SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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SYNTHESIS AND CHARACTERIZATION OF TUNGSTEN OXIDE – ZINC OXIDE HYBRID PARTICLES AND THEIR PHOTOCATALYTIC STUDY IN REMOVAL OF RhB DYE.

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitles "**Synthesis of tungsten oxide - zinc oxide hybrid particles and their photocatalytic study in removal of RhB dye**". I also declared that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF ABBREVIATIONS

Ag	Silver
Au	Gold
Aop	Advanced Oxidation Process
Bq	P-Benzoquinones
BOD	Biochemical oxygen demand
Cb	Conduction Band
COD	Chemical oxygen demand
DI	Distilled
Edx	Energy Dispersive X-Ray Spectroscopy
FESEM	Field Effect Scanning Electron Microscopy
Hcl	Hydrochloric Acid
HMT	Hexamethyltetramine
ICCD	International Centre For Diffraction Data
IPA	Isopropanol
KI	Potassium Iodide
NHE	Normal Hydrogen Electrode
nm	Nanometer
Pd	Palladium
Ph	Potential Of Hydrogen
Pt	Platinum
PVP	Polypyrolidone
Rhb	Rhodamine B
Rpm	Rotation Per Minute
RTPL	Room Temperature Photoluminescence
SPR	Surface Plasmon Resonance

TMO_s	Transitition Metal Oxides
Uv-Vis	Ultraviolet-Visible
Uv	Ultraviolet
Vb	Valence Band
Vl	Visible Light
W	Tungsten
Xrd	X-Ray Diffraction
Zn	Zinc
Zno	Zinc Oxide
0 D	Zero-Dimensional
1 D	One-Dimensional
2 D	Two-Dimensional

LIST OF SYMBOL

A	Concentration Of Solution
Ao	Initial Concentration
Å	Armstrong
k	Rate Constant
k	Molar Absorption Coefficient
s	Scattering Coefficient
R	Absolute Reflectance Of The Layer
d_{hkl}	Interplanar Spacing
µm	Micron Meter
λ	Lambda
n	Integer
Ɵ	Degree
g	Grams
O_i	Oxygen Interstial
Zn_i	Zinc Interstitial
M	Molarity
hr	Hours
Wo_x - Zno	Tungsten oxide - Zinc Oxide Hybrid Particles
Wo_x	Tungsten Oxide Particles
$^{\cdot}OH$	Hydroxyl Radical
mins	Minutes

ml	Mililiter
e^-	Electrons
h^+	Hole
O^{2-}	Superoxide Anion Radicals

SINTESIS DAN KARAKTERISASI TUNGSTEN OKSIDA - ZINK OKSIDA PARTIKEL HIBRID DAN KAJIAN FOTOPEMANGKIN DALAM PENYINGKIRAN RhB PEWARNA

ABSTRAK

Kajian mengenai prestasi fotopemangkin dalam penyingkiran pewarna organik telah dilakukan secara meluas. Namun, kajian mengenai mekanisme penyingkiran menggunakan hibrid semikonduktor fotomangkin yang mempunyai teras dengan nilai jurang kecil semikonducktor yang dikupelkan dengan lapisan luar yang mempunyai nilai jurang lebar jarang dikaji oleh penyelidik. Dalam penyelidikan ini, partikel WO_x (semikonduktor nilai jurang kecil, 2.80 eV) telah disintesis terlebih dahulu menggunakan kaedah mendapan larutan. Keputusan XRD menunjukkan partikel tersebut terdiri daripada partikel WO_3 dan partikel WO_2 (WO_x, x = 2, 3). Kekurangan efisiensi pancaran oleh partikel WO_x pada gelombang 401 nm, 511 nm dan 696 nm telah dijangka dalam RTPL analisis kerana WO_x merupakan jurang tidak langsung semikonduktor. Apabila dibandingkan dengan penyepuhlindapan partikel WO_x (650°C untuk 4 jam), partikel WO_x yang tidak melalui penyepuhlindapan menunjukkan prestasi yang lebih baik dalam aktiviti fotopemangkin dengan kecekapan penyingkiran sebanyak 27.60 % berbanding penyepuhlindapan partikel WO_x dengan hanya 8.53 % di bawah sinaran ultraungu untuk 80 minit. Seterusnya, partikel WO_x tanpa penyepuhlindapan telah dimasukkan dalam larutan zink nitrat untuk deposit zink oksida. Prestasi fotopemangkin oleh partikel-partikel tersebut yang telah disediakan dengan menggunakan berbeza (i) kepekatan zinc nitrat tetrahydrat (0.08 M, 0.12 M, 0.50 M dan 1.00 M) dan (ii) waktu pemendapan (4 jam, 24 jam. 48 jam dan 72 jam) telah dikaji. Umumnya, prestasi fotopemangkin oleh partikel WO_x di bawah sinaran ultraungu telah berkurang kerana zink oksida yang telah dideposit. Namun, ia telah dikenal pasti bahawa dengan peningkatan kepekatan zink nitrat tetrahydrat dan waktu pemendapan telah membantu dalam aktiviti fotopemangkin menjadi lebih baik untuk partikel hibrid. Ujian skavenger telah dijalankan pada WO_x – ZnO partikel hibrid yang telah disintesis pada 72 jam. Ujian tersebut menunjukkan bahawa reaktif spesis dalam penyingkiran pewarna RhB adalah elektron dan $^{\cdot}OH$ radikal bebas. Melalui keputusan ini, mekanisme penyingkiran pewarna RhB oleh WO_x – ZnO partikel hibrid telah dibincang.

SYNTHESIS AND CHARACTERIZATION OF TUNGSTEN OXIDE - ZINC OXIDE HYBRID PARTICLES AND THEIR PHOTOCATALYTIC STUDY IN REMOVAL OF RhB DYE.

