# STUDY ON PHOTOCATALYTIC PERFORMANCE OF RUTILE PHASED TiO2 MICRO SIZE RODS/FLOWERS FILM TOWARDS METHYL ORANGE DEGRADATION

A thesis submitted in
fulfillment of the requirement for the award of the
Degree of Master of Electrical Engineering



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*Special dedication to My…*

*Beloved husband;*
*Syaiful Ariff bin Amar@Omar*

*Son and daughter;*
*Hazim Annas and Iman Ryhana*

*Mom and mother in-law*

*Supportive families*

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# ABSTRACT

Pure rutile titanium dioxide ($TiO_2$) film was fabricated at low temperature of 150°C by hydrothermal method. $TiO_2$ film was developed on Fluorine doped tin oxide (FTO) by using titanium butoxide (TBOT) as a precursor, hydrochloric acid (HCl) and deionized (DI) water. The surface morphology of rutile phased $TiO_2$ films were studied by Field Emission Scanning Electron Microscopy (FESEM). X-ray Diffraction (XRD) was used to analyze the structural property of the films. Energy-dispersive spectroscopy (EDX) was used to verify the elemental property of the films. The photocatalytic degradation of methyl orange (MO) was observed by using UV-vis spectroscopy. The photocatalytic analysis was conducted to compare the ability of rutile phased $TiO_2$ film and P25 film (commercial $TiO_2$). The pH solution was varied from pH 3 to 10 to study the favorable pH of $TiO_2$ film. The MO concentration was varied from 5 to 15 ppm to find the limited reaction of $TiO_2$ film. The optimum amount of HCl concentration was 15.88 mol/L while the optimum amount of $TiO_2$ loading was 0.123 mol/L. The optimize reaction time was obtained at 10 hours. No degradation was observed after 10 hours. The result shows, 0.123 mol/L TBOT concentration of 1225 $mm^2$ has the highest degradation of MO. The degradation was up to 65.6 % while P25 film was 8.07 % only. MO degradation became insignificant at high concentration. From the experiments, it was found that the rutile phased $TiO_2$ has the higher photocatalytic activity in lower MO concentration and favorable in acidic environment.

# ABSTRAK

Fasa rutil filem nipis asli titanium dioksida ($TiO_2$) telah dihasilkan pada suhu rendah 150°C dengan kaedah hidroterma. Filem nipis $TiO_2$ telah dibangunkan pada florin atas didopkan timah oksida (FTO) dengan menggunakan titanium butoxide (TBOT) sebagai pelopor, asid hidroklorik (HCl) dan air ternyahion (DI). Permukaan morfologi fasa rutil filem nipis $TiO_2$ telah dikaji oleh Pancaran Medan Mikroskop imbasan Elektron (FESEM). Serakan sinar-X (XRD) digunakan untuk menganalisis ciri struktur filem nipis. Tenaga serakan spektroskopi (EDX) telah digunakan untuk mengesahkan unsur pada filem. Kemusnahan foto pemangkin metil jingga (MO) diperhatikan dengan menggunakan UV-vis spektrofotometer. Analisis foto pemangkin dijalankan untuk membandingkan keupayaan fasa rutil filem nipis $TiO_2$ dan filem nipis P25 ($TiO_2$ komersial). Larutan pH diubah daripada pH 3 hingga pH 10 untuk mencari pH yang terbaik untuk filem $TiO_2$. Kepekatan MO diubah dari 5 ppm hingga 15 ppm untuk mencari reaksi terhad untuk filem $TiO_2$. Jumlah optimum HCl adalah 15.88 mol/L manakala jumlah optimum $TiO_2$ adalah pada 0.123 mol/L. Masa tindak balas terbaik telah diperolehi pada 10 jam. Tiada penurunan diperhatikan selepas 10 jam. Hasil kajian menunjukkan 0.123 mol/L isipadu TBOT 1225 $mm^2$ mempunyai penurunan MO tertinggi. Penurunan adalah sehingga 65.6% manakala penurunan filem nipis P25 adalah 8.07% sahaja. Penurunan MO menjadi tidak penting pada kepekatan yang tinggi. Dari eksperimen, didapati bahawa fasa rutil $TiO_2$ mempunyai aktiviti foto pemangkin yang lebih tinggi dalam kepekatan MO yang lebih rendah dan positif pada persekitaran berasid.

