STUDY ON PHOTOCATALYTIC PERFORMANCE OF RUTILE PHASED TiO_2 MICRO SIZE RODS/FLOWERS FILM TOWARDS METHYL ORANGE DEGRADATION

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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^oC 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^oC 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^{o}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.

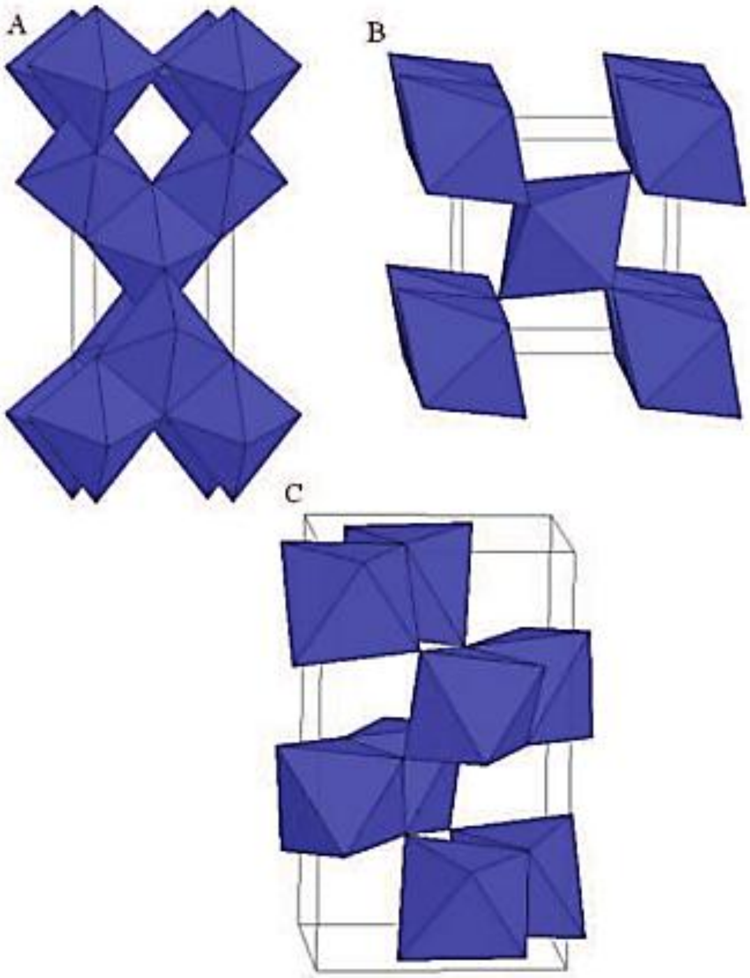


Figure 2.1: Crystal structure of (A) Anatase (B) Rutile (c) Brookite [20]

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).

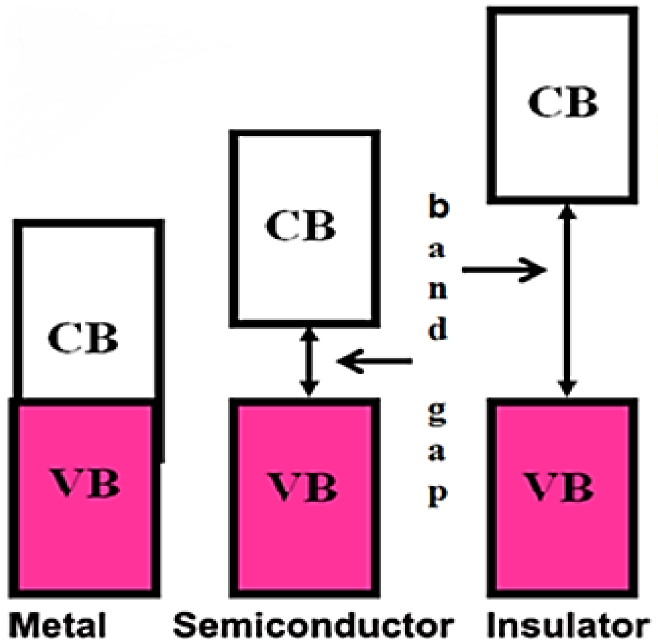


Figure 2.2: Valence band and conduction band for metal, semiconductor and insulator [21]

2.2 Different method for the preparation of nanostructure TiO_2 film

The preparation of nanostructured TiO_2 will be discussed in this section. TiO_2 film can be fabricated using many different methods such as hydrothermal [22], sol-gel [4] and spray pyrolysis deposition (SPD) method [25].