ABSTRACT

There are widely research has been done on the photocatalytic performance in organic dye removal. However, study regarding photodegradation mechanism by hybrid semiconductor photocatalysts with a narrow band gap core semiconductor coupled with a shell layer of wide band gap semiconductor is rarely explored by researchers. In this work, the WO_x particles (narrow band gap semiconductor, 2.80 eV) were pre-synthesized using solution precipitation method. The XRD analysis shows that the particles composed of WO_3 particles and WO_2 particles (WO_x, $x = 2, 3$). The poor emission efficiency of WO_x particles at wavelength of 401 nm, 511 nm and 696 nm is expected in RTPL analysis as WO_x is an indirect band gap semiconductor. As compared to annealed WO_x particles (650°C for 4 hours), the unannealed WO_x particles shows better photocatalytic activity with photodegradation efficiency of 27.60 % than annealed WO_x with only 8.53 % under UV irradiation for 80 minutes. Subsequently, the unannealed WO_x particles were immersed into zinc nitrate solution at required synthesis condition for the deposition of ZnO. The photocatalytic performances of these particles prepared using different (i) concentration of Zn nitrate tetrahydrate (0.08 M, 0.12 M, 0.50 M and 1.00 M) and (ii) deposition duration (4 hours, 24 hours, 48 hours and 72 hours), were studied. Generally, the photocatalytic performance of WO_x particles under UV irradiation was retarded with the deposition of ZnO. However, it is noted that the increase of concentration of Zn nitrate tetrahydrate and deposition duration generally provided better photocatalytic activity for the hybrid particles. The scavenger test was performed on WO_x – ZnO hybrid particles synthesized at 72 hours. The study suggests

that the reactive species for RhB dye removal were electrons and OH^- free radicals. Based on these findings, the photodegradation mechanisms of RhB dye by WO_x – ZnO hybrid particles is proposed.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The environmental problem is the main concern in the world in order to maintain quality of life of people. One of the main environmental problems is water pollution. Water pollution occurs when harmful chemicals from factories, industrial and domestic waste containing organic pollutants are discharged directly into the rivers, lakes and streams without undergoing wastewater treatment process. These activities not only cause dangerous effect to the aquatic and marine life, but it will eventually affect human health as it will pollute fresh water supply. Owing to these factors, fresh water has become a competitive resource for humans.

In particular, one of the common sources of organic pollutants in wastewater is untreated organic dyes. Organic dyes have been widely used especially in the paints, inks, textile and paper industries to enhance the appearance of product. Dyes are divided into two general classifications which are natural dyes and synthetic dyes. Natural dyes are matter that extracted from the natural resources such as in plants. For example, brown dyes are obtained from the maple trees whereas black color dyes are extracted from the logwood and soot. The application of natural dyes in industry are limited due to the flexibility of natural dyes to be used only in certain type of fabrics such as natural silk, wool and linen. The lack of natural resources that can be extracted as dyes also limited in amount that been the main reason towards the use of synthetics dyes. (Gulrajani, 2001). The use of these natural organic dyes would not cause any threat to the human and environment as they would decompose naturally, either by sun or microbes in later stage.

Synthetic dyes have several chemical classes such as anthraquinone, indigoid, azo, triphenlmethyl (trityl) and phthalocyanine derivatives. Amongst all of these classes, azo derivates are the major dyes that used in industrial application. For instances, Congo red, Acid Orange 7, Rhodamine B and Reactive black are common chemical dyes that used in industry (Oros et al., 2004). Despite the wide range of color and flexibility that offer by the synthetic dyes, these dyes demonstrated good chemical stability due to complex aromatic molecular structure. Attribute to this property, these synthetic dyes are difficult to decompose naturally from the water. The complex structures of synthetic dyes cause them to be resistant to decolorize even when expose to light.

Apart from textile industrial, other sectors such as agriculture industry and domestic waste also contributes to the water pollution. Generally, the presence of poisonous materials in wastewater contains numerous toxic substances such as cyanides, alkaline cleaning agents, degreasing solvents, oil, fats and metals (Noor et al., 2016). Existences of these harmful compounds can make water pollution become severe over the years.

Water pollution increases with year due to the growing of textile industries, agriculture industry and human population. The presence of hazardous dye compounds and the toxic raw materials that used to manufacture dyes, even in low concentration, could affect the visibility of water where these organic pollutants obstruct sunlight (Pekakis et al., 2006). This will hinder the photosynthesis process that eventually affects the aquatic life. Apart from that, decomposing of dyes compounds will produce carcinogenic by-products that can cause harmful effects on human health.

There are several development that been done by the researchers in order to manage water pollution cause by organic pollutants. These methods are chemicals method such as coagulation and the Fenton process. Coagulation method is effective, quick and compact but the disadvantage of coagulation method often produces excess amount of chemical sludge that create problems during disposal (Behel and Kumar, 2013). Meanwhile, Fenton process is considered to be the most advanced oxidation process in removal efficiencies due to the formation of strong hydroxyl radicals (OH^-) and the oxidation of Fe^{2+} to Fe^{3+} with formation of ferric hydro complexes which simultaneously acts as coagulant and oxidant (Lin et al., 2008). Nevertheless, this technique leaves a yellowish color in treated wastewater.

Advanced oxidation process (AOP) using semiconductor materials as photocatalysts, is the recent technique that gaining considerable attention of scientists. This is proven by the increase of number of publications from 1125 before year 2000 to 2905 in year 2016 as shown in Figure 1.1. The photocatalyst process does not produce secondary pollutants. Instead, it degrades the dyes efficiently. In the presence of UV or visible light irradiation, optical excitation causes generation of electrons and holes in semiconductor materials. Subsequently, these charge carriers interact with the solvent to produce chemically active hydroxyl free radicals and superoxide anions free radicals. The formation of these free radicals attacks specific bonds of the organic compounds. This leads to the decomposition of organic compounds. The reaction eventually decomposes the organic compounds into less harmful byproducts such as water, carbon dioxide and mineral acids (Chan et al., 2013). The common understanding of semiconductor photocatalyst is illustrated in Figure 1.2. AOP using semiconductor photocatalysts provides alternative way for engineers and scientists for wastewater treatment.

