SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
UNIVERSITI SAINS MALAYSIA

ASSESSING OPTICAL AND PHOTOCATALYTIC PROPERTIES OF METAL COUPLED TiO_2 PARTICLES

By
ATIIKAH BINTI ISHAK
Supervisor: Dr Sivakumar A/L Ramakrishnan
Co-Supervisor: Assoc Prof Ir Dr Pung Swee Yong

Dissertation submitted in partial fulfillment
of the requirements for the Degree of Bachelor Engineering with Honours
(Materials Engineering)

UNIVERSITI SAINS MALAYSIA

JUNE 2018

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitles "**Assessing Optical and Photocatalytic Properties of Metal Coupled TiO_2 Particles.**" 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.

Name of Student : Atiikah binti Ishak Signature :

Date : 25th June 2018

Witnessed by,

Supervisor : Dr Sivakumar A/L Ramakrishnan Signature :

Date : 25th June 2018

ACKNOWLEDGEMENTS

I am grateful to my supervisor, Dr Sivakumar A/L Ramakrishnan, whose expertise, understanding, generous guidance, and support make it possible for me carried out this project. It was pleasure working with him. I am truly indebted to my co-supervisor, Assoc Prof Ir Dr Pung Swee Yong for finding out time to keep track with my progress and also offered support in this project.

I also would like to thanked all technician and staff that have involved in this project directly and indirectly; specially to Mr Mohammad Azrul bin Zainol Abidin for helping me to run the ICP-OES test, Mrs Haslina bt Zulkifli that help me to run for UV Spectrophotometer, Mr Muhammad Khairi bin Khalid and Mr Abdul Rashid bin Selamat for SEM test and also Mr Mohamad Zaini bin Saari for XRD test. Besides that, thanks for the help and guidance from post graduate students, Lee Anh Thi, Yuri and Qurratul Aini.

Finally, I also placed my gratitude to all my course mates and friends that assist me throughout this project and this whole academic year. Last but not least, special thanks to my family for their encouragement and moral support throughout my research work. Without their support, I would not be able to complete this project with ease.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

eV	electronVolt
C_o	Initial concentration
1 D	One - dimensional
λ	Wavelength

LIST OF ABBREVIATIONS

NHE	Normal Hydrogen Electrode
UV	Ultraviolet
Vis	Visible
IL	Ionic Liquid
VLA	Visible Light Active
LUMO	Lowest Unoccupied Molecular Orbital
HUMO	Highest Occupied Molecular Orbital
DOS	Density of State
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
ICP-OES	Inductively Coupled Plasma –Optical Emission Spectrometry
PE	Photocatalytic efficiency
RhB	Rhodamine B
e^-	Electron
h^+	Hole

MENGENAI SIFAT-SIFAT OPTIK DAN FOTOPEMANGKIN OLEH LOGAM GANDINGAN BERSAMA ZARAH-ZARAH TITANIUM DIOKSIDA

ABSTRAK

Titanium dioksida (TiO_2) terkenal dengan prestasi fotopemangkin yang cemerlang dalam bahan pencemar organik dan penyingkiran logam berat. Walau bagaimanapun, pemendapan logam berat (selepas penyingkiran dari larutan) pada permukaan zarah TiO_2 mungkin sama ada memperbaiki atau merosakkan prestasi zarah TiO_2 dalam kemerosotan pencemar organic seterusnya. Dalam projek ini, logam berat terpilih telah dimendapkan ke permukaan zarah TiO_2 di bawah pendedahan cahaya UV dan cahaya nyata. Kecekapan penyingkiran setiap ion logam oleh zarah TiO_2 telah ditentukan. Pada amnya, zarah TiO_2 lebih berkesan dalam pengalihan logam berat di bawah sinaran UV daripada penyinaran cahaya nyata kerana ia mempunyai ruang yang lebar. TiO_2 menyingkirkan ion-ion Cu dari larutan adalah yang paling berkesan, diikuti oleh Ag, Ni, Cd, Mn dan Cr. Ion-ion logam ini dimendapkan di permukaan zarah TiO_2, menghasilkan zarah TiO_2 yang digabungkan dengan logam. Dalam kajian fotopenurunan pewarna RhB, zarah Cr-, Cu- dan Mn-TiO_2 merendahkan pewarna RhB dalam kadar yang lebih cepat (kadar pemalar yang lebih besar) daripada zarah TiO_2 dengan logam yang lain. Diperhatikan bahawa penurunan pewarna RhB mengikuti tindak balas kinetik urutan pertama tanpa mengira jenis logam yang digabungkan dengan zarah TiO_2. Pemantulan logam zarah TiO_2 yang digabungkan telah diukur. Zarah Ni-TiO_2 didapati mempunyai pemantulan tertinggi tetapi kadar fotopenurunan yang perlahan. Batasan untuk menggunakan zarah TiO_2 dalam kegunaan sebenar untuk rawatan sisa air kerana sisa air bukan sahaja mengandungi bahan pencemar organik tetapi juga ion logam berat yang boleh merosakkan prestasi zarah TiO_2.

ASSESSING OPTICAL AND PHOTOCATALYTIC PROPERTIES OF METAL COUPLED TIO_2 PARTICLES

ABSTRACT

Titanium dioxide (TiO_2) is famous of its excellent photocatalytic performance in organic pollutants and heavy metal removal. However, deposition of heavy metal (after removal from the solution) on the surface of TiO_2 particles might either improve or deteriorate the performance of TiO_2 particles in subsequent degradation of organic pollutants. In this project, selected heavy metals were deposited onto the surface of TiO_2 particles under both UV and visible light exposure. The removal efficiencies of each metal ions by TiO_2 particles were determined. Generally, TiO_2 particles were more effective in removal the heavy metals under UV light than visible light irradiation attributed to its wide bandgap. The TiO_2 particles removed Cu ions from solution most effectively, followed by Ag, Ni, Cd, Mn and Cr. These metal ions were deposited onto the surface of TiO_2 particles, producing metal-coupled TiO_2 particles. In the photodegradation of RhB dye study, Cr-, Cu- and Mn-TiO_2 particles degraded the RhB dye in faster rate (larger rate constants) than the other metal-coupled TiO_2 particles. It was noted that the degradation of RhB dye followed 1^{st} order kinetic reaction regardless the type of metal coupled to TiO_2 particles. he reflectivity of metal coupled TiO_2 particles was measured. It was found that Ni-TiO_2 particles have the highest reflectance but slow photodegradation rate. Limitation to use TiO_2 particles in real application for waste water treatment as waste water is not only contained organic pollutants but also heavy metals ions that could deteriorate the performance of TiO_2 particles.

