PHOTOCATALYTIC STUDIES OF Bi$_2$O$_3$/POROUS g-C$_3$N$_4$ COMPOSITE FOR DEGRADATION OF REACTIVE BLACK 5 UNDER UV-VIS LIGHT IRRADIATION

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by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

xi

Page

LIST OF SYMBOLS

		Unit
C	Concentration at time t	mg/L
C_o	Initial concentration	mg/L
e^-	Electron	-
E_g	Band gap energy	eV
h^+	holes	-
hv	Photon energy	-
$O_2\bullet^-$	Superoxide radical	-
OH•	Hydroxyl radical	-
pzc	Point of zero charge	-

LIST OF ABBREVIATIONS

AOP   Advance oxidation process

Bi_2O_3 Bismuth oxide

CO_2 Carbon dioxide

EDX   Energy Dispersive X-ray

FTIR   Fourier Transform Infrared Spectroscopy

$g-C_3N_3$ graphitic carbon nitride

CB   Conduction band

HCl   Hydrochloric acid

H_2O Water

H_2O_2 Hydrogen peroxide

HRTEM   High Resolution Transmission Electron Microscopy

NaOH   Sodium hydroxide

NHE   Normal hydrogen electrode

O_2 Oxygen

PL   Photoluminescence

RB 5   Reactive Black 5

SEM   Scanning Electron Microscope

UV   Ultraviolet

UV-Vis DRS   Ultraviolet-Visible Diffuse Reflectance Spectra

VB   Valence band

XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy

KAJIAN MENGENAI PEMFOTOMANGKINAN KOMPOSIT Bi_2O_3/g-C_3N_4 BERLIANG UNTUK PENYINGKIRAN *REACTIVE BLACK 5* DI BAWAH SINARAN UV-VIS

ABSTRAK

Di antara semua pemangkin cahaya yang terkini, g-C_3N_4 telah menerima banyak pertimbangan di dalam degradasi bahan cemar organik. Malangnya, penggunaan g-C_3N_4 tulen menghadapi masalah penyatuan semula e^-/h^+ dan penyerapan cahaya yang terhad disebabkan oleh jurang tenaga yang sederhana iaitu 2.7 eV. g-C_3N_4 tulen boleh dibaik pulih melalui pengubahsuaian struktur dan gabungan bersama semikonduktor lain yang mempunyai jurang tenaga yang sederhana seperti Bi_2O_3 untuk mencipta bahan baru agar mempunyai prestasi yang lebih baik. Untuk tujuan ini, gandingan di antara g-C_3N_4 berliang dan pelbagai peratusan berat Bi_2O_3 (3-15 berat%) telah berjaya disediakan menggunakan kaedah rawatan haba dan pengisitepuan. Tujuan utama kajian ini adalah untuk menyediakan komposit Bi_2O_3/g-C_3N_4 berliang untuk degradasi *Reactive Black 5* (RB 5). Di sini, tiga pemboleh ubah telah dikendalikan dan mekanisme di sebalik degradasi RB 5 telah dikaji. Kejayaan dalam menghasilkan komposit Bi_2O_3/g-C_3N_4 berliang telah dibuktikan melalui beberapa analisa, manakala ciri-ciri optik telah dikaji menggunakan Lingkungan UV-Vis Pantulan (UV-Vis DRS) dan Fotopendarcahaya (PL). Tambahan lagi, kajian seterusnya membuktikan bahawa zarah-zarah Bi_2O_3 telah menghiasi g-C_3N_4 berliang melalui Mikroskop Pengimbas Elektron (SEM) dan Mikroskop Penghantaran Elektron (TEM), manakala analisa daripada Mikroskop Penghantaran Elektron Beresolusi Tinggi (HRTEM) menunjukkan bahawa wujudnya

hubungan yang rapat antara Bi_2O_3 dan g-C_3N_4 berliang. Tambahan pula, aliran cas ini sememangnya terjadi seperti mana dibuktikan melalui analisa Spektroskop Fotoelektron Sinar-X (XPS). Aktiviti pemfotomangkinan komposit Bi_2O_3/g-C_3N_4 berliang membuktikan bahawa komposit 9wt% Bi_2O_3/g-C_3N_4 berliang adalah pemangkin cahaya yang terbaik di mana kadar degradasi pemfotomangkinan mencapai peratusan yang paling tinggi (84%) di bawah 2 jam sinaran UV-Vis. Di sini, kriteria yang paling penting yang menyumbang kepada peningkatan dramatik adalah disebabkan oleh pembaik pulih penyerapan cahaya dan pemisahan pasangan e^-/h^+, seperti mana yang terbukti melalui analisa UV-Vis DRS dan PL. Tambahan lagi, kajian pembolehubah proses menunjukkan bahawa keadaan optimum telah diperoleh menggunakan 1 g/L beban pemangkin cahaya, kepekatan awal RB 5 dengan angka 10 ppm dan pada pH 5.7. Selain itu, kajian penyahradikal membuktikan bahawa aliran cas mengikut mekanisme Z-skema dimana radikal superoksida ($O_2\bullet^-$) adalah spesies yang bertanggungjawab dalam penyingkiran RB 5. Dan yang paling penting, kestabilan komposit 9wt% Bi_2O_3/g-C_3N_4 berliang dikekalkan selepas digunakan beberapa kali (3 kitaran) untuk degradasi RB 5, di mana 84%, 80% dan 76% telah disingkir pada kitaran 1, kitaran 2 dan kitaran 3.