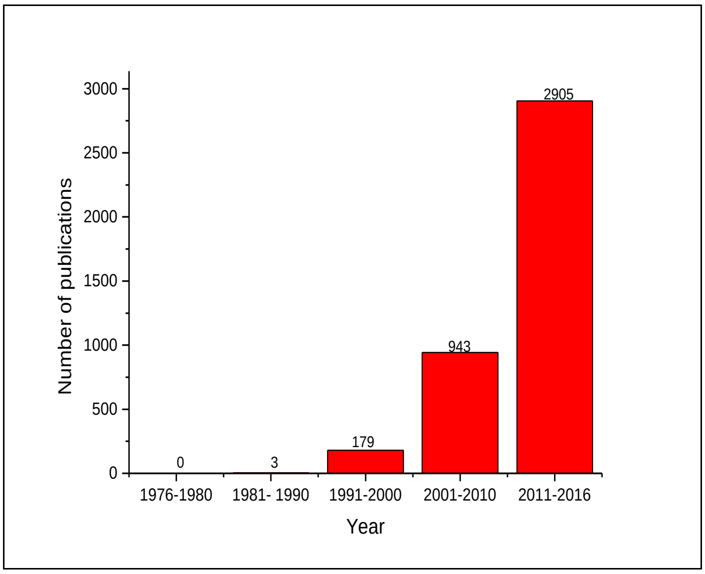

Figure 1.1: The number of publications related to semiconductor photocatalysts (Source of data: Web of Science).

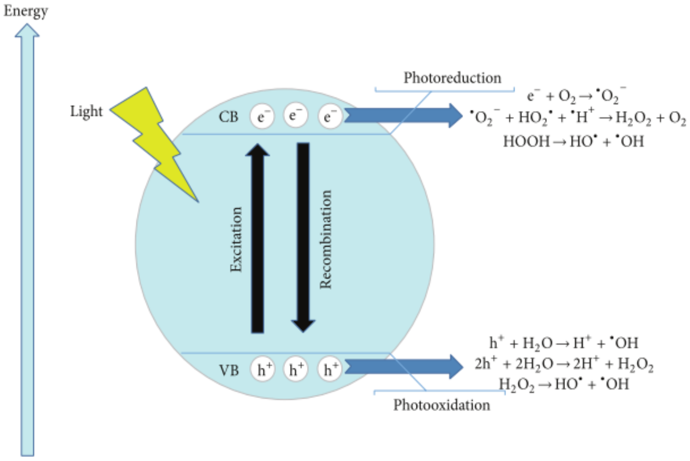

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Figure 1.2: Schematic of photodegradation mechanism of organic compounds by semiconductor photocatalysts (Johar et al., 2015).

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1.2 Problem statement

Wide band gap semiconductors such as ZnO (3.37 eV) (Lozada et al., 2015) and TiO_2 (3.20 eV) (Dette et al., 2014) are well known photocatalysts for organic pollutants removal under UV light irradiation. However, these semiconductors have weak photocatalytic activities under visible light attribute to their wide band gap (Al-Sabahi et al., 2016). The constraint in visible light absorption by wide band gap semiconductors restrict their application because solar spectrum only consist 5% of UV light (Johar et al., 2015). Another problem that occurs in wide band gap semiconductors photocatalysts is the rapid recombination of charge carriers. The photogenerated electron-hole pairs tend to recombine within pico-seconds in the semiconductor materials (Colmenares et al., 2009). The recombination will produce unproductive heat (Park et al., 2016). Since there is less number of charge carriers available for the production of free radicals in the subsequent step, the rapid recombination rate will affect the efficiency of the photodegradation of dyes.

Many attempts have been made by researchers to overcome the above problems. This includes (i) coupling of semiconductor material with metal e.g. Ni – ZnO (Thein et al., 2016), Ni – TiO_2 (Xin et al., 2008) and Fe- TiO_2 (Concrete, 2014); (ii) doping e.g. Cu on $InVO_4$ (Wetchakun et al., 2017), ZnO doped SnO (Rashad et al., 2014) and Ag doped TiO_2 (Harikishore et al., 2014) and Fe doped ZnO (Bousslama et al., 2017) (iii) coupling of semiconductor material with another semiconductor material (nanocomposites). It is notably that most of the studies were conducted by coupling a narrow band gap semiconductor (shell) onto a wide band gap semiconductor (core). The common examples are WO_3 – TiO (Cybula et al., 2014), CuS- TiO_2 (Khanchandani et al., 2016a) and ZnO – SnO_2 (Tripathy et al., 2007).

It is worth mentioning that not many research have been done to study the photodegradation efficiency of nanocomposites composes of coupling a wide band gap semiconductor (shell) onto a narrow band gap semiconductor (core). The photodegradation mechanism of organic pollutants (dyes) by these nanocomposites, whether the coupled wide band gap semiconductor is in the form of particle, porous layer or shell layer, is yet to be established.

1.3 Research objectives

This project aims to assess the photocatalytic performance of WO_x (core) -ZnO hybrid particles ($x = 2$ and 3) in organic dye removal as well as to establish its photodegradation mechanism by performing scavenger tests. The band gap of WO_x is 2.5-3.1 eV (Ahmadi et al., 2014) and the band gap of ZnO is 3.37 eV (Lozada et al., 2015). To achieve this aim, the following objectives are formed:

(i) To synthesize and characterize WO_x particles, ZnO particles and WO_x (core) - ZnO hybrid particles by solution precipitation method,

(ii) To assess the photocatalytic performances of WO_x particles, ZnO particles and WO_x (core) - ZnO hybrid particles in organic dye removal under both visible light and UV light irradiation.

1.4 Project overview

This project has been divided into three phases. In first phase of the project, WO_x particles and ZnO particles were synthesized using solution precipitation method. Part of the semiconductor photocatalysts were annealed at 650^oC for 4 hrs under ambient condition. The physical property, optical property and photocatalytic performance of these photocatalysts (without and with annealing) were analyzed using X-Ray diffraction (XRD), Field Effect Scanning Electron Microscopy (FESEM), Energy Dispersive X-Ray (EDX), room temperature photoluminescent (RTPL) spectroscopy and UV-Vis spectroscopy. Since WO_x photocatalyst without annealing demonstrated better photodegradation efficiency, it was used in the subsequent phase.

In second phase of the project, pre-synthesized WO_x particles without annealing were added into chemical solution (used to prepare ZnO). The aim of this process was to deposit ZnO onto the WO_x particles. Two deposition parameters were studied, i.e. concentration of zinc nitrate tetrahydrate and deposition duration. By varying the deposition parameters, ZnO could deposit onto the surface of WO_x particles in the form of (i) particles, (ii) porous layer or (iii) shell layer. These effects could change the physical property, optical property and photocatalytic performance of nanocomposites differently.