INTRODUCTION

1.1 Background

Titanium dioxide (TiO_2) is an excellent semiconductor photocatalyst to break down organic compounds into less harmful by-products such as water and carbon dioxide. In 1977, an experiment done by Frank and Bard have shown that TiO_2 has increasing interest in environmental applications (Fujishima et al., 2000). TiO_2 has the most productive photoactivity, the best stability and the lowest cost (Kazuhito et al., 2005). It has been used as a white pigment from earliest times, therefore its safety to people and the atmosphere is assured. TiO_2 is one of the most promising materials due to its high oxidation efficiency, nontoxicity, high photostability, chemical inertness and environmentally friendly to our nature (Daghrir et al., 2013). In the past decade, nanostructured materials have been of great interest as catalyst and other application because of their unique textural and structural characteristics.

This research highlights the importance of TiO_2 photocatalyst for environmental applications. A number of research studies have focused on the development of a new TiO_2 photocatalyst able to absorb visible light as a main part of solar spectrum. The limitations of pure TiO_2, which require the use of UV light and its high photogenerated electrons and holes recombination rate, can be overcame by introducing foreign species into the TiO_2 matrix. The doping of TiO_2 with either cationic or anionic metals and coupling TiO_2 with other narrow bandgap semiconductors are the major approaches that have been reviewed. Up to now, the successful applications of TiO_2 photocatalyst under visible light for water and waste water treatment were carried out

at the laboratory scale. Future research should be focused on the use of novel TiO_2 photocatalyst (doped TiO_2 or photosensitization TiO_2) for large-scale applications.

1.2 Problem Statement

In reality, the waste water contains large amount of organic and inorganic pollutants such as heavy metals (e.g. Copper, Cadmium, Nickel, Magnesium, Silver and Chromium). These heavy metals tend to deposit onto the surface of TiO_2 particles and remove from wastewater. Nevertheless, deposition of these heavy metals might improve or deteriorate the performance of TiO_2 particles in subsequent photocatalytic to decompose organic pollutants (e.g. organic dye). Till to date, systematic study on the coupled of heavy metals and its subsequent photocatalytic activities to decompose organic pollutants by TiO_2 particles has not been properly investigated.

In this project, various metal ion solutions with same concentration were prepared. These metal ions were deposited by TiO_2 particles under UV irradiation. The deposition of TiO_2 particles on these metal ions from solutions were calculated via the ICP-OES measurement. Next, the photocatalytic performance of metal-coupled TiO_2 particles in Rhodamine B degradation was determined under UV and visible light irradiation.

1.3 Research Objectives

In order to achieve the project aim, two objectives have to be fulfilled. The objectives are listed below:

i) To investigate the properties and photocatalytic activity of TiO_2 particles for heavy metal removal.

ii) To determine the effect of metals coupling on TiO_2 particles particularly on their photocatalytic efficiency and performance in RhB dye removal.

1.4 Scope of Research

This project has been divided into two phases. In the first phase of the project, the physical properties and optical properties of TiO_2 particles were characterized using Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD) analysis and UV-Visible Spectrophotometer. The photocatalytic performance of TiO_2 particles in RhB dye removal and also in heavy metals was assessed using the method of absorption from difference time intervals.

1.5 Dissertation Outline

There are five chapters that compiles in this dissertation. First chapter describes the introduction, problem statement and research objectives of this project. Second chapter covers the background study of TiO_2 semiconductor, photocatalysis, effect by coupling with heavy metals, recent development of photocatalysts and their applications. Chapter three presents the materials and procedures used in synthesizing the TiO_2. 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 TiO_2 with heavy metals. Chapter 5 concludes with the key findings of this research work and suggestions for the future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter reviews the development of photocatalytic TiO_2. It also discusses on the use of semiconductor photocatalysts for organic pollutants removal, general mechanism of photocatalysis, methods in improving photocatalytic activity, comparison in efficiency of degradation between core-shell structure and particles of photocatalyst.

2.2 TiO_2 structures and properties

TiO_2 is an n-type semiconductor (Zhou et al., 2018), it exists in three different polymorphs; anatase, rutile and brookite as illustrated in Figure 2.1 (Pelaez et al., 2012). The most stable form of TiO_2 is rutile. All three polymorphs can be synthesised in the laboratory and typically the metastable anatase and brookite will change to the thermodynamically stable rutile upon calcination at temperatures exceeding ~600 °C (Pelaez et al., 2012). Titanium (Ti^{4+}) atoms are co-ordinated to six oxygen (O^{2-}) atoms, making TiO_6 octahedral.

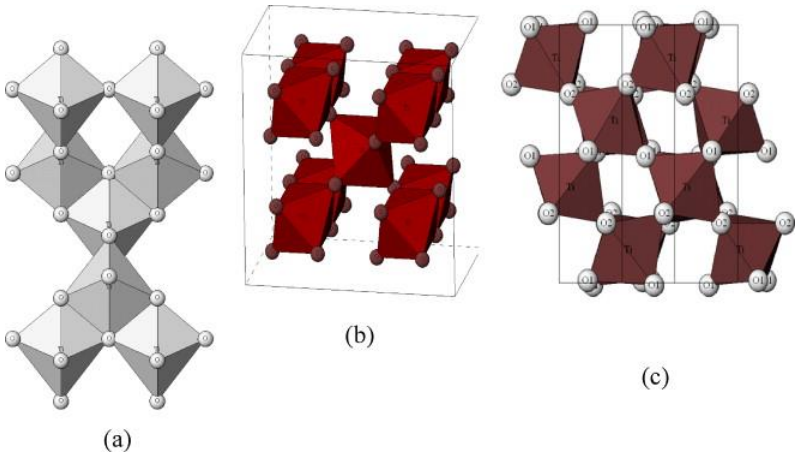

Figure 2.1: Crystalline structures of TiO_2; (a) Anatase resulting in tetragonal structure, made up of corner (vertical) sharing octahedra which form (0 0 1) planes. (b) Rutile resulting in octahedral share edges at (0 0 1) planes to give a tetragonal structure and (c) Brookite resulting both edges and corners are shared to give an orthorhombic structure (Pelaez et al., 2012).