PHOTOCATALYTIC STUDIES OF Bi_2O_3/POROUS g-C_3N_4 COMPOSITE FOR DEGRADATION OF REACTIVE BLACK 5 UNDER UV-VIS LIGHT IRRADIATION

ABSTRACT

Among all recent photocatalyst, g-C_3N_4 has received so much consideration in the degradation of organic pollutants. However, the use of bulk (pure) g-C_3N_4 faced the problems of high recombination of e^-/h^+ pairs and limited absorption of visible light due to its moderate band gap energy of about 2.7 eV. Pure g-C_3N_4 could be improved by structural modification and coupling with another semiconductor having moderate band gap energy such as Bi_2O_3 to develop new material for a better photocatalytic performance. For this purpose, Bi_2O_3/porous g-C_3N_4 composites with different loading of Bi_2O_3 (3-15 wt%) were successfully synthesized using thermal treatment and wet impregnation method. The specific objective of this study is to synthesize Bi_2O_3/porous g-C_3N_4 composite for the degradation of Reactive Black 5 (RB 5). Here, different process parameter studies were conducted and mechanism behind the degradation of RB 5 was studied. The successful synthesis of Bi_2O_3/porous g-C_3N_4 composites was proven using certain characterizations while optical properties were characterized using UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS) and photoluminescence (PL). Moreover, further characterizations revealed that Bi_2O_3 particles were decorated on top of the porous g-C_3N_4 based on the Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analysis, while High Resolution Transmission Electron Microscopy (HRTEM) analysis showed that intimate contact were formed between

Bi$_2$O$_3$ and porous g-C$_3$N$_4$. In addition, the charge transfers indeed occurred as proven from XPS analysis. The photocatalytic activity of Bi$_2$O$_3$/porous g-C$_3$N$_4$ composites proved that 9wt% Bi$_2$O$_3$/porous g-C$_3$N$_4$ composite is the best photocatalyst with highest degradation percentage of RB 5 (84%) under 2 h of UV-visible light irradiation. Here, the most important criteria that contributed to dramatic improvement are due to the improved light absorption and separation of e$^-$/h$^+$ pairs, which were proven using UV-Vis DRS and PL analysis, respectively. Moreover, process parameter studies concluded that the highest degradation efficiency using 9wt% Bi$_2$O$_3$/porous g-C$_3$N$_4$ composite was achieved using 1 g/L of photocatalyst, 10 ppm of initial RB 5 aqueous solution and at pH 5.7. Besides that, radical scavenger test proved that the photo-generated charge carriers followed Z-scheme mechanism where superoxide radical (O$_2$•$^-$) was found as the most active species. And most importantly, the stability of 9wt% Bi$_2$O$_3$/porous g-C$_3$N$_4$ composite is preserved after being reused for multiple times (3 cycles) for the degradation of RB 5, in which 84%, 80% and 76% of RB 5 have been degraded at cycle 1, cycle 2 and cycle 3, respectively.

CHAPTER 1

INTRODUCTION

This chapter presents the background of the current research work which covers the topic of environmental crisis, wastewater treatment and graphitic carbon nitride (g-C_3N_4) and bismuth oxide (Bi_2O_3) for dye removal. All topics are separated in different sections. The significance of this current work is expressed by outlining a set of objectives and major contributions by performing this research. Finally, the scope of this study is given by outlining the chapters in this thesis.

1.1   Environmental Crisis

The concern on the environmental contamination caused by the growth in industries urged the need for renewable energy generation and environmental decontamination. Most industries release toxic and organic pollutants to the air and water which eventually caused air and water pollution (Chen *et al.*, 2014b). For example, dyeing industries is one of the main causes in contributing to water pollution. Every single thing around us is colored to enhance its beauty, even the medicine itself (Padhi, 2012). Dyes have been produced in a very large amount of up to 800, 000 tons per year and used in various productions such as in textile industry, pharmaceutical, food coloring, cosmetics and food coloring (Hassaan & El Nemr, 2017b). In textile industry alone, it is used up to two thirds of the total dyeing industries, hence making it as the largest consumer of dyes (Ananthashankar, 2012; Hassaan & El Nemr, 2017a). The various types of dyes which have been used for fabrics coloring are mainly acidic, basic and reactive dyes, in which different fabric

types are colored with different types of dyes, as shown in Table 1.1 (Gita *et al.*, 2017; Lellis *et al.*, 2019).

Table 1.1: Percentage of discharged dyes in different types of fiber dyeing (Gita *et al.*, 2017; Lellis *et al.*, 2019).

Fiber	Type of dye	Discharged dye (%)
Wool and nylon	Acid dyes/reactive dyes for wool	7-20
	Pre-metallized dyes	2-7
Cotton and viscose	Azoic dyes	5-10
	Reactive dyes	20-50
	Direct dyes	5-20
	Pigment	1
	Vat dyes	5-20
	Sulfur dyes	30-40
Polyester	Disperse	8-20
Acrylic	Modified basic	2-3

Table 1.1 shows the various types of dye which are used for different types of fiber with the amount of discharged dye. In the production of clothes, the used dyes do not all perfectly bind to the fabrics (Table 1.1) and more than 5% (acid, azoic, reactive, direct, vat, sulfur and disperse dyes) of the used dyes are released into water stream without having been treated properly (Gita *et al.*, 2017; Kant, 2011; Rehman *et al.*, 2018). In fact, more than 11 % out of 450,000 dyes are wasted from industrial processes, and some of these dyes are toxic, carcinogenic and mutagenic like methyl red (MR), methyl orange (MO) and methylene blue (MB) that may decompose to naphthalene and other aromatic compounds (Derudi *et al.*, 2007; Forgacs *et al.*, 2004; Jyoti & Singh, 2016). Figure 1.1 shows the chart illustrating the general amount of synthetic dyes used in industries, showing that in textile industries alone, more than 10% of the un-used dyes were discharged into water stream. As reviewed by Yaseen *et al.* (2018), most of the dye level in textile effluents all over

the world is more than 10 ppm while the intensity of the dye is between 1000 and 1500 American Dye Manufacturers Institute (ADMI) units (Yaseen & Scholz, 2019).
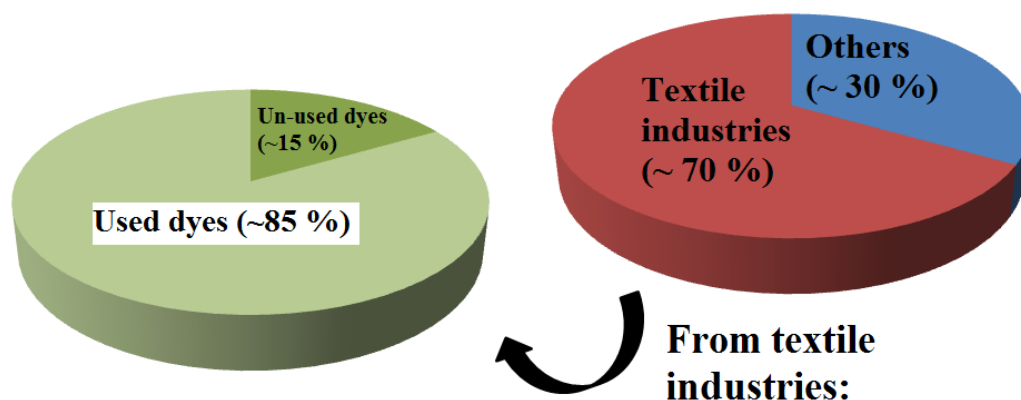
Figure 1.1: General percentage of synthetic dyes used in textile industry and discharged dyes into water stream (Gita *et al.*, 2017; Hassaan & El Nemr, 2017b).