Lastly, scavenger tests were performed on WO_x particles, ZnO particles and selected WO_x-ZnO hybrid particles in order to determine the dominant reactive species that responsible for the photodegradation of organic dye under UV light and visible light, respectively. The finding helps to establish the photodegradation mechanism of organic dye particularly the WO_x-ZnO hybrid particles.

1.5 Thesis outline

There are five chapters that compiles in this thesis. First chapter describes the introduction, problem statement and research objectives of this project. Second chapter covers the background study of WO_x particles, ZnO particles, recent development of photocatalysts and their applications. Chapter three presents the materials and procedures used in synthesizing the ZnO particles, WO_x particles and WO_x - ZnO hybrid particles. This chapter also discuss the working principles and sample preparation of characterization techniques used in this project. Chapter 4 discusses the characterization results and photodegradation mechanism of ZnO particles, WO_x particles and WO_x - ZnO hybrid particles. Chapter 5 concludes with the key findings of this research work and suggest future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides overview of water pollution globally as well as in Malaysia. In addition, it reviews types of organic pollutants commonly found in wastewater, its impact to environment and the recent developments of wastewater treatment techniques available in the market. Next, this chapter also discussed the use of semiconductor photocatalysts for organic pollutants, principle of photocatalytic oxidation, general mechanism of photocatalysis, methods in improving photocatalytic activity, comparison in efficiency of organic dyes degradation between core-shell semiconductor and semiconductor particles of photocatalyst. Lastly, synthesis of WO_x particles and ZnO particles and analyzed their properties and crystal structure is presented.

2.2 Water pollution

Preserving water quality is essential as water is one of the most important component for living things such as human, animals and plants. However, due to the growing population, demand for fresh water supply also increase. Level of polluted water around the world has risen to the concern number as according to the United Nations, estimate there are around 783 million populations still use contaminated water in daily life and around 2.5 billion that does not have sufficient hygiene routine (WHO, 2015). Proper treatment of wastewater will help to keep sewage and other contaminants from entering the water supply.

There are three main sources of water. The first pollutants are a natural source that comes from the volcanic area which rarely in the case. The other two sources are domestic waste which comes from the household areas and industrial waste which contributes from the factories and production area. High water pollution mainly recorded from the industrial waste because generation of contaminated materials that consists of acids, metals and alkalis (Alrumman et al., 2016). Commonly, disposal of the chemical waste may contributes from the textile industries (Jaganathan et al., 2014) and heavy metal industries (Chowdhury et al., 2016).

The health hazard arise from the water pollution caused by dyes was studied by (Halder and Islam, 2015) at Dhaka, Bangladesh that deal with environmental issues regarding water pollution. It reveals that water pollution in the area is highly polluted and the amount of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and turbidity is higher than the standard limit. Majority of people in that area has skin problem which in contact with the water in the area that identify to be highly alkaline. This related to the use of caustic soda and alkalis soda ash in textile industry that has been discharged in the river without treatment.

Growing country such as Malaysia makes it has no exception from facing with the water pollution problems. Demand of fresh water supply increase with population. It is noted that the highly polluted area in Malaysia are located especially in industrial area. One of the contributors to the water pollution in Malaysia is textile industry. Textile industry especially in Kelantan and Terengganu has undeniably provides economic growth but there are adverse effect of this industry which is the release of harmful chemical to the streams (Pang and Abdullah, 2013). The level of polluted water in Malaysia has been monitor by government body which is Department of Environment (DOE). DOE reported the status of river quality 2005 to 2012 as shown in Figure 2.1.

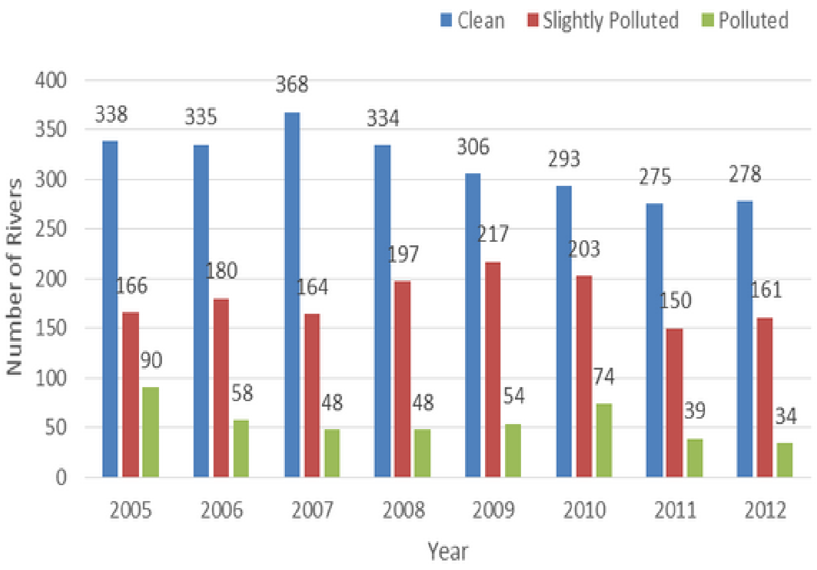

Figure 2.1: Number of rivers polluted in Malaysia from year 2005 to 2012 (Environment, 2012).

As mentioned previously, dyes residual that leached in the stream will lead to harmful effect. However, the applications of dyes in industry are continuously used due to high intensity colour that is able to impart by dyes. The colour presence is due to the chromophores and auxochromes structure. The chromophores structure is used to control the colour of dyes meanwhile the auxochromes is used for enhancing the colour of dyes. Generally, the colour can only be able to impart if there are combination of these structure. Specifically, dyes can be classified according to their application and mainly, xanthene dyes is one of the predominantly dyes that used in the textile industry production. One example of xanthene dyes are Rhodamine B (RhB).

RhB is an organic dye which dissolves easily in water, producing pink colour solution. It is an important representative of xanthene dyes. Industries widely used RhB for manufacturing of textile, paper, printing, pharmaceutical and food. It is also a well-recognized water tracer fluorescent and therefore it is usually used as a dye laser material because of its good stability. Unintentionally taken of RhB dye could cause allergic to the respiratory system, skin and eyes of human being. Research shows that RhB dye could be decomposed via N-de-ethylation process as illustrated in Figure 2.3 (Al-Kahtani, 2017).