The band gap of TiO_2 is 3.2 eV for anatase, 3.0 eV for rutile, and ~3.2 eV for brookite. Anatase and rutile are the main polymorphs and their key properties are summarized in the Table 2.1.

Table 2.1: Physical and structural properties of anatase and rutile TiO_2 (Pelaez et al., 2012).

Property	Anatase	Rutile
Molecular weight (g/mol)	79.88	79.88
Melting point (°C)	1825	1825
Boiling point (°C)	2500–3000	2500–3000
Light absorption (nm)	<390	<415
Mohr's Hardness	5.5	6.5–7.0
Refractive index	2.55	2.75
Dielectric constant	31	114
Crystal structure	Tetragonal	Tetragonal
Lattice constants (Å)	$a = 3.78$	$a = 4.59$
	$c = 9.52$	$c = 2.96$
Density (g/cm^3)	3.79	4.13
Ti—O bond length (Å)	1.94 (4)	1.95 (4)
	1.97 (2)	1.98 (2)

Photocatalysis is a science of retaining catalyst that is operated for moving up chemical reactions that needs or involves light (Khan et al., 2015). A photocatalyst is a material that is capable of absorbing light and producing electron-hole pairs that allow chemical transformations of the reaction contain. There are two types of photocatalytic reaction i.e. homogeneous photocatalysis and heterogeneous photocatalysis (Khan et al., 2015). Table 2.2 shows the optical bandgap and their band edges position in Normal Hydrogen Electrode (NHE) diagram of the common semiconductor photocatalysts. Generally, based on its optical bandgap, two main categories of semiconductor photocatalysts, i.e. (i) UV responsive and (ii) visible light responsive are reported in literature. The generation of electrons and holes in the band gap of these semiconductor photocatalysts is illustrated in Figure 2.2.

Table 2.2: Common semiconductors used in photocatalytic processes (Daghrir et al., 2013).

Semiconductor	Band gap (eV)	Wavelength (nm)	Light absorption	Valance band (V vs NHE)	Conduction band (V vs NHE)
TiO_2	3.2	387	UV	+3.1	-0.1
SnO_2	3.8	318	UV	+4.1	+0.3
ZnO	3.2	387	UV	+3.0	-0.2
ZnS	3.7	335	UV	+1.4	-2.3
WO_3	2.8	443	Visible	+3.0	+0.4
CdS	2.5	496	Visible	+2.1	-0.4
CdSe	2.5	729	Visible	+1.6	-0.1

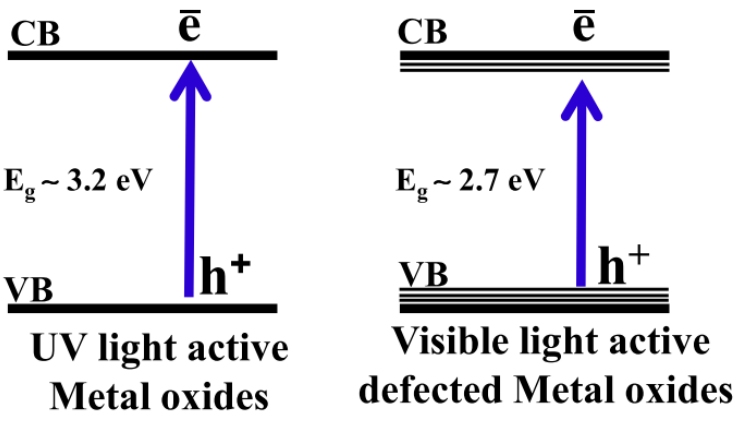

Figure 2.2: UV light active metal oxides and visible light active metal oxides showing photo excitation (Khan et al., 2015).

TiO_2 is the most efficient photocatalyst. It is cheap and demonstrated excellent chemical however no absorption in the visible region is possible attributed to its wide bandgap (Kazuhito et al., 2005). A typical photocatalytic study of TiO_2 in degradation of RhB under various wavelengths of light sources is shown in Figure 2.3. In this study, TiO_2 achieved best photodegradation efficiency under sunlight. The inset shows the time trend of the Rhodamine B absorption spectrum, upon irradiation with the yellow lamp. The spectral modifications with time suggest the occurrence of colored conversion intermediates, which would cause an underestimation of the dye degradation. Limited to negligible transformation of Rhodamine B was observed upon irradiation without TiO_2, under all conditions. It was noted that dyes have the ability to inject an electron into the conduction band of a semiconductor when photo-excited (Barbero and Vione, 2016).