Azo dyes such as Reactive Black 5 (RB 5) is the largest class of dyes that have been used in the textile industry comprising of up to 70 % (Molinari *et al.*, 2004). Without proper treatment, the breakdown of azo dyes releases aromatic amines which are highly carcinogenic (Zhang *et al.*, 2007). Waste water having untreated dyes not only causes water crisis and affect human life, but also alters transparency of water and harm the aquatic life (Erdemoğlu *et al.*, 2008). Even when they appear in small concentration of less than 1 ppm, sunlight penetration into water stream is reduced hence leading to the slower rate of photosynthesis reaction (Chung, 1983). Moreover, the dissolved oxygen (DO) in water is disturbed where the water-consisting dyes were found to have higher biological oxygen demand (BOD) and chemical oxygen demand (COD) due to the presence of organic molecules which are the dye molecules itself (Imran *et al.*, 2015; Kant, 2011; Padhi, 2012). These carry-forward effects of discharge waste water-containing dyes thus

affect the entire biological cycles of aquatic biota and harms the marine lives (Kant, 2011). Therefore, there is a need for these organic pollutants to be mineralized from industrial plants to reduce the pollution problems.

1.2   Wastewater Treatment

The problem of water crisis and its serious effects to aquatic and human life lead to the higher restrictions in the industrial activities especially in the implementation of laws regarding the discharge of waste water-containing dyes into water stream (Kant, 2011). Hence, an economical solution in the mineralization of synthetic dyes is still being investigated until now. Although the three common methods of water treatment such as physical, chemical and biological methods have been used before, they are still lacking in efficiency in mineralizing organic pollutants. As an example, physical and chemical methods only decolorize the dyes without decomposing the dyes into less hazardous molecules, produce secondary sludge and involve high cost due to the use of electricity (Imran *et al.*, 2015; Lellis *et al.*, 2019). Meanwhile, although biological method seems to be the most economical and environmental friendly, the degradation of dyes takes too long and hence is not efficient enough (Babel & Kurniawan, 2003; Hassaan & El Nemr, 2017a). Now, researches pay most intention to advanced oxidation processes (AOP) for decontamination of organic pollutants (Guillard *et al.*, 2003; Mamba & Mishra, 2016). Generally, AOP is the process of generating active radicals such as hydroxyl radical with oxidizing potential of 2.8 V versus NHE, the second highest oxidizing agent after fluorine (Al-Kdasi *et al.*, 2004; Mamba & Mishra, 2016). The method is developed by using different oxidants such as hydrogen peroxide (H_2O_2) and was found to have a great effect in accelerating oxidation process and being able to

4

destroy various organic compounds (Babel & Kurniawan, 2003). This method can be classified under photocatalytic and photochemical processes as the radicals could be generated by using irradiation and chemical energies (Chung, 1983; Hassaan & El Nemr, 2017b).

AOP brings numerous advantages due to its inexpensive method and able to mineralize organic pollutants to carbon dioxide and water (Ruzmanova *et al.*, 2013; Stoller *et al.*, 2011). Since AOP generates active radical such as hydroxyl radical, most of the organic pollutants are mineralized after interaction with the radicals (Al-Qaradawi & Salman, 2002). AOP is a green technology method because no solid wastes are generated and is time efficient (Kaur & Singh, 2012). Besides that, AOP has been reported to be effective at ambient temperature and pressure, and able to provide an almost total degradation to soil and water organic soluble wastes (Mounir *et al.*, 2007; Torres *et al.*, 2007). Various AOP methods are:

i.   Photolysis

ii. Photocatalysis

iii. Ozone

iv. Hydrogen peroxide

Among all AOP methods, water treatment by using photocatalysis reaction employing semiconductor materials has received numerous attractions among researchers. This is because photolysis reaction without photocatalyst has low efficiency in degradation of organic pollutants, while the use of ozone and hydrogen peroxide are not safe enough for the waste water treatment.

1.3   g-C$_3$N$_4$ and Bi$_2$O$_3$ as a Photocatalyst

Since last decades until now, zinc oxide (ZnO) and titanium dioxide (TiO$_2$) are the most common used semiconductor photocatalyst for the abatement of pollutants. They have been recognized as being non-toxic in nature and able to degrade various pollutants under sunlight (Obregón *et al.*, 2012; Regmi *et al.*, 2017) However, both ZnO and TiO$_2$ can only utilize less than 5 % of solar light due to high band gap energy (> 3.0 eV), thus bring less practical usage in industry (Regmi *et al.*, 2017). Since about 45% of solar light comes from the visible light region, the development of an efficient semiconductor photocatalyst in pollutants degradation is highly important. Hence, the studies now are more focused on another type of semiconductor such as g-C$_3$N$_4$ and Bi$_2$O$_3$ in which both are capable of absorbing large portion of UV-visible light.

g-C$_3$N$_4$ has a moderate band gap energy of approximately 2.7 eV for a pristine g-C$_3$N$_4$ (Regmi *et al.*, 2017; Yang *et al.*, 2016). It is known to be a reduction-type semiconductor due to its high reduction potential, where the level of CB is about -1.13 V versus NHE, negative enough for the reduction of oxygen (O$_2$) to superoxide radical (O$_2$•-) (Li *et al.*, 2015). Meanwhile, the monoclinic phase of Bi$_2$O$_3$ also has a moderate band energy of about 2.8 eV, and known to be an oxidation-type semiconductor with high oxidation potential, where the level of VB is about +2.90 V versus NHE, positive enough for the oxidation of water (H$_2$O) into hydroxyl radical (OH•) (Xiong *et al.*, 2015). Both O$_2$•- and OH• were reported as the major species responsible for the degradation of various organic pollutants (Mamba & Mishra, 2016). Based on the matching band edge levels, it is believed that the coupling of g-C$_3$N$_4$ and Bi$_2$O$_3$ would have good photocatalytic performance due to their synergistic effect.