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## LIST OF SYMBOLS AND ABBREVIATIONS

| | | |
|---|---|---|
| CB | - | Conduction band |
| CdS | - | Cadmium sulfide |
| $CeO_2$ | - | Cerium oxide |
| $Cr_2O_3$ | - | Chromium oxide |
| CuO | - | Copper Oxide |
| DI water | - | Deionized water |
| XRD | - | Dispersion X-ray |
| DSSC | - | Dye sensitized solar cells |
| $Fe^{3+}$ | - | Ferric |
| FESEM | - | Field emission scanning electron microscope |
| FTO | - | Fluorine doped tin oxide |
| HCl | - | Hydrochloric acid |
| $H_2O_2$ | - | Hydrogen peroxide |
| $InO_2$ | - | Indium oxide |
| MO | - | Methyl orange |
| mm | - | Milimeter |
| ml | - | Milliliter |
| $O_3$ | - | Ozonation |
| POME | - | Palm oil Mill Effluent |
| ppm | - | Parts per million |
| pH | - | Potential of hydrogen |
| SPD | - | Spray pyrolysis deposition |
| $SnO_2$ | - | Tin oxide |
| TBOT | - | Titanium butoxide |
| $TiO_2$ | - | Titanium dioxide |
| $WO_3$ | - | Tungsten trioxide |
| UV | - | Ultra violet |

| | | |
|---|---|---|
| UTHM | - | Universiti Tun Hussien Onn Malaysia |
| VB | - | Valence band |
| $V_2O_5$ | - | Vanadium oxide |
| ZnO | - | zinc oxide |

# LIST OF APPENDICES

# LIST OF PUBLICATIONS

**Journal / Proceedings:**

(a) **Noor Kamalia Abd Hamed**, Nafarizal Nayan, Mohd Khairul Ahmad, Noor Sakinah Khalid, Fatin Izyani Mohd Fazli, Muhammad Luqman Mohd Napi. "Influence of Hydrochloric Acid Concentration on Titanium Dioxide ($TiO_2$) Film by Using Hydrothermal Method."Conference on Nano-& Biosource Technology 2015 (NBT 2015), UKM Bangi, Selangor, 28-29 February 2015, concentration 45, pp. 1669-1673, Sains Malaysiana.

(b) **Noor Kamalia Abd Hamed**, Nur Ain Adam, Mohd Khairul Ahmad. "Effects of Annealing Temperature of $TiO_2$ Film Deposited by Spray Pyrolysis Deposition Method for Dye-Sensitized Solar Cell (DSSC) Application", Proceeding of International Integrated Engineering Summit (IIES 2014), UTHM, Batu Pahat, Johor, 1-4 December 2014, Advanced Materials Research Concentration 773-774, pp. 652-656, 2015, Trans Tech Publications, Switzerland.

(c) **Noor Kamalia Abd Hamed**, Rizal Mahat, Noor Sakinah Khalid, Fatin Izyani Mohd Fazli, Muhammad Luqman Mohd Napi, Salina Mohammad Mokhtar, Ng Kim Seng, Soon Chin Fhong, Nafarizal Nayan, A.B. Suriani, Mohd Khairul Ahmad. "Fabrication Of Cobalt Doped Tin Oxide Film For Dye-Sensitized Solar Cell Using Spray Pyrolysis Deposition Method", Proceeding of Malaysian Technical Universities Conferences on Engineering and Technology (MUCET 2015), KSL Hotel, Johor, 11-13 October 2015, (pending publication in ARPN Journal of Engineering and Applied Sciences with Scopus indexed).