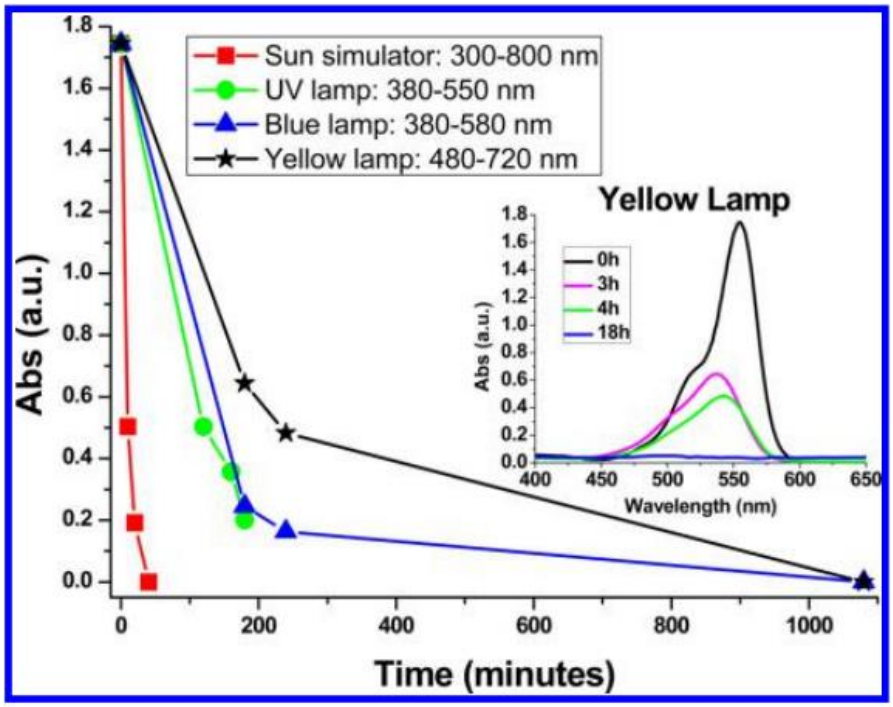

Figure 2.3: Time trend of Rhodamine B (initial concentration 20-25 µM evaluated at the wavelength of maximum absorption) under different irradiation conditions, in the presence of $2gL^{-1}$ TiO_2.

The reactivity of TiO_2 powder investigated was enhanced by the addition of small amounts of Pt which initiates an effective charge separation of the photo-formed electrons and holes. The highly dispersed TiO_2 species prepared and encapsulated exhibit high photocatalytic activities due to the high activities of their charge transfer excited states. Metal coupled into TiO_2 powder such as Cr, has been found to modify electronic state of TiO_2 that results in the shift of absorption band to longer wavelength regions. The extent to the shift depends on the type and concentration of the metal (Anpo, 1997).

(Ghasemi et al., 2009) have investigated that transition metal such as copper, nickel, manganese, silver and chromium doped with nanoparticles have smaller crystalline size and higher surface area than pure TiO_2. It is proven that dopant ion in the TiO_2 structure caused significant absorption shift into the visible region as shown in the XRD analysis of Figure 2.4. The results of photodegradation of Acid Blue92 (AB92) in aqueous medium under UV light showed that photocatalytic activity of TiO_2 nanoparticles was significantly improved by the occurrence of some transition metal ions.

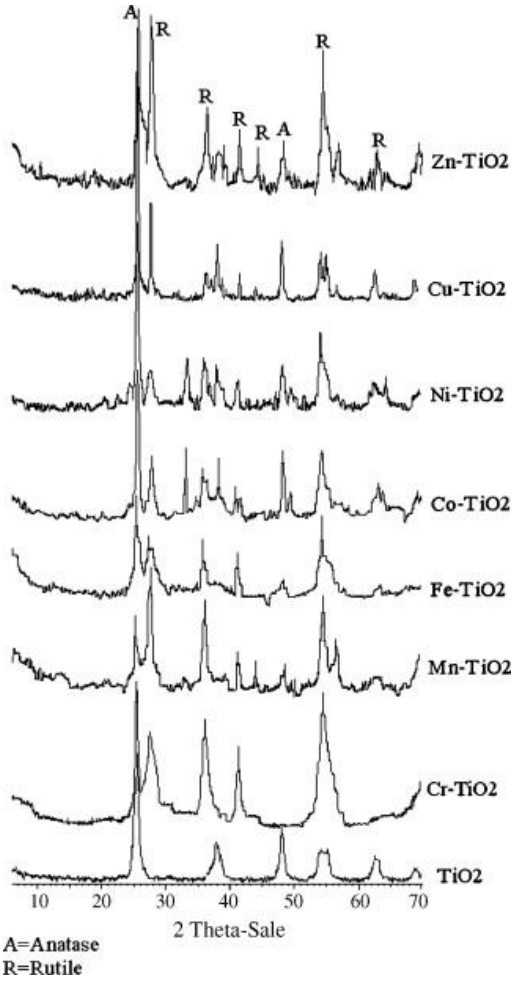

Figure 2.4: XRD patterns of the pure and transition metal doped TiO_2 particles in an ionic liquid (IL) and calcined at 500°C (Ghasemi et al., 2009).

TiO_2 samples were prepared by calcination $Ti(OH)_4$ in air from 500 to 800°C. With increasing calcination temperature and calcination time, the anatase TiO_2 transformed slowly to rutile phase (Zhang et al., 2008). The anatase phase in the bulk begins to transform into the rutile phase at only 550°C, while the surface region maintains the anatase phase when the calcination temperature was below 680°C (Zhang et al., 2008).

2.3 Strategies for improving TiO_2 photoactivity

Several approaches have been used for improving the photocatalytic efficiency of TiO_2. They can be summarized as either chemical adjustments by incorporation of additional components in the TiO_2 structure or morphological adjustments such as growing surface area and porosity. Although visible light active (VLA) TiO_2 photocatalysts involve chemical adjustments, their overall efficiencies have been improved by adjusting the semiconductor morphology (Pelaez et al., 2012).

The most frequently used TiO_2 morphology is that of monodispersed nanoparticles where the diameter is organized to give paybacks from the small crystallite size (high surface area, reduced bulk recombination) without the detrimental effects related with very small particles (surface recombination, low crystallinity). One dimensional (1D) TiO_2 nanostructures (nanotubes, nanorods, nanowires, nanobelts, nanoneedles) have been also designed by hydrothermal synthesis but high emphasis was given to TiO_2 self-assembled nanotubular films developed by electrochemical anodization on titanium metal foils.

Benefits of such structures is their controlled porosity, tailored morphology, low recombination at grain boundaries and vectorial charge transfer that result in improved performance in photoinduced applications, mainly in photocatalysis. Another exciting use of TiO_2 nanotubes in photocatalytic applications is the evolution of freestanding flow-through membranes (Pelaez et al., 2012).