In this study, the performance of g-C_3N_4 is improved by introducing porosity to make a porous g-C_3N_4 and the development of a binary composite with a visible light-responsive semiconductor, which is bismuth oxide (Bi_2O_3). The purpose is to develop a better photocatalyst for the wastewater treatment such as for the degradation of organic pollutants specifically for the degradation of azo dyes. In this study, Bi_2O_3/porous g-C_3N_4 composites are synthesized using wet impregnation method and the performance was tested on the degradation of RB 5.

1.4   Problem Statement

Since there is a need for an efficient waste water treatment, the synthesis of a light-driven photocatalyst that may absorb wide region of UV-visible light are in demand (Song *et al.*, 2015). Now, the studies on an efficient catalyst moved towards the use of semiconductors which have good band gap energy (1.5-3.0 eV) that may absorb large portion of visible light (Mamba & Mishra, 2016). Among all recent catalysts, g-C_3N_4 has received so much consideration in the degradation of organic pollutants. Wang *et al.* (2009) first reported on g-C_3N_4 for its ability to split water into hydrogen and oxygen under visible light irradiation (Wang *et al.*, 2009). With a band gap of less than 3.0 eV, g-C_3N_4 is considered as a suitable catalyst to be used in photocatalytic water splitting with its additional criteria for having good thermal and chemical stability. However, the use of pristine g-C_3N_4 is inefficient due to the low surface area, thus having limited active sites available for the adsorption of organic pollutants and absorption of light (Yang *et al.*, 2015). Here, surface modification of g-C_3N_4 by introducing porosity is one of the approaches to improve the performance of photocatalyst as it may increase surface area, increase light scattering effect and

active sites, thus enhancing the oxidation of organic pollutants into less hazardous compounds (Yang *et al.*, 2015; Yu *et al.*, 2014).

However, there are still some major problems faced by every singular photocatalyst which are ineffective charge carriers separation and limited visible light absorption (Habibi-Yangjeh *et al.*, 2019; Wen *et al.*, 2015; Yu *et al.*, 2017a; Zhang *et al.*, 2013). For the first point, ineffective charges carrier separation means that the excited electron recombines with its hole, hence reducing the efficiency of producing the radicals responsible for the degradation of organic pollutants. If the recombination of photo-generated charge carriers could be reduced, it will lead to the enhancement of photocatalytic activity due to higher production of active species. For the second point, the limited visible light absorption means that the photocatalyst can only absorb small portion of visible light region. If the visible light absorption could be extended to a higher wavelength, more portion of sunlight could be absorbed by the photocatalyst, which means that more photons could be absorbed thus leading to a higher production of electron-hole pairs and followed by the production of radicals. Here, apart from the surface modification, development of a binary photocatalyst would be helpful in reducing these two major problems. Another recent photocatalyst, Bi_2O_3, was also reported to greatly enhance photocatalytic activity due to its moderate band gap energy (2.8 eV) (Liu *et al.*, 2010). Development of Bi_2O_3/g-C_3N_4 as binary composite would improve photocatalytic activity by improving the charge separation and broaden the utilization of visible light (Li *et al.*, 2015). They have a matched band structure that brings the synergistic effect in both photocatalysts. Besides that, both g-C_3N_4 and Bi_2O_3 fulfill the criteria of a good photocatalyst which are stable at high temperature,

highly abundant, non-toxic in nature, easily prepared, inexpensive, and yet able to perform in photocatalytic activity effectively (Chen *et al.*, 2011).

1.5   Research Objectives

The aim of the research is to study the photocatalytic activity of Bi_2O_3/porous g-C_3N_4 composite for degradation of RB 5 under UV-Visible light irradiation. The specific objectives are:

1. To prepare and characterize the physical and chemical properties of Bi_2O_3/porous g-C_3N_4 composite which were synthesized using wet impregnation method.

2. To investigate the effect of mass ratio of Bi_2O_3/porous g-C_3N_4 composite with different amount of Bi_2O_3 on the photocatalytic degradation of RB 5.

3. To determine the optimum process parameters in photocatalytic reaction which are amount of photocatalyst, initial concentration and pH of RB 5 solution using the best photocatalyst.

4. To study the mechanism of the photo-degradation of RB 5 over Bi_2O_3/porous g-C_3N_4 composite using different sacrificial reagents.

1.6   Scope of Study

The purpose of this study is to improve the performance of g-C_3N_4 by surface modification which is introduction of porosity, and semiconductor coupling with Bi_2O_3. By introducing porosity, it is expected that the available adsorption sites of organic pollutants and light harvesting will be improved. Herein, pre-thermal treatment is easy as the precursor which is melamine, just need to be calcined at two different temperatures without involving any template agents such as silica and acid.

Besides that, it is proposed that semiconductor coupling will improve the performance of singular photocatalyst as the recombination of photo-generated charge carriers could be reduced. As these two modifications (porosity and semiconductor coupling) are believed can enhance the photocatalytic behaviors of g-C_3N_4, certain characterizations which are X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and UV-visible diffuse reflectance spectroscopy (DRS) were performed to reveal the properties of Bi_2O_3/porous g-C_3N_4 composites. The photocatalytic activity of Bi_2O_3/porous g-C_3N_4 composites was tested for degradation of RB 5. Here, RB 5 was chosen as the model pollutant because previous studies involving Bi_2O_3 and g-C_3N_4 photocatalysts were more focused on the degradation of cationic dyes such as MB and Rhodamine B (RhB). Subsequently, process parameter studies involving different amount of photocatalyst loading, initial concentration and pH of RB 5 were also conducted to obtain the best conditions needed in the degradation of RB 5. Scavenger tests were also performed to reveal the mechanism involved behind the degradation of RB 5 using the best Bi_2O_3/porous g-C_3N_4 composite. Lastly, reusability test was conducted to determine the stability of the synthesized Bi_2O_3/porous g-C_3N_4 composite.