2.2.1 Spray pyrolysis deposition method

In spray pyrolysis deposition film process, at appropriate pressure the solution was atomized to deposit on the substrate in tiny droplets. The produced film is depending on spray rate, droplet size, distance of nozzle spray to substrate and deposition temperature [22]. The selection of the solution is important to ensure only unwanted elements will be evaporated during the deposition. Figure 2.3 shows a typical spray deposition setup.

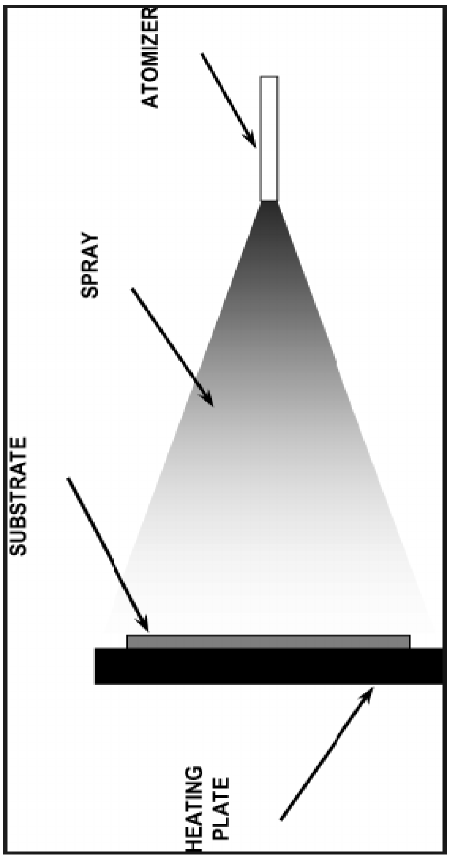


Figure 2.3 : A typical spray deposition setup [23].

The fabricated TiO_2 film by using spray pyrolysis deposition method is producing high porosity but with anatase phased instead of rutile phased [24]. Thus, this method is suitable for gas sensor application.

2.2.2 Sol-gel method

Sol-gel process can be defined as the process of transiting solution into gel phase. A series of hydrolysis and condensation process of precursor will formed a sol. Then, the condensed sol particle will be formed a gel. Sol-gel process usually use condensation, hydrolysis and solvent reaction [25]. From the previous study reported that, nanostructured TiO_2 from sol-gel preparation only produce the anatase phase and the film was coarse [26]. In addition, it was reported that to obtain the anatase phase, the nanostructured TiO_2 must undergone calcination process at 300oC and rutile phase at 800^{o}C [27]. This method has a difficulty in producing rutile phase. The calcination process at higher temperature will cause the surface morphology devastated.

2.2.3 Hydrothermal method

Hydrothermal is a process of a solution which is reacted under controlled pressure and temperature in a closed system and water as a solvent [28]. Normally, hydrothermal process is conducted in steel vessel pressure called teflon line stainless steel autoclave under controlled temperature or pressure with the chemical reaction happened in the aqueous solution. The temperature can be inflated above the boiling point of water, reaching the pressure of vapour saturation. The temperature and the amount of solution combined to the teflon autoclave determine the internal pressure produced. Figure 2.4 shows the autoclave for hydrothermal system in the oven.

Hydrothermal method gives a homogeneous film assisted with stable temperature and pressure. Hydrothermal synthesis is a simple yet effective method among other various strategies to produce a wide diversity of hierarchical TiO_2 architectures. The variation of hydrothermal conditions such as temperature, pH, concentration and molar ratio of reactants and additives imparts tunable morphologies and crystalline films of TiO_2 at the nano-scale and micro-scale [29]. In addition, hydrothermal method is an advantageous method to fabricate materials as it can synthesize at low temperature with high pressure in a closed system compared with other fabrication method.