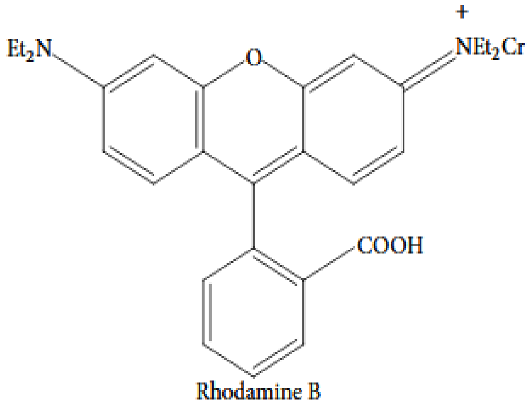

Figure 2.2: Molecular structure of RhB dye (Yan et al., 2016)

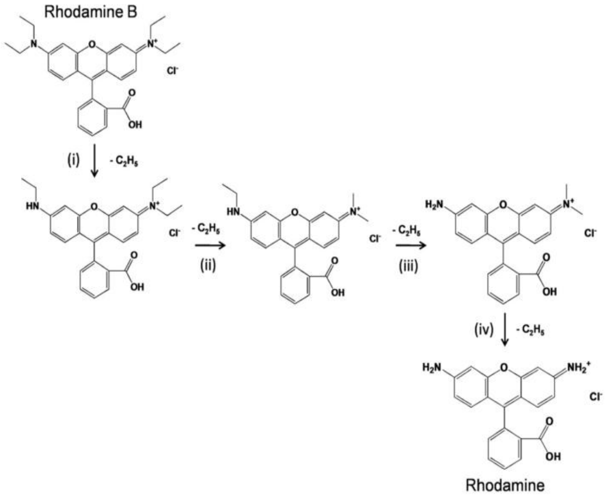

Figure 2.3: N-de-ethylation of RhB molecule under visible light irradiation (Sridharan and Park, 2013)

2.3 Methods for current wastewater treatment

Synthetic dyes are chemically stable. They are difficult to breakdown into smaller molecules which are less harmful to environment. Release of these dyes into the stream is highly undesirable. This is because they will produce carcinogenic products such as benzidine, napthalene and other aromatic compounds even these dyes molecules could be breakdown (Zaharia et al., 2009). These by-products are threat to the human and aquatic life. Several methods have been proposed in treating these wastewater e.g. adsorption, sedimentation, chemical analysis, chemicoagulation, biological methods, water chlorination and advanced oxidation process (Vijayaraghavan, et al, 2013)

2.3.1 Chemicoagulation method

This method is used to separate between the dissolved and suspended particles in the water. It is applied prior to the sedimentation and filtration stages. Naturally, the suspended particles have negative charges. They tend to repels each other and eventually remain as suspension in water. These will cause a problem during the sedimentation and filtration stage later. Chemicoagulation process overcomes those forces that stabilizing the suspended particles by adding chemical such as alum. As a consequence, the particles collide and develop flocs that can be set and expel through the sedimentation process. Nonetheless, this technique produces secondary pollutants attributed to the creation of colloids in wastewater (Pirkarami and Olya, 2017).

2.3.2 Biological method

Biological methods are economic alternatives approach as compared to other methods. Generally, biodegradation methods use fungal decolourisation (e.g., Phanerochaeta chrysosporium and Trametes), microbial degradation or bioremediation system to treat this industrial wastewater. For anaerobic biological method, bacteria that been used are Eubacterium, Cclostridium and Clostridium to remove the azo dye solutions by splitting the azo bond, producing aromatic amines as by-product. Dyes from other classes have been successfully decolourized by aerobic bacteria although they does not totally degrade. The reason they are not totally degraded is because of their xenobiotic nature (Lokesh and Kiran, 2013).

2.3.3 Water Chlorination

Water chlorination treatment is a conventional way that has been used in treating wastewater for years. The strength of this method is because chlorination of wastewater is able to reduce the effect cause by the untreated wastewater such as oxidation of metal ions, elimination of colours and odours, and destruction of cyanides and phenols. Chlorine is added to the water with the intention to eliminate bacteria and other microorganism. However, main drawback of this method is that it takes long processing time and requires hazardous reactive chemicals (Daneshvar et al., 2004).

2.3.4 Advanced oxidation process

Advanced oxidation process (AOP) is referred to the process oxidative treatment. It is commonly used to treat toxic effluents from the industrial. The priority of this process is to remove the organic or inorganic materials by oxidation via reactions with hydroxyl radicals. Under AOPs, the regularly used processes are Fenton-based processes, ozonation or photocatalysis using semiconductor materials. The Fenton-based process and ozonation have its own drawbacks. For Fenton process, the effectiveness for generation of hydroxyl radical is only at acidic pH condition. Thus, it is restricted in use in wastewater treatment (Deng and Zhao, 2015). Ozonation process provides no germicidal or disinfection residual that prevent re-growth of bacterial. The drawbacks of the Fenton and ozonation processes have led the development of AOP based on semiconductor materials.

2.4 Semiconductor photocatalysts

This process utilizes semiconductor materials and light to decompose organic pollutants. The photodegradation mechanism involves in photocatalytic are oxidation and reduction. This process converts the organic compounds into less harmful by-products. Thus, it has attracted a great deal of attention for its simplicity, efficiency, low cost and low secondary pollution. Other applications of semiconductor photocatalysts are water splitting (Jafari et al., 2016) for the production of hydrogen gas, inactivation of bacterial and fungal, and solar cell application.