(e) Noor Sakinah Khalid, Fatin Izyani Mohd Fazli, **Noor Kamalia Abd Hamed**, Muhammad Luqman Mohd Napi, Chin Fhong Soon, Mohd Khairul Ahmad. "Biocompatibility of $TiO_2$ Nanorods and Nanoparticles on Hela Cells." Proceeding of Conference on Nano-& Biosource Technology 2015 (NBT 2015), UKM Bangi, Selangor, 28-29 February 2015 (pending publication in Sains Malaysiana).

(g) Fatin Izyani Mohd Fazli, Nafarizal Nayan, Mohd Khairul Ahmad, Noor Sakinah Khalid, **Noor Kamalia Abd Hamed**, Muhammad Luqman Mohd Napi. "Effect of Annealing Temperature on $TiO_2$ Film Prepared by Spray Pyrolysis Deposition Method." Proceeding of Conference on Nano-& Biosource Technology 2015 (NBT 2015), UKM Bangi, Selangor, 28-29 February 2015 (pending publication Sains Malaysiana).

(h) Noor Sakinah Khalid, Indah Fitriani Hamid, **Noor Kamalia Abd Hamed**, Fatin Izyani Mohd Fazli, Soon Chin Fhong, Mohd Khairul Ahmad. "Application of $TiO_2$ Nanostructure Using Hydrothermal Method For Waste Water Treatment." Proceeding of International Conference on Electrical and Electronic Engineering 2015 (IC3E2015), Equatorial Hotel, Melaka, 10-11 August 2015 (pending publication in ARPN Journal of Engineering and Applied Sciences with Scopus indexed).

# LIST OF AWARDS

(i) **Silver Medal in Research and Innovation Festival 2014 (R&I Fest UTHM)**

Noor Kamalia Abd Hamed, Wan Suhaimizan Wan Zaki, Mohd Khairul Ahmad. "Optimization of Rutile-phased $TiO_2$ Nanorods/nanoflowers film for Palm Oil Mill Effluent (POME) Treatment."

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of study

Fabrication of nanostructured titanium dioxide ($TiO_2$) received great attention to many researchers due to their excellent potential in many applications. $TiO_2$ is widely used for a variety of application for example photo-catalyst, gas sensor, optical filter, antireflection and dye-sensitized solar cell (DSSC) [1]. In addition, $TiO_2$ with nanostructure provide more surface area and has a low recombination rate of electron-hole pair compared to nanoparticle $TiO_2$ [2]. Numerous fabrication techniques such as sol-gel [3], DC magnetron sputtering [4], spin-coating [5], spray pyrolysis deposition (SPD) method [6] and hydrothermal method [7] can be used to fabricate $TiO_2$ nanostructure. However, hydrothermal method shows a great ability to produce a homogenous film with a cost effective method.

$TiO_2$ exists in three minerals form which are brookite, anatase and rutile [1]. Anatase and rutile phase are most studied compared to brookite phase. This is because brookite has problems in preparing pure nanocyrstalline forms. Anatase is widely used as a catalyst in photocatalytic. However, rutile has a stable phase and has a smaller band gap than anatase phase. In some circumstances, rutile was discovered to be more active for photocatalytic activity than anatase [8]. First discovery of photocatalysis was the "Honda-Fujishima Effect" first described by Fujishima and Honda in 1972 [9]. Fujishima et al. discovered $TiO_2$ is an excellent photocatalyst material for environmental purification. They found $TiO_2$ could use light irradiation in breaking water molecules to hydrogen and oxygen gas.

Recently, nanotechnology of $TiO_2$ is a promising technology for waste water treatment. In order to overcome the increasing pollution, waste remediation and pollution control technology are on demand. An ideal waste water treatment process should offer cost effective product and the process does not leave any hazardous residues. $TiO_2$ is widely known as a low cost, chemically stable and has large redox potential with respect to water [10].