1.7   Thesis Organization

This thesis consists of five chapters which are introduction, literature review, materials and methods, results and discussion, and lastly conclusions and recommendations. Chapter 1 (Introduction) gives a general description of

environmental crisis, wastewater treatment and g-C_3N_3 and Bi_2O_3 for dye removal. Chapter 1 also includes the problem statement which clarifies the purpose of this study, and followed by the scope of this study.

Chapter 2 (Literature review) describes the background of this study which are the principle of photocatalysis, description about dyes and the properties of RB 5, the use of g-C_3N_4 as a semiconductor photocatalyst including its modifications by the introduction of porosity and coupling with Bi_2O_3, and catalyst preparation. In this chapter, the summary on the use of g-C_3N_4 with other materials as the photocatalysts are also given for comparison.

Chapter 3 (Materials and Methods) describes the materials, chemicals and all characterizations involved in the synthesis of Bi_2O_3/porous g-C_3N_4 composites. Detailed methodology starting from the photocatalyst preparation, characterizations, experimental set-up, photocatalytic experiments, process parameter studies and scavenger tests and reusability test were also included.

Chapter 4 (Results and Discussion) provides the findings of the current research studies in terms of the photocatalytic behaviors of Bi_2O_3/porous g-C_3N_4 composites. This chapter plays the major role in determining the contributions of this work for future study. It consists of five sections starting with the characterizations of the porous g-C_3N_4 and Bi_2O_3/porous g-C_3N_4 composites, photocatalytic experiments, process parameter studies, scavenger tests and reusability test.

Chapter 5 (Conclusions and Recommendations) concludes the findings of this current research study and recommendations for future works were also provided.

CHAPTER 2

LITERATURE REVIEW

This chapter provides the background that lead to this current research. The chapter starts with the literature of dyes, photocatalysis and semiconductor photocatalyts with an emphasis on structural modification of g-C_3N_4 and coupling with Bi_2O_3, and preparation of binary photocatalyst.

2.1 Dyes as Organic Pollutants

Dye is a substance that can produce color and shows affinity to the fabrics owing to its auxotrophic groups which are highly polar (Wardman, 2017). Synthetic dyes started to be manufactured in the late nineteenth century to replace the use of natural dyes in the dyeing industries and are widely used in textile industry. The discharge of dyes into water stream leads to the reduction in the photosynthesis reaction and DO content in water bodies (Imran *et al.*, 2015). Compared to natural dyes, synthetic dyes have toxic effects in which the intermediates of synthetic dyes are carcinogenic. There was a report made by Christie *et al.* (2017) where an incidence of bladder cancer happened involving the intermediates of synthetic dyes which are benzidine and 2-naphthylamine (Christie, 2015). In fact, dyeing process wasted about 12 % of dyes and out of this value, 20 % of dyes enter the water system (Rauf & Ashraf, 2009). Here, special mention should be given to azo dyes where more than 15 % of azo dyes do not bind to fabrics, and is discharged together with water during the washing step. Without treatment, these dyes remain in the environment due to their complex structure having half-lives of between 2 and 13 years (Copaciu *et al.*, 2013; Pandit *et al.*, 2015). Here, due to its high solubility in

water, conventional water treatments were found to be ineffective in treating the discharge dyes (Hassan & Carr, 2018). And even if some of the discharged dyes could be broken down partially, they are not mineralized completely and the intermediates could be much more hazardous compared to its parent structure (Lellis *et al.*, 2019).

2.1.1 Reactive Black 5 (RB 5)

According to the National Center for Biotechnology Information, PubChem Compound Database, RB 5 is a heterocyclic aromatic compound which belongs to azo dyes with 2 chromophoric azo (R_1-N=N-R_2) attached to aromatic rings and sulfonate groups (Saratale *et al.*, 2011). Complexity of its aromatic structure makes RB 5 and other dyes to have high stability and are non-biodegradable in natural conditions. Table 2.1 shows the properties of RB 5.

Among all types of azo dyes, reactive dyes are preferred to be used in textile industries because of its bright color, easy application and high stability against light, heat, water, detergent and bleach (González-Gutiérrez *et al.*, 2009; O'mahony *et al.*, 2002). RB 5 is one of the most commonly used reactive dyes which can form covalent bonds with textile fibers such as cotton, wool and nylon (Asad *et al.*, 2007). Other than textile industry, RB 5 is also suitable to be used in paper, pharmaceutical and chemical industries.

The example of azo dyes is RB 5, which falls under the group of reactive dyes. In this study, RB 5 was chosen as the model pollutant because previous studies which employed the use of g-C_3N_4 and Bi_2O_3 as the photocatalyst were mostly only focused on the degradation of cationic dyes such as MB and RhB (Dang *et al.*, 2015; Li *et al.*, 2015; Liu *et al.*, 2018a). By also studying the interaction between

Bi_2O_3/porous g-C_3N_4 and dye having anionic property such as RB 5, the reasons behind the increased or decreased photocatalytic activity at different pH could be understood better.

Table 2.1: Properties of RB 5.

Chemical structure	
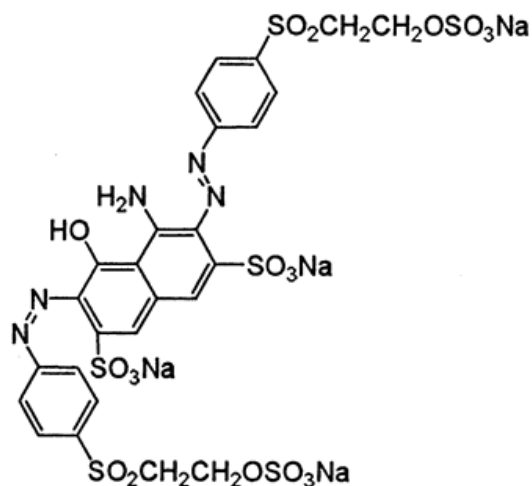
Molecular weight	991.789 g/mol
Molecular formula	$C_{26}H_{21}N_5Na_4O_{19}S_6$
Solubility	High solubility in water
Color	Black powder
Odor	Odorless
Form	Powder

Improper treatment of RB 5 releases intermediates which are toxic, mutagenic and carcinogenic (Weisburger, 2002). The color would remain in water bodies for a long period of time because the complexity of aromatic compounds makes them stable against microbial attack. The toxicity of synthetic dyes brings much concern and now, manufacturers are strictly required to mineralize the wastewater-consisting dyes before they are discarded into water bodies.