Photocatalysis is a process that speeds up the production of hydroxyl radical ($^{\cdot}OH$) with the presence of catalyst to produce less harmful molecules or at least makes it's biodegradable. Presence of catalyst and photons (e.g, UV and visible light) can trigger the formation of OH^- radicals. In photocatalysis, generation of hole and pairs plays important roles. The frequently uses catalyst in photocatalysis is wide band gap semiconductor, i.e. TiO_2. TiO_2 (3.2 eV) has been extensively studied by the researches because it has strong oxidizing capability and low cost (Wang et al., 1997). The photocatalytic performance of TiO_2 is evaluated by the formation of the photogenerated charge carriers which are holes and electrons. These charged carriers are developed during the irradiation of UV. The formation of holes in the valence band diffuse to the TiO_2 surface and react with adsorb water molecules to form $^{\cdot}OH$ radical. These photogenerated holes and $^{\cdot}OH$ radicals oxidize the organic molecules near or on the surface of TiO_2. Electrons in the conduction band react with oxygen molecule in the air to generate superoxide radical anions (O^{2-}) (Fujishima, 2012). These O^{2-} free radicals could also decompose organic pollutants. The photocatalytic mechanism is displayed in Eq. (2.1) to Eq. (2.5).

$$TiO_2 + hv \rightarrow e^-_{cb} + hv^+_{vb} \qquad \text{Eq. (2.1)}$$

$hv^{+} + OH^{-}_{(surface)} \rightarrow {}^{\cdot}OH$ Eq. (2.2)

$hv^{+}_{vb} + H_2O_{(adsorbed)} \rightarrow {}^{\cdot}OH + H^{+}$ Eq. (2.3)

$e^{-}_{cb} + O_{2(adsorbed)} \rightarrow O_2^{-}$ Eq. (2.4)

$\text{dyes} + {}^{\cdot}OH \rightarrow \text{Degraded product}$ Eq. (2.5)

Apart from TiO_2, another frequently used wide band gap photocatalyst is ZnO. ZnO has a band gap of 3.37 eV, which is similar to the band gap of TiO_2. Thus the performance of ZnO in organic pollutants removal is expected to be quite similar to the TiO_2. Wide band gap of ZnO makes it as a UV driven photocatalyst. Use of ZnO as photocatalyst can only be performed when wavelength of optical excitation source is smaller than 380 nm. The performance of wide band gap semiconductor photocatalysts under sunlight is rather limited as the solar spectrum contains only 3-5% of UV radiation. The performance of the photocatalyst towards visible light application and low recombination rate can be improved through several modifications. Generally, there are four strategies could be used to improve photodegradation efficiency of wide band gap semiconductor photocatalysts, i.e. noble metal loading, ion doping, sensitization, and semiconductor coupling.

2.4.1 Noble metal loading

Noble metal (Pd, Ag, Pt, Au) have been used as photocatalyst because of good absorption of visible light related to the surface plasmon resonance (SPR) effect. Surface plasmon resonance effect is the oscillation which able to propagate at the region between the semiconductor and metal. This SPR effect improves the photogenerated carriers by the transfer of electron from noble metal to the semiconductor. Another preference of noble metal as photocatalyst is due to Schottky junction that formed at region between the metal and semiconductor. Schottky barrier developed internal electric field that assist the movement of electron and holes to moves in opposite direction (Bumajdad and Madkour, 2014).

Ni et al reported that loading of noble metals such as Rh, Pd, Au, Pt, Ni, Ag and Cu could enhance photodegradation efficiency of TiO_2 as shown in Figure 2.7 (Ni et al., 2007). This is because the Fermi level of noble metal is lower than TiO_2. The excited electrons of TiO_2 could be transferred to the noble metals that deposited on the surface of TiO_2. This transfer of electron will prolong the charge carrier lifetime. Thus, this allows more holes diffuse to the surface of TiO_2 particles, producing more hydroxyl free radicals. Although deposition of Pt could improve the photocatalytic performance of TiO_2, it is an expensive noble metal. This increases the cost of raw materials and hinders its usage for organic pollutants removal.

2.4.2 Ion doping

Transitional metal ion doping is another method in enhancing photocatalytic activity of photocatalysts. According to the study done by Wetchakun et al., (2017), Cu doping on $lnVO_4$ improved visible-light-induced photocatalytic activity. In fact, $lnVO_4$ sample that doped with 1.0 mol% of Cu has the highest photocatalytic activity as displayed in Figure 2.8. Cu, as dopant, has the ability to lengthen the optical absorption toward longer wavelengths and has a larger surface area. The result also showed that a higher concentration of Cu doping decreased the distance of the trapping sites of electrons in $lnVO_4$ sample. This somehow increased the photocatalytic efficiency of the doped $lnVO_4$. The disadvantages of doping is it reduces the reduction and oxidation potentials of the excited charge carriers that eventually has a poorer efficiency of photocatalytic reaction.

2.4.3 Sensitization

Dye-sensitized photocatalysts could enhance the photocatalytic properties. The selected dyes were attached to the surface of semiconductor to increase the efficiency of electron transfer. During irradiation with visible light, the excited electrons from the dyes were injected to the conduction band (CB) of the semiconductor for the catalytic reaction (Ni et al., 2007). Disadvantages by sensitization method of semiconductor is that it is self destructive which means it can be self degraded due to the natural state of organic dyes that have inclination toward redox reaction process.

2.4.4 Coupling with another semiconductor

Coupled semiconductor, which is also known as hybrid semiconductor, is another method that is used in increasing the photocatalytic activity of semiconductor photocatalysts. Justifications of using coupled semiconductor in the photocatalyst application are (i) to prolong the photo-response by coupling of wide band gap to narrow band gap and (ii) to hinder the recombination process by the photogenerated carrier with the movement of electron to the wide band gap of conduction band that positioned lower in the coupled system. This approach makes the hydrogen production using visible light possible. As shown in Figure 2.4, there are three possible configurations of semiconductor coupling, i.e. (i) type I (core: wide band gap semiconductor, shell: narrow band gap semiconductor), (ii) type II (shell: wide band gap semiconductor, core: narrow band gap semiconductor) and (iii) type III (same as type II but the band position is located further and is called broken-gap situation) (Marschall, 2014).

Until now, most of the researches have been worked on type I semiconductors. In this scenario, careful selection of semiconductors coupling is needed. This is because semiconductors with different energy levels could affect the transfer of electrons and holes to other semiconductor. Eventually, it increases the charge separation duration (Kuo and Lin, 2004). Some of examples are discussed in details in the following sections.

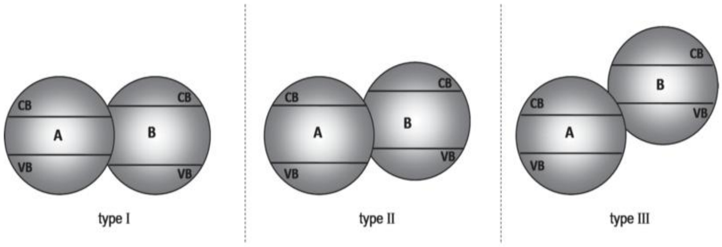

Figure 2.4: Different types of heterojunction in coupled semiconductor, A = semiconductor 1, B = semiconductor 2, (i) type I (core: wide band gap semiconductor, shell: narrow band gap semiconductor), (ii) type II (shell: wide band gap semiconductor, core: narrow band gap semiconductor) and (iii) type III (broken-gap situation) (Marschall, 2014).