These past two decades, photocatalysis process has been found as one of the most effective green technology for waste water treatment by removing the organic contaminants [11]. Photocatalytic degradation is a process where the ultra violet (UV) light will degrade the organic contaminant in water in the present of $TiO_2$ catalyst. The formation of highly oxidizing hydroxyl and superoxide radicals from the photocatalytic activity may oxidize and destroy organic pollutant. Generally, photocatalytic process was conducted in slurry system. However, several problems had risen by using slurry system which were the post separation between powder and treated water after treatment process, the powder became aggregate when applied at high concentration and the powder form is not suitable at continuous flow system [12]. The immobilization of the catalyst such as film gives outstanding advantages to the post separation in photocatalytic activity and overcome the difficulties. Therefore, photocatalytic activity of flowerlike rutile-phased titanium dioxide film was studied for degradation of methyl orange (MO) because it is a dominant practice in industrial waste water treatment.

The awareness on environmental issues related to the treatment of water pollutant has increased as the public become more affluent. Therefore, the regulations concerning the industrial effluent have been restricted towards the environment for the sake of future generations.

In this study, low temperature hydrothermal system was approached to fabricate rutile $TiO_2$ film on fluorine doped tin oxide (FTO) substrate. The temperature is set at 150°C. This study was the first report about the rutile film for photocatalytic application for MO degradation. The rods and the flowers structure of rutile $TiO_2$ film show an excellent photocatalytic activity on photodegradation of methyl orange (MO) under UV light irradiation. The rutile $TiO_2$ thin was characterized by using field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), electron dispersive spectroscopy (EDS) and UV-Vis spectroscopy. This study serves to find the most favorable pH value and concentration of MO to achieve the optimum degradation by rutile $TiO_2$ film.

## 1.2 Problem statements

In this 21st century, the world is facing a severe environmental problem. The rapid development in science and technology lead many industries for examples chemical, textile, food and etc. producing polluted effluent and contaminate the natural water resources. The contaminated drinking water sources with the present of harmful organic substances are hazardous to health. Malaysia is one of the countries who faces serious water pollution [13]. Water is the most important thing to the living creatures and industrial development. The increasing of the population leads to the increasing in demand of water supply and safe water. The water pollution can cause inadequate supply of clean water to all users and future generation.

The conventional water treatment process cannot remove all the contaminants easily. There are varieties of conventional method such as physical, chemical and biological methods are used for waste water treatment. However, these conventional methods are inefficient enough to destroy the contaminants completely. Recently, numerous new technologies in waste water treatment have been invented. One of the new technologies are the use of photocatalytic effect of semiconductor metal oxide. Semiconductor metal oxide has shown a good performance of photocatalytic activity for environmental application. Normally, the photodegradation of organic compound were conducted in colloidal and powder catalyst suspension. The photocatalytic activity of powder catalyst shows a strong oxidative power. For example, P25 is a commercial powder $TiO_2$ which is widely used in the industries. However, the powder catalyst faced several practical problems which are separation of the catalyst from the suspension after the reaction is difficult, the suspension particle tend to aggregate especially when they are present at high concentration and particle suspension are not easily applicable to continuous flow system [14].

Thus, the preparing of rutile phased $TiO_2$ micro size rods/flowers film on FTO substrate may replace commercial P25 powder catalyst in photodegradation of waste water.

## 1.3 Objectives of the study

In this research, several objectives have been considered to make this research done successfully. The objectives are:

1) To grow a rutile phased $TiO_2$ micro size rods/flowers film using hydrothermal method.
2) To determine the effect of HCl concentration on rutile phased $TiO_2$ micro size rods/flowers film in morphology and structural property.
3) To determine the effect of surface area on rutile phased $TiO_2$ micro size rods/flowers film in elemental, morphology, structural and photocatalytic property.
4) To compare the photodegradation of rutile phased $TiO_2$ micro size rods/flowers film with P25 film.
5) To investigate the limitation of rutile phased $TiO_2$ micro size rods/flowers film on different MO concentration and pH.