Based on the previous studies, degradation of RB 5 was mainly done using TiO$_2$-based photocatalysts. One of the studies were conducted by Tang *et al*. in which about 99 % of RB 5 was successfully degraded using commercial TiO$_2$ Degussa P25 under UV light irradiation for 150 min (Tang & Chen, 2004). In another study, Song *et al*. synthesized graphene-titanium nanotube using hydrothermal method which also successfully degraded 100 % of RB 5 under UV light irradiation for 180 min (Song *et al.*, 2015). However, both studies employed the use of UV light as the artificial light source, hence are not feasible for photocatalysis reaction involving large volume of slurry (Chowdhury *et al.*, 2017; Regmi *et al.*, 2017).

The degradation of RB 5 using other photocatalysts are shown in Table 2.2, where it is obvious that most photocatalysts employed the use of UV light to degrade RB 5. Here, the use of UV light portion is limited under sunlight irradiation (only 5 %), hence is not practical for real-life application.

Table 2.2: Degradation of RB 5 using various photocatalyst.

Catalyst	Method of preparation	Type of Light	Catalyst amount (g/L)	Concentration of Dye (ppm)	Results	Reference
Graphene-titanium nanotube composite	Hydrothermal treatment	UV-Vis	0.4 g/L	10	100 % of RB 5 was degraded after 180 min of irradiation, where highest achievement obtained using 15 wt% graphene-titanium composite.	(Song *et al.*, 2015)
TiO$_2$ Degussa P25	Not stated	UV	2 g/L	50	99 % of RB 5 was degraded after 150 min of irradiation	(Tang & Chen, 2004)
N-doped TiO$_2$ nanoparticles	Sol-gel method	UV-Vis	1 g/L	6	88.4 % of RB 5 was degraded after 360 min of light irradiation.	(Kamaludin *et al.*, 2018)
ZnO and lanthanum (La) doped nanoparticles	Sol-gel method	UV	0.12 g/L	10	99.43 % of RB 5 was degraded after 180 min of irradiation, where highest achievement obtained using 1wt% La-doped ZnO nanoparticles.	(Kaneva *et al.*, 2016)
Immobilized TiO$_2$ nanoparticle composite	Electro-spinning	UV	2	10	Almost 100 % of RB 5 was degraded after 240 min of irradiation.	(Sugiyana *et al.*, 2014)

2.2   Photocatalysis

Among all AOP methods, the most investigated technologies belong to the heterogeneous photocatalysis reaction which can be done using photocatalytic oxidation (Belver *et al.*, 2019). Here, heterogeneous photocatalysis is a reaction having a system with two phases involving the solid catalyst and polluted water. The catalyst is called as photocatalyst because it could be activated under light illumination. One type of heterogeneous photocatalysts is semiconductor photocatalyst, where the electronic and optical properties depend on the band structure of the semiconductor itself (Mamba & Mishra, 2016; Serpone & Emeline, 2012). The semiconductor behaves in between a metal and insulator, where electrons could move and be excited to conduction band (CB) after it receives enough energy given by the photons, leaving holes at the valence band (VB) (Serpone & Emeline, 2012). The history of semiconductor photocatalysis started in 1972, where Fujishima and Honda first discovered that TiO_2 can be used as a photocatalyst in water splitting reaction (Fujishima & Honda, 1972; Serpone & Emeline, 2012). Semiconductor photocatalysis provides several advantages such as being able to provide a complete mineralization of organic pollutants into inorganic ions, carbon dioxide and water (Mamba & Mishra, 2016; Serpone & Emeline, 2012). Besides that, it has high stability towards photolysis and applicable at ambient condition, thus allows for multiple oxidative conversions which can enhance the efficiency of the conversion process (Pekakis *et al.*, 2006). Moreover, this method can be classified as green technology as renewable energy (sunlight) could be employed, hence consuming less cost in terms of the usage of UV-visible lamp (Belver *et al.*, 2019).

Apart of hydrogen production and water purification which are the dominant applications of heterogeneous photocatalysis reaction, the concern on global

warming also attracted the use of photocatalysis reaction for the reduction of CO_2 gas into useful fuels. In the air purification alone, various organic pollutants such as Volatile Organic Compounds (VOC) and inorganic gases such as nitrogen dioxide (NO_2) have been successfully removed using photocatalysis reaction (Boyjoo *et al.*, 2017). The importance of photocatalysis reaction can be shown in the huge number of paper publications where 10 % corresponds to the abatement of water pollutants by using photocatalysts (Belver *et al.*, 2019).

Generally, photocatalysis employs the use of light to speed up any chemical reaction. As for the light source, natural or artificial lights may be used to initiate the production of active species for redox reactions (Yu *et al.*, 2017b). Previously, UV light is the main artificial light source in photocatalysis reaction. However, the use of UV light is neither practical nor economical as only 5 % of UV light comes from the sunlight and the use of UV lamp is rather expensive (Chowdhury *et al.*, 2017; Yu *et al.*, 2017b). With regard to this issue, the use of visible or UV-visible light becomes more prominent in today's technology as sunlight contains big fraction of visible light region of up to 45% (J. Hu *et al.*, 2017). With the presence of light source such as visible light, absorption of energy of equal or more than the band gap energy of semiconductor excites the electrons from the VB to the CB (Mamba & Mishra, 2016). The semiconductor has unique criteria that enable it to act as photocatalyst, where the VB is fully occupied with electrons while conduction band is empty and unoccupied with electrons (Devi & Kavitha, 2013). Band gap determines electrical conductivity of material based on the difference between highest occupied energy state of VB and lowest unoccupied CB, where a small band gap needs low energy for the excitation of electrons. In a photocatalysis reaction, the position of VB and CB of the semiconductor matters as it determines the potential capability in producing

active radicals which are responsible for the photocatalytic reaction (Belver *et al.*, 2019). As reviewed by Mamba *et al.* (2016), visible light can be absorbed by semiconductors which have band gap energy of between 1.5 and 3.0 eV (Mamba & Mishra, 2016).