Generally, there are two different arrangement regarding joining of two semiconductor together. That is the different between coupled and capped semiconductor (core-shell). The different structures result in different interfacial charge transfer. In coupled semiconductor, the particles are in contact with each other and enable for electron and hole to complete the oxidation and reduction process that occur on the surface particles. For capped semiconductor (core-shell) it only allow one charge to carried out the reaction on the surface of the particles while the other charge is trapped inside the core structure.

Coupled semiconductor can be synthesis by co-precipitation in the solution medium. Example coupled semiconductor is (TiO_2 – $NiTiO_3$) which both of these oxide semiconductor have wide band gap. Coupling of these wide band gaps has good photodegradation efficiency in degradation of methylene blue. The CB of the $NiTiO_3$ is positioned at -4.70 eV which is more negative than TiO_2 (-4.21 eV) which makes TiO_2 can trap the photogenerated electron during electron injection while the holes moves towards opposite direction and accumulate at $NiTiO_3$ that eventually improve the charge separation (Xin et al., 2008).

Core – shell structure is prepared by pre-synthesized the core materials and followed with the second layer with controlled deposition. Example of core-shell structure is TiO_2@SiO_2. The formation of band structure by core shell makes the electron generated from TiO_2 to the conduction band of SiO_2 while the holes remains in the valence band of TiO_2 during illuminated with light. This separation hinders the recombination and enhanced photocatalytic activity as proposed by Gholami and Bazarganipour, (2015). The increase in charge separation efficiency makes core shell structures are more favourable compared to the normal coupling by semiconductor. Next section will discussed thoroughly the example of core-shell semiconductor and the comparison for photodegradation efficiency between core shell structure and particles structure for photocatalyst application.

2.4.4.1 TiO_2@CuS core-shell

Khanchandani et al reported the photocatalytic performance of TiO_2 particles and TiO_2@CuS core shell particles in removal methylene blue (MB) dye (Khanchandani et al., 2016). These particles were synthesized via surface functionalization route. As shown in Figure 2.12, rod-shape particles were obtained for both types of samples. The average length and diameter of these particles are 700 ± 15 nm and 100 ± 6 nm, respectively. As compared to TiO_2 particles, a rougher surface was found on the surface of TiO_2@CuS core shell particles. This was attributed to the deposition of CuS particles, forming a shell layer on the surface of TiO_2 particles.

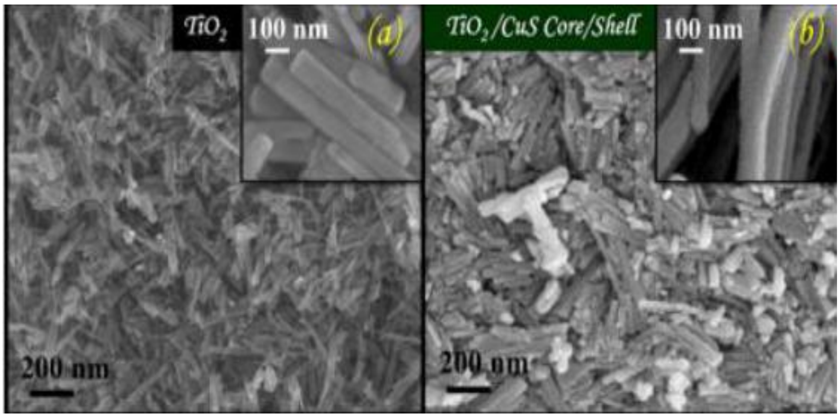

Figure 2.5: FESEM images of (a) TiO_2, and (b) TiO_2/CuS core/shell particles (Khanchandani et al., 2016).

The photocatalytic efficiency of TiO_2/CuS core/shell particles was better as compared to TiO_2 particles. As summarized in Table 2.1, core shell structure exhibit higher photocatalytic efficiency (90%) in removal of MB dye under visible light irradiation (λ = 420 nm, t = 60 min) compared to TiO_2 particles (13%). The rate constant (k) of core shell structure is one order magnitude larger ($k = 3.6 \times 10^{-2}$ min^{-1}) as compared to TiO_2 particles (1.9×10^{-3} min^{-1}). The core-shell particles had a better photocatalytic due to its structure that could confine the electrons in one component and holes in the other component. This retarded the recombination of charge carriers and allowed more free radicals to be generated for organic dye decomposition. Another factor that gives impact on photocatalytic performance of the core shell structure is the present of type II of heterojunctions in TiO_2@Cus core/shell structure. The type-II core/shell nanostructures result in a spatially indirect transition, which occurs at longer wavelengths that cannot be accessible with one of the two materials (either core or shell) alone.

Table 2.1: The photocatalytic properties of TiO_2 particles and TiO_2@CuS for core shell particles in removal of MB dye under visible light irradiation (Khanchandani et al., 2016)

Sample	Shell thickness (nm)	Band gap (eV)	Photocatalytic efficiency (%)	Rate constant (min^{-1})	CB (eV)	VB(eV)
TiO_2	-	3.18	13	1.9×10^{-3}	-0.28	2.90
TiO_2/CuS core /shell	20	2.62	90	3.6×10^{-2}	-0.28, -0.39	2.90, 1.61

2.4.4.2 NiO@ZnO core-shell

Another case study for the effect of coupling was done by the Thein et al., (2016). In their work, NiO was coupled with ZnO nanorods using solution precipitation technique. However, the photocatalytic activity of NiO@ZnO core-shell particles was not as expected as shown in Figure 2.6. The core shell structure demonstrated a lower photocatalytic efficiency (12%) in removal of RhB dye under UV light irradiation (λ = 325 nm, t = 75 min) compared to ZnO particles (98.8%). The rate constant (k) of core shell structure is one order magnitude larger (k = 0.0015 min^{-1}) as compared to ZnO particles (0.058 min^{-1}). The present of localized surface plasma resonance (LSPR) effect was the cause of this observation as it consumed most of the charge carriers which were needed for the formation of free radicals.