Figure 2.4: Autoclave for hydrothermal system in the oven

For this experiment, the temperature was fixed at150˚C because from the previous study Meidan Ye proved that 150˚C is an ideal temperature for TiO_2 nanorod/nanoflower to growth. If the temperature is below 100 ˚C, the flower morphological cannot be developed and if the temperature is too high the TiO_2 film started to detach from the substrate [30]. Then, reaction time was fixed for 10 hours. Previous study shows it takes 10 hours to grow nanoflower morphology. If the reaction time less than 10 hours the flower morphology cannot be grown [31]. Thus, if the reaction time extended more than 20 hours, the TiO_2 film will start to detach from FTO substrate because the competition between the crystal growth due to the hydrolysis rate of titanium [30].

As stated in the previous study, base environment will lead to anatase phased TiO_2 [32]. Thus, in this research, by using hydrothermal method in acidic solution will produce rutile phased TiO_2.

The possible growth process of rutile phased TiO_2 can be proposed as follows. From the hydrothermal process, $[Ti(OH)_4]$ is produced from TBOT in the solution and becomes the important point of growth in the TiO_2 on the FTO (SnO_2) substrate. Since the SnO_2 layer also has the rutile phased crystallinity resulting in an epitaxial growth of the rutile phased TiO_2 [29]. SnO_2 and rutile phased TiO_2 has a similar tetragonal crystal and the lattice parameter for SnO_2 and rutile TiO_2 is SnO_2 a=

4.687Å, c=3.160Å and rutile TiO_2 a= 4.594Å, c=2.959Å, respectively. $[Ti(OH)_4]$ also set off the growth of TiO_2 in the solution. The growth of the rutile phased TiO_2 could be originated from a high concentration of HCl. In high acidic solution, pH < 7, TiO_2 becomes soluble, which suggests that a dissolution-precipitation process can occur rapidly. Since the hydrothermal condition under the free space, the flourish rutile flower are grown and deposited on the top of the rutile rod TiO_2 due to gravity. Figure 2.5 show the growth mechanism of rutile phased TiO_2 using hydrothermal method.

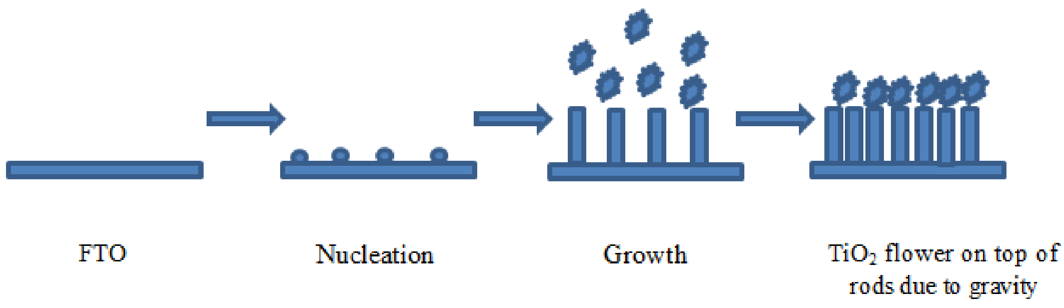


Figure 2.5: The growth mechanism of rutile phased TiO_2 by hydrothermal method

2.3 Photocatalysis

Photocatalysis can be defined as a "catalytic reaction involving the production of a catalyst by absorption of light" [28-29]. In general, there are two types of photocatalysis which are homogenous photocatalysis and heterogenous photocatalysis. For homogenous photocatalysis, the catalysts that used in the process is Fe^{3+} (ferric), O_3 (ozonation) or H_2O_2 (hydrogen peroxide) under powerful irradiation of UV lamp [19]. While, heterogenous photocatalysis is the process of generation of electron and hole pair under light irradiation of semiconductor materials. There are lists of homogeneous photocatalysis such as ozonation and UV irradiation (O_3/UV), hydrogen peroxide and UV irradiation (H_2O_2/UV) and photo-fenton system ($fe^{3+/}H_2O_2$/UV). Table 2.1 summarized the advantages and disadvantages between homogenous photocatalysis and heterogenous photocatalysis.