Upon excitation of electrons, valence band carries a positive charge called as holes (h^+) while the conduction band carries a negative charge called as electron (e^-), as shown in Figure 2.1 (Molinari *et al.*, 2004).
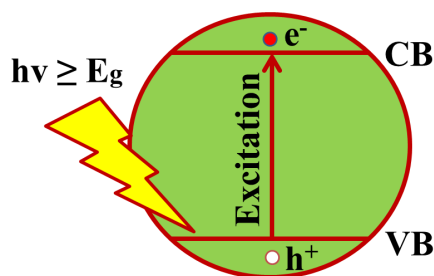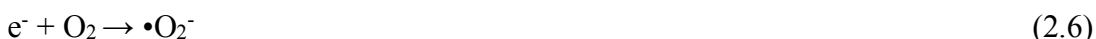

Figure 2.1: Excitation of electron under light irradiation (Molinari *et al.*, 2004).

The formation of this e-/h+ pair occurs in femtoseconds depending on the energy barrier between the VB and CB of the semiconductor (Belver *et al.*, 2019). Hydroxide ions (OH^-) or water (H_2O) are then captured by h^+ hence forming a powerful oxidizing agent, $OH\bullet$. Meanwhile, molecular oxygen (O_2) traps the available e^- to produce superoxide radicals ($O_2\bullet^-$) (Mamba & Mishra, 2016; Tseng *et al.*, 2010). Formation of these radicals ($OH\bullet$ and $O_2\bullet^-$) help to reduce electron-hole recombination, thus lead to efficient photocatalytic activity. The mechanism of radical attack is depicted in Equation (2.1-2.8)

$$Catalyst + hv \rightarrow h^+ + e^- \tag{2.1}$$

$$h^+ + H_2O \rightarrow \bullet OH + H^+ \tag{2.2}$$

$$h^+ + OH^- \rightarrow \bullet OH \tag{2.3}$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \tag{2.4}$$

$$H_2O_2 + hv \rightarrow 2\ \cdot OH \tag{2.5}$$

$$e^- + O_2 \rightarrow \cdot O_2^- \tag{2.6}$$

$$\cdot O_2^- + H_2O_2 \rightarrow \cdot OH + O_2 + OH^- \tag{2.7}$$

$$e^- + H_2O_2 \rightarrow \cdot OH + OH^- \tag{2.8}$$

Hydroxyl radicals which have strong oxidation potential help in the degradation of various compounds including dyes which having a stable and complex structure (Teoh *et al.*, 2012).

One of the most likely scenarios that would unfold or reduce the efficiency of the photo-degradation of organic pollutants is due to the recombination of electron and hole pairs after absorption of light. Specifically, there are various types of electron-hole recombination that may occur, which could be divided into bulk and surface recombination. Here, bulk recombination occurs when the excited electron recombine with its hole which then emits a photon having energy similar with the band gap energy (Appavoo *et al.*, 2015; Weiss *et al.*, 2019). Meanwhile, surface recombination occurs at any defect at the surface or interface due to the severe disruption of the crystal lattice, such as due to the dangling bonds that induce a high local recombination of electron-hole pairs (Appavoo *et al.*, 2015; Weiss *et al.*, 2019). The recombination of this photo-generated charge carriers occur very fast up to few nanoseconds resulting in lesser formation of active species or radicals responsible in photocatalysis reaction for the degradation of organic pollutants. Upon recombination of electron-hole pairs, energy is lost in the form of heat or light, which occurs almost 90 % for every photocatalyst (Hernández-Alonso *et al.*, 2009; Molinari *et al.*, 2004; Soutsas *et al.*, 2010). Besides that, capability in absorbing large portion of visible light is also one of the main concerns for a good photocatalyst. As

about 45% portion of the sunlight is visible light, the important criteria of a good photocatalyst must have a band gap energy of between 1.5 and 3.0 eV, which corresponds to a wavelength of higher than 400 nm (Mamba & Mishra, 2016; Wang *et al.*, 2013).

In photocatalysis reaction, there are five basic general steps (Figure 2.2) involved for the pollutants mineralization (Devi & Kavitha, 2013; Herrmann, 1999), which are:

i. Mass transfer of solution onto semiconductor surface.

ii. Adsorption of pollutants, which occurs simultaneously with the excitation of semiconductor electrons.

iii. Oxidation of pollutants by radical species.

iv. Desorption of degraded products from the photocatalyst surface.
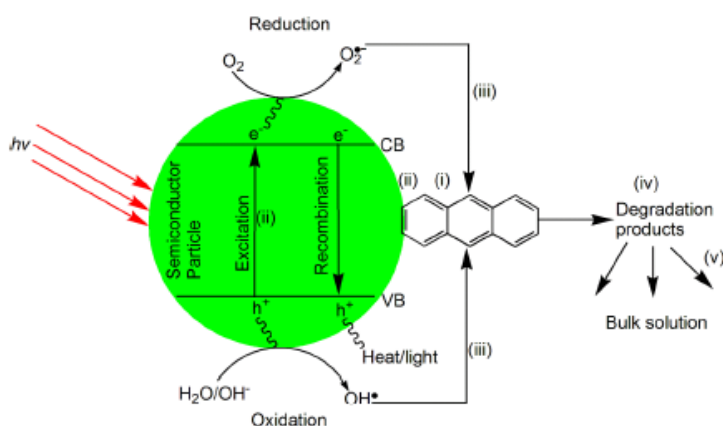
v. Diffusion of degraded products into bulk solution.

Figure 2.2: Photocatalysis reaction (Mamba & Mishra, 2016).