Another strategy for improving TiO_2 photoactivity is by sol-gel method and consequently heated to precipitate fine anatase crystals from TiO_2 based powders

doped with a small amount of SiO_2. The SiO_2 doped TiO_2 powders were preserved chemically with aqueous NaOH. Infrared reflection spectra indicated that the action reduced the amount of SiO_2 in the powders. The photocatalytic property of the powders was particularly improved by the treatment, and the powders presented advanced activity than the undoped TiO_2 powders (Kasuga et al., 1997).

The greatest photocatalytic activity was perceived by a mixture of rutile (15%) and anatase (85%) prepared by high-temperature hydrolysis of aqueous $TiOSO_4$ solution (Kolen'ko et al., 2004). Photocatalysis has been regarded as one of greatest solutions use of sunlight to produce hydrogen from water and to eliminate organic pollutants from the environment and that TiO_2 nanomaterials was treated as the major photocatalyst for these resolution (Liu et al., 2017).

The efficiency of photocatalytic reactions, including the decomposition of contaminants and water splitting for H_2 production for environmental purification, depends on three factors, that are the efficient optical absorption by the photocatalyst, efficient use of the charge carriers and efficient construction of charger carriers, in the photocatalytic processes. UV light and visible light establish roughly 47% of solar irradiation which creates better target photocatalytic efficiency (Tang et al., 2008).

2.4 Formation of TiO_2

Different bulk and surface crystalline phases of TiO_2 samples were prepared by the process of calcination of $Ti(OH)_4$ in air from about 500°C to 800°C. As illustrated in Figure 2.5, the anatase of TiO_2 transforms to the rutile phase when the calcination temperature or calcination time is being increased (Zhang et al., 2008). With a combination of surface-sensitive practices, the photocatalytic activity of TiO_2 was found to be connected to the surface-phase structure, and can be improved when anatase TiO_2 nanoparticles are highly dispersed on the surface of rutile TiO_2 to form anatase–rutile surface phase junctions (Zhang et al., 2008).

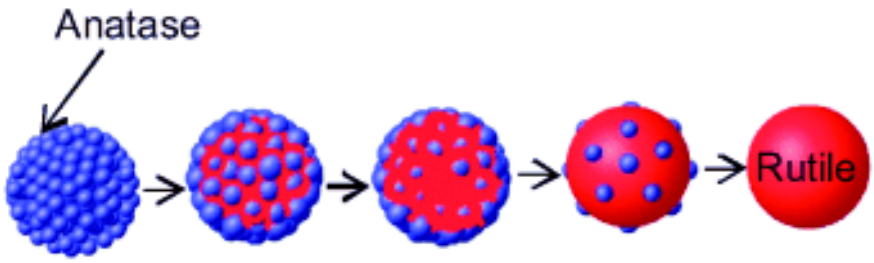

Figure 2.5: Calcination progression from anatase become rutile phase (Zhang et al., 2008).

When the surface phase of TiO_2 is directly exposed to light and the reactants, contributes to photocatalysis and solar energy adaptation because the photocatalytic reaction or photoelectron transformation takes place only when photoinduced electrons and holes are presented on the surface. The crystalline phase of TiO_2 particles in the surface region unlike from the bulk region, predominantly when TiO_2 in transition stage of the phase transformation from anatase to rutile. A relationship between the surface phases of TiO_2 and its photocatalytic is a great impact, but has endured to the

characterizing the surface phase of TiO_2, mainly of TiO_2 nanoparticles, which have been useful as photocatalysts and catalysts (Zhang et al., 2008).

A higher photocatalytic action can be reached for a TiO_2 photocatalyst with a surface junction made between anatase and rutile TiO_2, anatase TiO_2 nanoparticles were deposited on rutile TiO_2 particles by a wet-impregnation method, and then the TiO_2 powder was calcined up to 400 °C to transform the deposited TiO_2 on the rutile surface into the anatase phase while observance the bulk still in the rutile phase. The impregnation technique was repeated (the loading of anatase deposited on the surface of the rutile particles was roughly 5 wt % for each time) to get the samples with different quantities of anatase phase on the surface of the rutile TiO_2 particles (Zhang et al., 2008).

2.5 Function of Metal Oxides such as TiO_2

From the recent research of (Khan et al., 2015) metal oxides can be used as a photocatalyst to prevent fogging of glass and decompose toxic organic compounds. As illustrated in Figure 2.6, applications of metal oxides are such as environmental remediation, solar cells, nanoelectronic devices, biological uses, sensors, clean energy production and photovoltaic applications (Khan et al., 2015).

Figure 2.6: Possible applications of metal oxides (Khan et al., 2015).

Previous research has also shown that metal oxides can be used as a photocatalyst to prevent fogging of glass and even split water into hydrogen and oxygen decompose toxic organic compounds and also photovoltaics. Thus, they are of excessive technological importance in areas of environmental remediation, storage, hydrogen manufacture and electronic industries. The heterogeneous photocatalysis is also being actively explored as a promising antibacterial, self-cleaning and deodorization system. The uses of such photocatalytic practice are generally required for the purification of waste water, by removal of bacteria and other pollutants, as this can extract water reusable (Khan et al., 2015).

It has been informed that the photodegradation rate increases as the light intensity increases during photocatalytic degradation response. Previous experimental analysis clearly designate that the UV irradiation reasons a higher rate of degradation than irradiation with sun light. This happen due to high intensity of light which is appropriate for the excitation of plenty electrons from the valence band to the

conduction band of the metal oxide semiconductor (Dina Mamdouh and Mona Bakr, 2011).