Table 2.1: The summarized of homogenous and heterogeneous photocatalysis

Photocatalysis	Advantages	Disadvantages	Ref
Homogenous	• Minimum sludge generation. • High absorption efficiency.	• To remove irons salt and hydrogen peroxide residue after the process • Has longer degradation process • Expensive generation for ozone • Ozone might be poisonous and must destroy before releasing to environment	[34] (1996) [35] (2005)
Heterogenous	• The process is more environmental friendly which produces CO_2 and H_2O after degradation process. • Low energy UV light/ solar light. • Only used atmospheric O_2 other than expensive chemical. • Cost effective process and reusable catalyst.	• Huge amount of catalyst is needed for industrial purposes.	[36] (1999) [37] (2010)

2.3.1 Photocatalytic activity of TiO_2

Among the decontamination techniques, the heterogeneous photocatalytic processes have received an increasing attention in the last decades because they are potentially able to completely oxidize many organic compounds present in waste water. Many aspects take into account in producing high photocatalysis process such as ability to utilize in UV light or visible light, biological and chemical inertness, photostability, ecofriendly and low cost [19].

There are a few semiconductors exist such as titanium dioxide (TiO_2), zinc oxide (ZnO), cadmium sulfide (CdS), tungsten trioxide (WO_3), tin oxide (SnO_2), iron oxide (Fe_2O_3), chromium oxide (Cr_2O_3), indium oxide (InO_2), vanadium oxide (V_2O_5), cerium oxide (CeO_2) and Copper Oxide (CuO). From the previous study, ZnO is unstable because of inappropriate dissolution to produce yield $Zn(OH)_2$ on ZnO particle and make inactivated catalyst over time [9] [30-33]. TiO_2 is unique in its chemical and biological inertness, photostability, and low cost production. Photocatalytic water and air purification using TiO_2 is a predominant advanced oxidation process (AOP) because of its efficiency and eco-friendliness [33]. TiO_2 is a multifunctional semiconductor photocatalyst which can be an energy catalyst (in water splitting to produce hydrogen fuel), an environmental catalyst (in water and air purification), or an electron transport medium in dye-sensitized solar cells.

Fundamental research regarding the preparation of catalysts with high photocatalytic activity and the improvement of photocatalyst performance are priorities to be considered.

Figure 2.6 shows the mechanism of photochatalytic of TiO_2 in waste water treatment. TiO_2 will be exposed under the UV light. If the TiO_2 is irradiated with photons with energy equal or greater than the band gap energy, electrons can absorb this energy and be promoted from the valence band to the conduction band [19]. At valence band, the holes which are positively charged will react with the water molecules and produce hydroxyl radicals (·OH). At the conduction band, the electron will react with the dissolved oxygen and will produce superoxide anions (·O2−).

Thus, these active oxygen species which are (·OH) and (·O2−) will attack the organic substance and will produce carbon dioxide and water which are harmless to environment. This cycle continues as long there is the presence of light. The mechanism of photocatalytic of TiO_2 is summarized by equation (2.1) to (2.5).