2.3   Semiconductor Photocatalysts

Photocatalysis using semiconductor received so much interest in waste water treatment as it may use renewable energy for pollutants abatement. It is worth to note that the properties of an excellent semiconductor should be photoactive, able to utilize UV and visible light, biologically and chemically inert, photo-stable (no leaching), inexpensive and easy synthesis, and non-toxic in nature. Hence, the choice of a semiconductor for photocatalysis reaction becomes more limited by following the specifications as mentioned above ((Obregón *et al.*, 2012; Regmi *et al.*, 2017). Figure 2.3 shows the examples of semiconductor photocatalyst and band energy position.
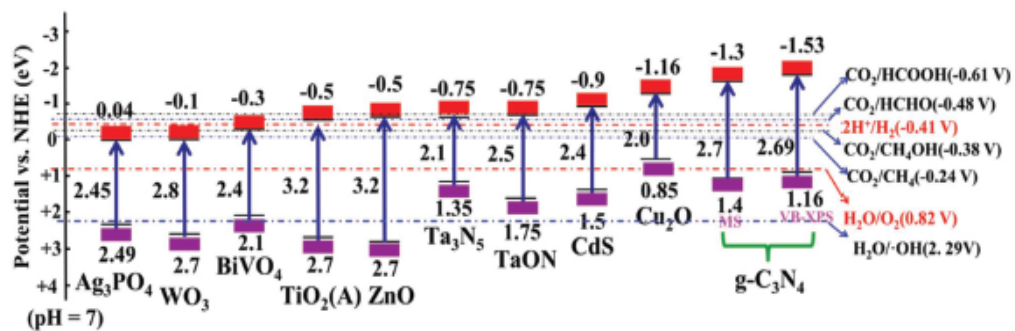

Figure 2.3: Band position of various semiconductor photocatalysts (Li *et al.*, 2016).

Based on Figure 2.3, it can be observed that there are various photocatalysts which can be used for the environmental remediation. For example, both ZnO and TiO_2 were used extensively as a photocatalyst due to their ability in harvesting UV light for the degradation of various azo dyes (Md Rosli *et al.*, 2017; Song *et al.*, 2015). However, they can only absorb UV light region hence limiting its application in photocatalysis reaction. Meanwhile, cadmium sulfide (CdS) is a toxic material, thus its application for green technology is limited. Moreover, although bismuth

vanadate ($BiVO_4$) and tungsten oxide (WO_3) can be considered as new findings in photocatalytic technology with great properties, their synthesis treatment is not easy and requires lots of chemicals and complicated procedures (Guan *et al.*, 2011; Yu *et al.*, 2017a; Zhao *et al.*, 2016). Hence, among all, g-C_3N_4 and Bi_2O_3 which have high level of CB and VB respectively, non-toxic in natures, easy to be synthesized with abundant precursors, photo-stable, and able to absorb both UV and visible light are chosen as the photocatalyst for the binary composites synthesis, which could enhance the performance of singular photocatalyst (Xu *et al.*, 2017; Zhang *et al.*, 2015b)

2.3.1   Graphitic carbon nitride (g-C_3N_4) as photocatalyst

2.3.1(a)   Properties of g-C_3N_4

Polymeric g-C_3N_4 is a 2D, metal-free, л-conjugated semiconductor with mild band gap energy of 2.7 eV (Mamba & Mishra, 2016; Yang *et al.*, 2016). The oldest C_3N_4 was reported to be melon which was synthesized in 1834 (Wang *et al.*, 2015). Since then, different allotropes of C_3N_4 were synthesized by using different methods such as α-C_3N_4, β-C_3N_4 and g-C_3N_4 (Semencha & Blinov, 2010). Among all allotropes, most researchers pay more intention to g-C_3N_4 due to its high stability at ambient temperature of up to 600 °C, concentrated acidic and alkali solution, and resistant (insoluble) in common solvents like water and alcohol as the stacked graphitic layers are strongly held by the Van der Waals forces (Mamba & Mishra, 2016; Zhou *et al.*, 2011; Zhou *et al.*, 2015). The building blocks that form the polymeric C_3N_4 was agreed to be tri-s-triazine units (Figure 2.4(b)) which are connected through tertiary nitrogen atom (Yang *et al.*, 2011). Although s-triazine (Figure 2.4(a)) units may also form g-C_3N_4, computational studies using Density

Functional Theory (DFT) revealed that tri-s-triazine unit is more thermodynamically stable than s-triazine unit (Zhang *et al.*, 2012).
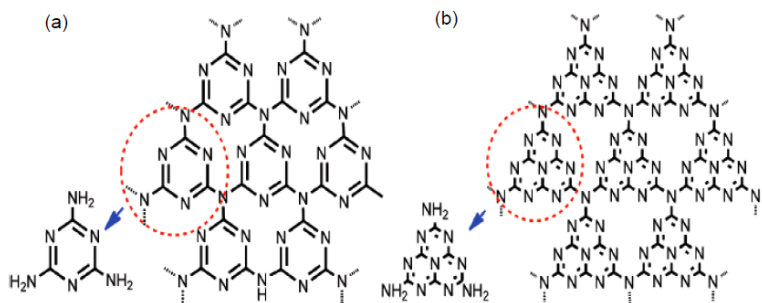

Figure 2.4: (a) S-Triazine unit and (b) Tri-s-triazine unit of g-C_3N_4 (Mamba & Mishra, 2016).

With band gap of ~ 2.7 eV, large portion of UV-visible light could be absorbed by g-C_3N_4 (Mamba & Mishra, 2016; Yang *et al.*, 2016). Here, the polymer-like g-C_3N_4 allows for the multiple excitation of electrons upon absorption of light, which would hence enhance the generation of active radicals (Cui *et al.*, 2016; Mamba & Mishra, 2016). In addition, the strong reduction capability of g-C_3N_4, where the level of CB is about -1.13 V versus NHE, is negative enough for the reduction of oxygen (O_2) to superoxide radical ($O_2\bullet-$), which is also one of the active species for the mineralization of organic pollutants (Li *et al.*, 2015). Since the discovery of g-C_3N_4 for hydrogen production in 2009, g-C_3N_4 was studied extensively for the degradation of dyes such as MB and RhB (Md Rosli *et al.*, 2017; Wang *et al.*, 2009). Due to good criteria of g-C_3N_4 which is easy to be synthesized, has abundant precursors, non-toxic in nature, and thermally and chemically stable, the properties of g-C_3N_4 are now still being explored and some modifications are made to improve some minor drawbacks of g-C_3N_4 such as structural modification, metal-doping and semiconductors coupling to increase surface area, separate the