2.6 Hybrid semiconductor photocatalysts

Hybrid semiconductor photocatalysts significantly improve the photocatalytic efficiency by reducing the recombination rate of the photogenerated electron-hole pairs and existing potential applications in water splitting, photovoltaic devices and organic decomposition. (Pelaez et al., 2012). In photocatalytic systems, coupling between different semiconductors with different energy levels is another exciting method, which has established great interest in the past decade. Coupling TiO_2 with others semiconductors was planned to prolong the absorption wavelength range into the visible light region and to improve the charge carrier recombination in individual photoelectrodes. It was shown by previous research that the good matching of the conduction band and valence band of the two semiconductors could ensure an effective transfer of the charge carriers from one band to another.

As illustrated in Figure 2.7, a small band gap semiconductor having more negative conduction band level. When this semiconductor coupled with TiO_2 semiconductor, the electron can be inserted from the small band gap of the semiconductor to the TiO_2. The energy gap between corresponding band levels allows the transfer of charge carriers from one particle to its neighbour and reassures the separation between the electron-holes photogenerated.

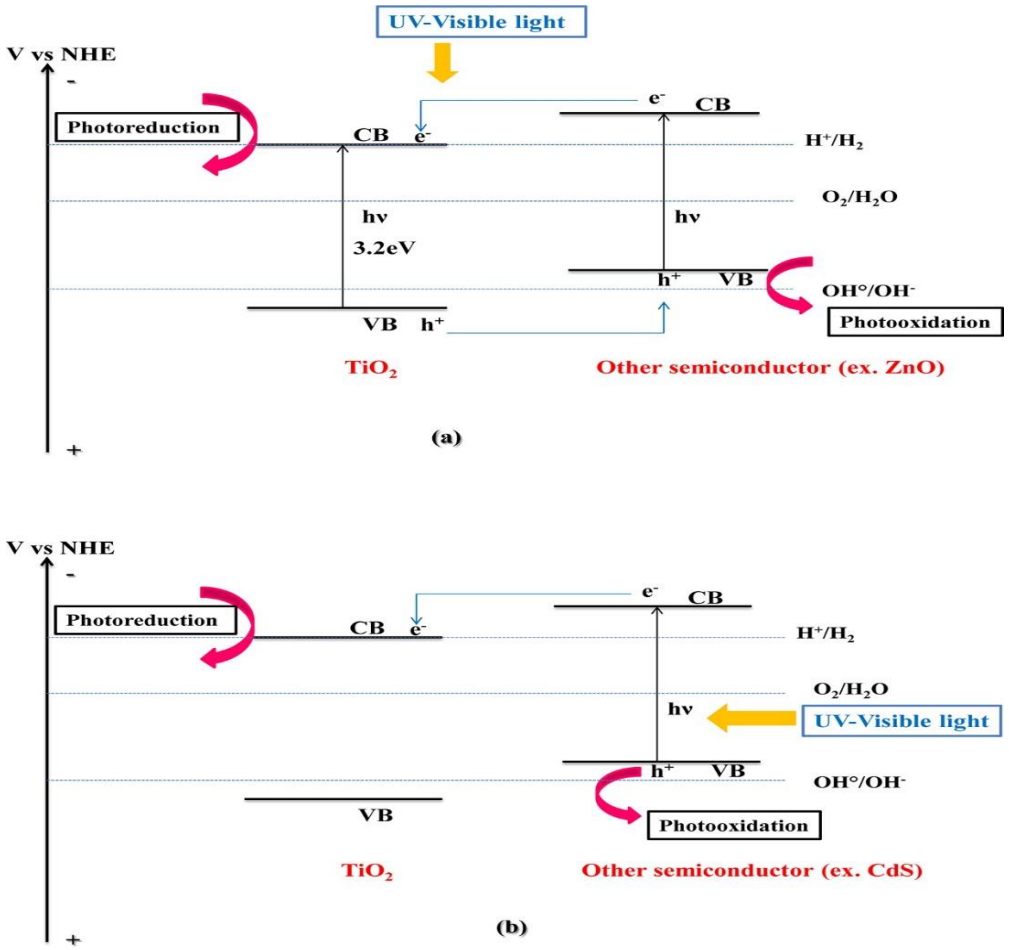

Figure 2.7: Vectorial transfer of electrons-holes (e^-/h^+) in coupled semiconductor system. (a) Under visible irradiation, only the sensitizer is excited and the electrons photogenerated will flow into the conduction band of the adjacent TiO_2. (b) If the valence band of the sensitizer is more cathodic than that of TiO_2, the holes photogenerated behind in the valence band of the sensitizer (Daghrir et al., 2013).

The effective transfer of electrons and holes photogenerated between TiO_2 and the semiconductor influenced by the difference between the conduction band and the valence band potentials of the two semiconductors. As shown in Figure 2.8, when the conduction band of TiO_2 is more anodic than the corresponding band of the semiconductor, then transfer of electron may happen.

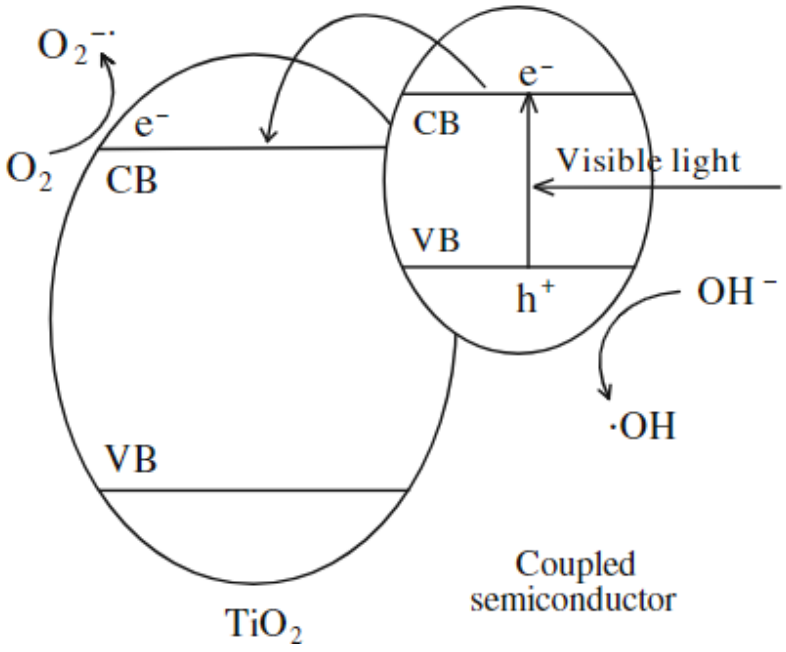

Figure 2.8: Schematic diagram for the visible light photocatalytic mechanisms of TiO_2 coupled with a semiconductor (Yang et al., 2011).