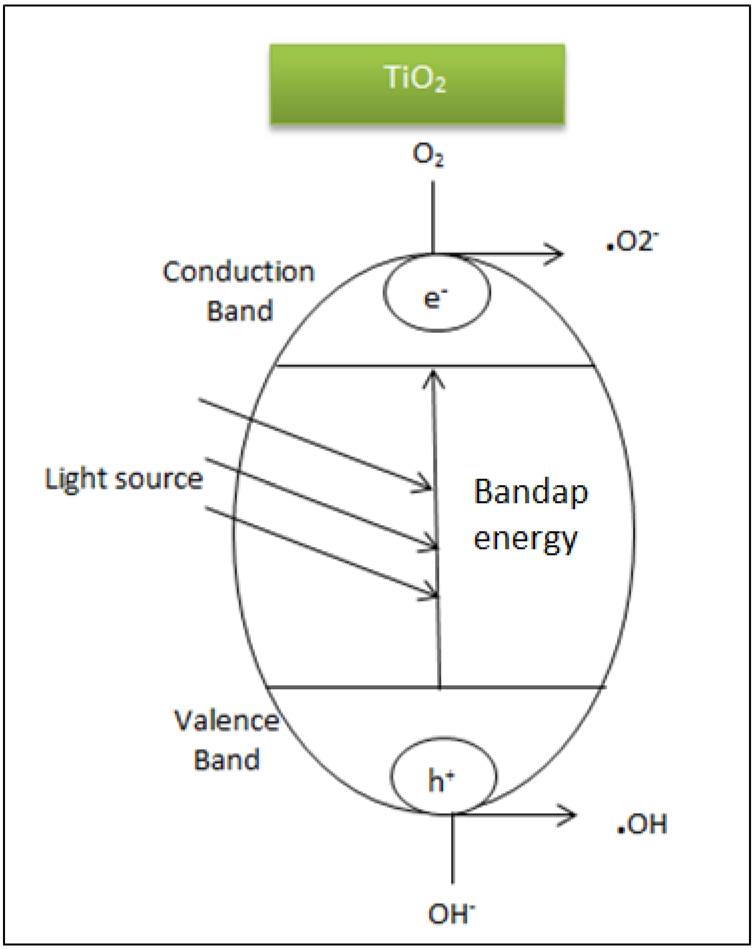


Figure 2.6: The mechanism of photocatalytic activity of TiO_2 (reproduce image)

The photocatalytic degradation of TiO_2 was started when the photon has equal or more energy than band gap of TiO_2 and thus leading the production of electron-hole pair:

$$TiO_2 \xrightarrow{hv} TiO_2\,(h^+ + e^-) \qquad (2.1)$$

At conduction band, the electron will react with molecular O_2 to produce superoxide anion:

$$e^- + O_2 \longrightarrow \cdot O_2- \qquad (2.2)$$

At valence band, the holes will react with H_2O or hydroxide ions to produce super hydroxyl radical:

$$h^+ + OH^- \longrightarrow \cdot OH \quad (2.3)$$

$$h^+ + H_2O \longrightarrow \cdot OH \quad (2.4)$$

These superoxide anion and hydroxyl radical will attack the organic substance and produce carbon dioxide and water which is harmless to environment;

$$\text{Organic substance} + \cdot O2- + \cdot OH \longrightarrow CO_2 + H_2O \quad (2.5)$$

In this study, the free radical produce from the photocatalytic activity will attack the organic substance in the contaminated water. MO will play as a model compound of waste water in evaluating the ability of rutile phased TiO_2 film [41].

2.4 Immobilization of photocatalyst

Generally, most of the reported work on heterogeneous photocatalysis has been performed by using it in powder form. Unfortunately, the post separation between the TiO_2 powder and treated water will lead to difficulty. It is difficult to control with high energy consumed and involve longer time. In order to overcome this problem, immobilized TiO_2 on various substrates are used.