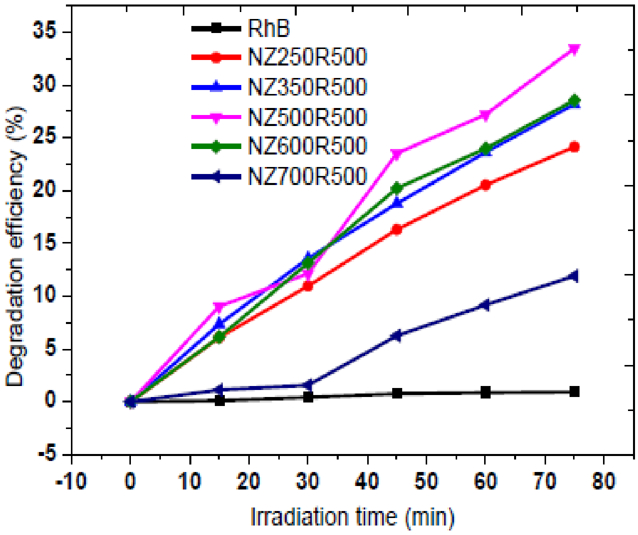

Figure 2.6: Performance of ZnO particles and NiO@ZnO core-shell particles in degradation of RhB dye under UV light (Thein et al., 2016).

2.4.5 Effect of main parameter on photocatalytic activity

The photocatalytic activities of semiconductor photocatalysts could easily affect by their synthesis condition and the testing condition. This section describes key parameters that influence the photocatalytic efficiency of semiconductor photocatalysts.

2.4.5.1 Effect of heat treatment (calcinations temperature)

Calcination temperature has great influence in the photocatalytic activity as it is able to modify the morphology and crystalline structure of materials. Cybula et al synthesized WO_3/TiO_2 coupled semiconductor using hydrothermal technique as shown in Figure 2.7. 8 mol% WO_3 loaded on TiO_2 was calcined at different temperature (Cybula et al., 2014). As shown in Table 2.2, calcination temperature below 500°C produced WO_3 (8%)/ TiO particles with high amorphous content, which was about 60%. The calcination temperature was rise up from 500°C to 900°C, crystalline structure was increased to 80%. However, there was a significant drop of photoactivity from 1.27×10^{-2} min $^{-1}$ to 0.81×10^{-2} min $^{-1}$ when the WO_3 (8%)/TiO_2 annealed at

800°C and 900°C. When sample was heated above the optimum calcination temperature, it generated a higher number of defects in the oxide structure that acted as charge carrier recombination centers. Generally, as reported by Yang et al., (2004) that structure of pure tungsten oxide was become more stable when it is heated above the 600°C. The crystal structure was transformed to the monoclinic structure. Thus, it shows different calcinations temperature plays critical role in enhancing photocatalytic activity.

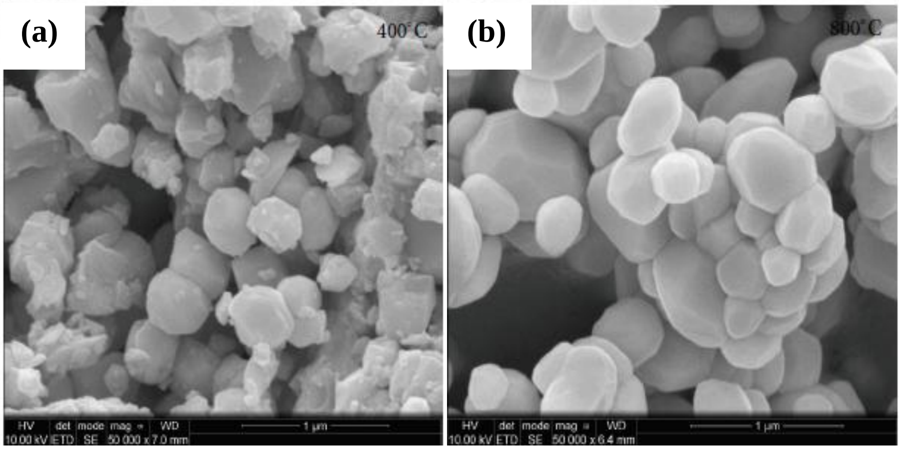

Figure 2.7: FESEM images of WO_3(8%)/TiO_2 particles calcinated (a) at 400°C and (b) 800°C (Cybula et al., 2014)

Table 2.2: The effect of calcinations temperature with the amount of crystallinity and amorphous (Cybula et al., 2014)

Sample	Calcination temperature (°C)	Crystalline phase content (%)	Amorphous phase content (%)
WO_3 (8%) without heat treatment	-	42	58
WO_3 (8%)	400	39	60
WO_3 (8%)	500	77	23

WO_3 (8%)	600	76	22
WO_3 (8%)	700	75	25
WO_3 (8%)	800	80	20
WO_3 (8%)	900	82	18

2.4.5.2 Effect of initial concentration of the dyes

Increasing the concentration of initial dyes will lower the photodegradation efficiency. The reason of this is because more attachment of dyes at the active sites of photocatalyst reduces the reaction and production of hydroxyl radicals which eventually reduce the photocatalytic activity. In addition, the increasing of concentration of dyes makes the fully attachment of dyes cause low energy or phonon to irradiate at the surface of photocatalyst. The low energy phonon that arrives at surface of photocatalyst makes the promotion of electron from the valence band to conduction band reduces which relates to lower the degradation efficiency.

2.4.5.3 Effect of pH

The compounds in wastewater could cause large variation of pH values in wastewater. The pH values in aqueous solution has huge impact in the photocatalytic activity because it affects the (i) charge surface of the photocatalyst, (ii) the amount of adsorption of dyes on the surface of photocatalyst which is critical reaction for the photocatalytic reaction to takes place and (iii) the amount of agglomeration of nanoparticles photocatalyst.

Akpan et al reported the effect of TiO_2 degradation of azo dyes with low pH and high pH value (Akpan and Hameed, 2009). At lower pH<6, the strong adsorption of dyes on the surface of TiO_2 was recorded. This was attributed to the electrostatic force between the positively charged TiO_2 and the dyes. However, at higher pH in alkaline