These combinations were also considered as encouraging materials to improve a high efficiency photocatalyst activated with visible light. They can also compensate the disadvantages of the individual components and persuade a synergistic effect such as an efficient charge separation and enhancement of photostability. Thus, visible light driven coupled photocatalysts that can decay organic material are of great attention (Pelaez et al., 2012). The existence of a metal–semiconductor interface encourages operative charge separation carrier allocations which afterward increase photocatalytic effect (Dina Mamdouh and Mona Bakr, 2011).

2.7 Surface sensitization of TiO_2

Visible light photocatalytic activity can be realize using surface sensitization because it is one of an effective method of modifying TiO_2 (Yang et al., 2011). As depicted in Figure 2.9, the adsorption of visible light could be greatly improved by using dye sensitizer. As a result, more photogenerated holes and electrons were generated, allowing subsequent generation of hydroxyl free radicals and superoxide anion free radicals. These reactive species are needed for the decomposition of organic pollutants.

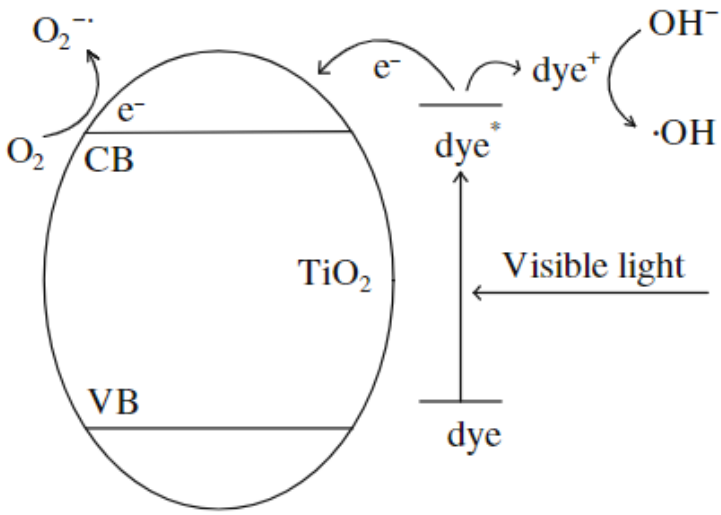

Figure 2.9: Schematic diagram for the visible light photocatalytic mechanisms of surface-sensitized TiO_2 (Yang et al., 2011).

2.7.1 Photosensitization of TiO_2 by M_XS_Y Nanoparticles

Photosensitizer is absorbed on the large surface of TiO_2 powered by high surface energy and form composite materials. Photosensitizer usually made from active compounds that can strongly absorb visible light, such as humic acid, polyunsaturated fatty acids and organics dyes. The photosensitizers excite and then

inject electrons into the conduction band of TiO_2 under visible light illumination. According to the most research on surface sensitization of TiO_2, the injection is favourable due to the more negative potential of the excited photosensitizers as compared to the conduction band potential of TiO_2 (Yang et al., 2011).

The coupling TiO_2 with CdS is highly encouraging approach in the area of investigation. Cadmium Sulfide is one of the very well-known semiconductors has a narrow bandgap of 2.4 eV. CdS has a higher conduction band and the valance band as compared to TiO_2. The conduction band potentials of TiO_2 and CdS versus Normal Hydrogen Electrode (NHE) at pH 7 are -0.5 and 0.95 V respectively (Daghrir et al., 2013).

The energy levels of the valence and conduction bands allow CdS to act as photosensitizer to generate electrons and holes and to absorb visible irradiation. Subsequently, the electrons are injected into the conduction band of the inactivated TiO_2 leaving the holes behind in the valence band of CdS. TiO_2 receives photoelectrons generated from the CdS, which could effectively prevent the recombination of photoelectrons and holes in CdS. Owing to this charge separation under visible light illumination, the couple TiO_2/CdS has been widely applied to improve the degradation of organic pollutants by photocatalytic and photoelectrocatalytic reactions (Daghrir et al., 2013).

The photocatalytic performance of the coupled semiconductors is associated to the geometry of the particles, the particle size and the contact surface between particles. These parameters intensely be influenced by the method with which the couples are arranged. Numerous core/shell type nanocrystals have been widely

investigated using different approaches. Higher temperatures, exacting inert atmosphere protection, longer times and complex reaction procedure are necessary by synthesis methods. There is probability of synthesizing nanocomposites in a short time, in air, under mild conditions and without calcination by applying ultrasound under definite conditions. For example, a core-shell configuration has been prepared with ultrasound treatment by TiO_2-coated nanoparticles (Pelaez et al., 2012).

The TiO_2 was found to be regularly coated on the surface of CdS and this led to an expansion of the nanoparticles. The creation of huge irregular aggregates was detected in the absence of ultrasound. As shown in Figure 2.10, the absorption band of CdS nanoparticles was found at around 450–470 nm in comparison with the bulk crystalline CdS which appeared at about 515 nm (Eg = 2.4 eV). The onset absorption for nanoparticles prepared under ultrasound was about 360 nm, while for the bulk it was about 385 nm (Eg = 3.2 eV) in the case of TiO_2.

It is proved that modification of TiO_2 with CdS particles spreads the optical absorption spectrum into the visible region in contrast with that of pure TiO_2. Increasing the amount of TiO_2 led to a further red-shift of the absorption band in composite photocatalysts. The red shift of spectra are typical features of core-shell nanocrystals, making from the efficient diminishing of the surface defects of core nanocrystals after covering them with higher band gap shells. The band gap of CdS employed in composite photocatalysts is lifted by an electronic semiconductor-support interaction (Pelaez et al., 2012).