## 1.4 Research scope

To achieve the objectives, the following scopes were investigated:

- The $TiO_2$ photocatalyst is fabricated by using hydrothermal method. The experiment was conducted under different amount of HCl concentration and different amount of $TiO_2$ surface area.
- The $TiO_2$ surface area was divided into two areas which is 250 and 1225 $mm^2$.
- The fabricated $TiO_2$ were characterized by using FESEM, EDX, XRD and Uv-Vis spectrophotometer to investigate the morphology, elemental, structural and photodegradation properties.
- The photodegradation activity of fabricated $TiO_2$ was investigated by degradation of MO by using UV-Vis spectrophotometer with different pH value (3-10) and different MO concentration (5-15 ppm).

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Titanium dioxide nanostructured

Titanium dioxide also known as $TiO_2$ is a semiconductor material widely used for a variety of application for examples photo-catalyst, gas sensor, optical filter, antireflection and dye-sensitized solar cell (DSSC) [7]. Titanium dioxide is known as a crucial material as it is extensively used as pigment in paints and coating materials in optical films. This is due to its high transparency and high refractive index and also its chemical durability in the visible and near infrared (IR) region [15]. The properties of $TiO_2$ like high stability, low cost and non-toxicity make $TiO_2$ widely used in many other fields [16]. Titanium dioxide films have useful electrical and optical properties and excellent transmittance of visible light [11].

Titanium dioxide occurs in nature as minerals rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) [17]. Figure 2.1 shows the crystal structure of anatase, rutile and brookite. Generally, brookite phase is only stable at very low temperature and not so useful for many applications. Anatase and rutile belong to different space groups but both have tetragonal crystal lattice.

Rutile phase is more stable in high temperature region whereas anatase and brookite phases are metastable and they can transform into rutile phase when they are prepared at high temperature [18]. Each crystalline has a different physical properties such as surface state, band gap and etc. The energy gap between valence band and conduction band is band gap [19]. The band gap of $TiO_2$ is different between the phased. Rutile has a lower band gap compared to anatase phased. The values are 3.2 eV and 3.0 eV for anatase and rutile respectively [15-19]. The electrons must have equal or more energy than band gap energy to excite from the valence band (VB) to the conduction band (CB) for photocatalytic process. Figure 2.1 shows is the illustration of band gap energy of metal, semiconductor and metal.