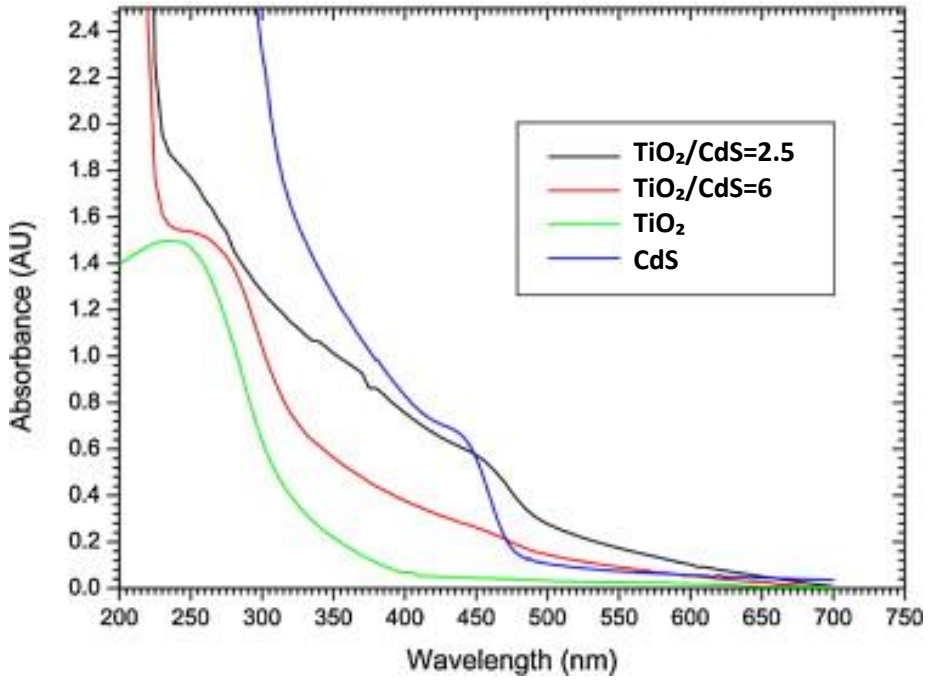

Figure 2.10: The UV-Vis absorbance spectra of pure and TiO_2 composite semiconductors (Pelaez et al., 2012).

The photocatalytic efficiency of the couple TiO_2/CdS depended on the proportion of CdS. For example, higher degradation of organic dye (more than 95%) has been verified when the TiO_2/CdS system comprising lower amounts of CdS (only 5%). In water, organic compounds were adsorbed on the CdS surface than the TiO_2, and the transfer of the electrons from the dye to CdS contributed to the degradation mechanism. Furthermore, the surrounding TiO_2 matrix protected the CdS against photocorrosion, which addressed the major problem of CdS photocatalyst in conservational application.

Photoanodic corrosion occurred when the photogenerated holes did not react quickly with the water molecular or with organic pollutants. This was because CdS photocatalyst was easily oxidized by photogenerated holes. This was accompanied by

the release of Cd^{2+} into the solution and the formation of the elemental sulfur layer on the surface of the CdS (eq 2.2). This occurrence could negatively disturb the photocatalytic reactions (Daghrir et al., 2013). Figure 2.11 shows the TEM image of CdS/TiO_2 hybrid semiconductor photocatalyst and its related charges transportation in the nanostructure.

$$CdS\ (e^- + h^+) + TiO_2 \rightarrow CdS\ (h^+) + TiO_2 \quad (2.1)$$

$$CdS + 2H_2O \rightarrow H_2 + Cd^{2+} + S + 2OH^- \quad (2.2)$$

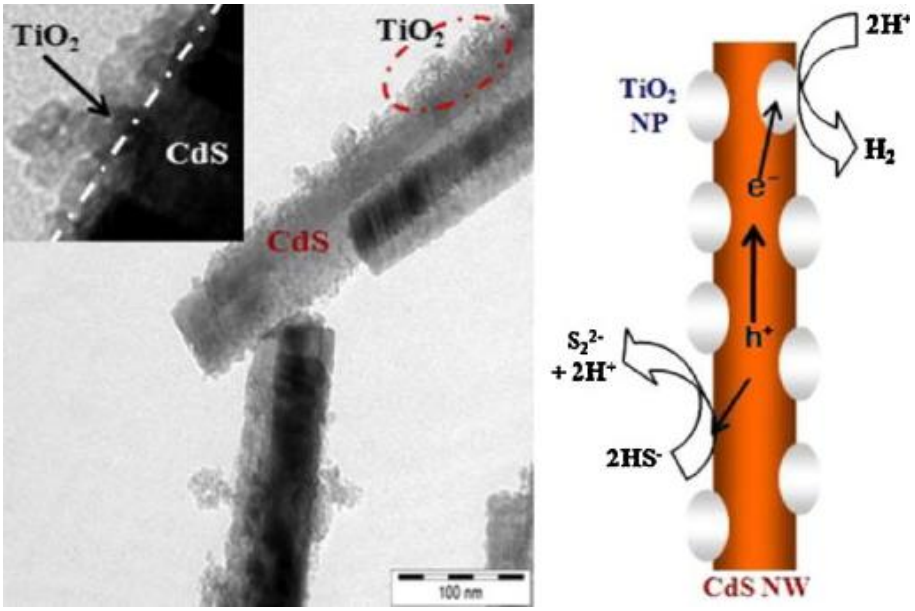

Figure 2.11: TEM and mechanistic image of the interface between CdS nanowires and TiO_2 nanoparticles. TiO_2 offer sites for collecting the photoelectrons created from CdS nanowires, allowing an efficient electron-hole separation (Pelaez et al., 2012).

Cadmium Selenide (CdSe) is another material that has been extensively used as photosensitizer in the CdSe/TiO_2 system. CdSe has a lower band gap (E_g = 1.74 eV) and has been reflected as potential material to form a composite semiconductor with TiO_2.