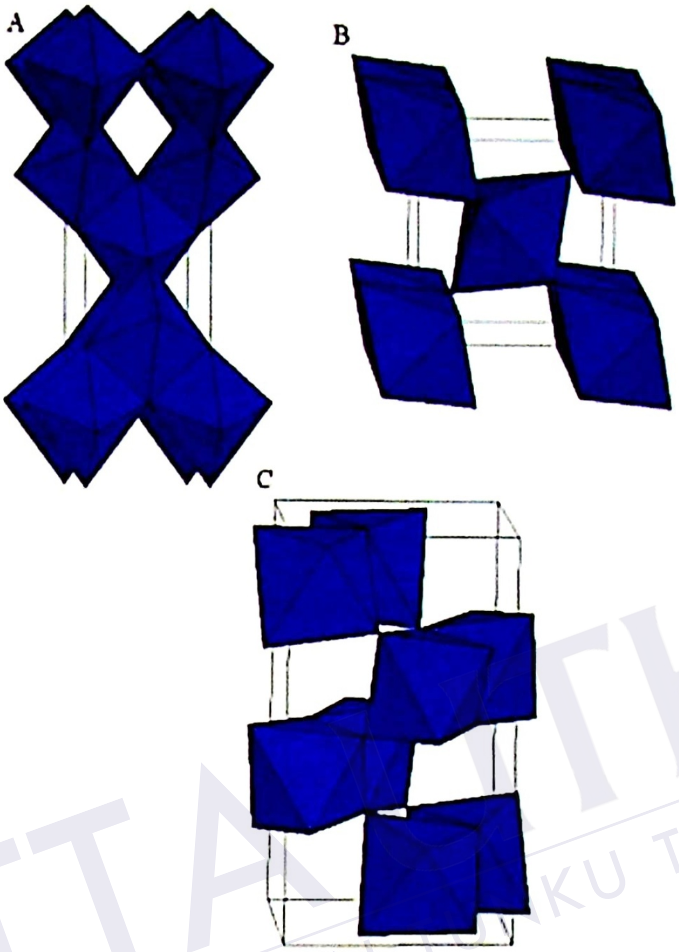


Figure 2.1: Crystal structure of (A) Anatase (B) Rutile (c) Brookite [20]



Even though the band gap energy of anatase is higher than rutile, many researchers claimed anatase phased has better response with ultraviolet photons used for photocatalysis [17]. Different opinion from Yawin wang. He claimed that rutile phased has a thermodynamically stable phase and has a smaller band gap than anatase phase [8].

Many reports have been reported on the nanostructures of $TiO_2$ in different area. There are varieties of $TiO_2$ nanostructured such as nanoparticles, nanorods, nanobelts, nanowires and nanoflowers. The structure and optical properties are depending to the application. Dense structure film is suitable for solar cell application while porous film is good for gas sensor application. Then, amorphous film is used in the biomedical field due to its biocompatibility in bloods while $TiO_2$ on the film is more convenient than powder form in photocatalysis application since it is very easy to remove from the solution [17]. In addition, the combination of rod and flower structure in rutile phased gives higher surface area and better electron mobility.

Several precursor are used to fabricate $TiO_2$ nanostructured such as titanium butoxide (TBOT), titanium isopropoxide(TTIP) and titanium tetrachloride. It was reported that the morphology of structure on film similar between TBOT and TTIP [7]. Titanium tetrachloride has a higher chemical reactivity and difficult to handle compared to other precursor. In order to fabricate rutile phase $TiO_2$ rods/flower film structure, TBOT is used as a precursor in this experiment.

Thus, the rutile phase $TiO_2$ rods/flower film structure was chosen to treat the waste water. This structure will be used as a photocatalyst agent to treat methyl orange dye (waste water model). It is expected that the combination of the rods/flowers $TiO_2$ will increase the degradation process of organics in MO due to the increase of surface area and better electron mobility compared to P25 (commercial $TiO_2$).

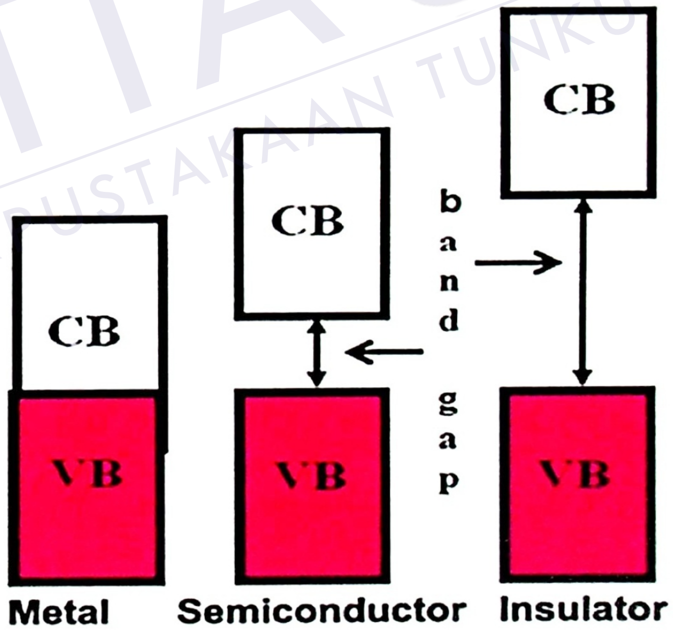


Figure 2.2: Valence band and conduction band for metal, semiconductor and insulator [21]

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