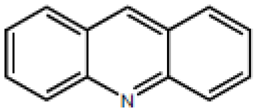
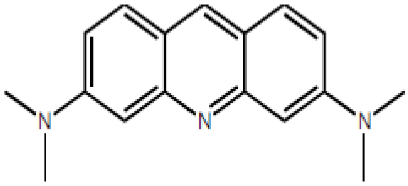
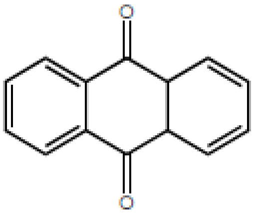
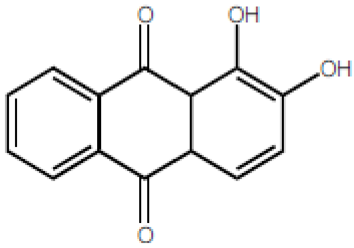
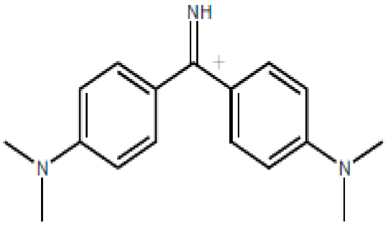
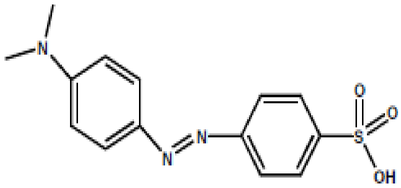
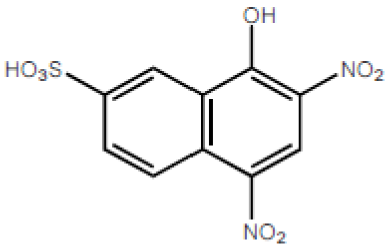
There are various substrates which have been used in the photocatalysis degradation in different applications such as glass [42], stainless steel woven meshes [43], sponge [44], carbon [45], polymeric material [46] and silica [47]. Various immobilization techniques for example sol gel [43-44], solvothermal [50], chemical vapour deposition [51], sputtering [51] and electrospinning [52] has been used to fabricate immobilized TiO_2. From the previous study, the researcher claimed the powder form photocatalysis has larger surface area than immobilized TiO_2 [33]. Although, some other author claimed immobilized TiO_2 does not affect the efficiency of photocatalysis degradation [9]. However, with flower-like rutile phased TiO_2 will contribute to high surface area due to the flower-like structured. This flower-like structure will provide more active surface area and enhanced the photocatalytic activity. High efficiency of photocatalysis degradation still remains elusive among the researchers. These differences may be caused by the preparation of fabricated catalyst, the condition of the photocatalysis environment and other factors. This study is aimed to fabricate the immobilize catalyst which is rutile phased TiO_2 film in order to overcome the stated problem above.

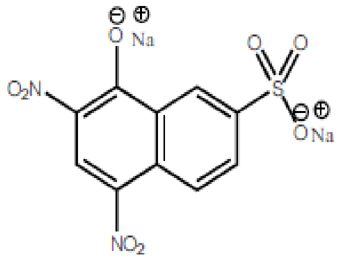
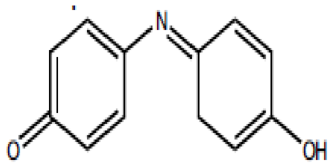
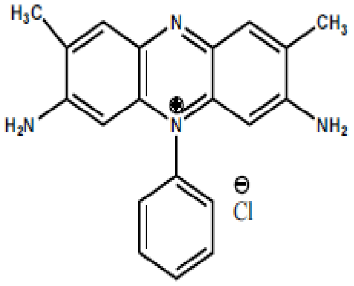
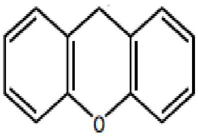
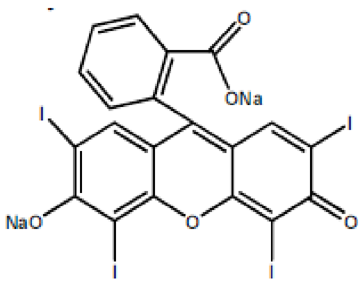
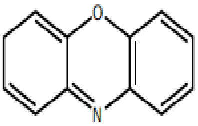
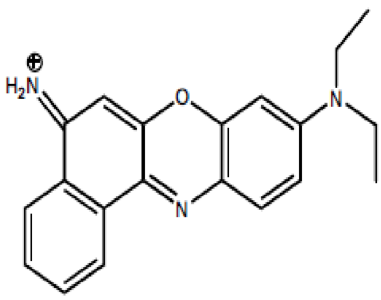
2.5 Dyes

Dyes are extensively utilized in various industries for example food, textile, plastics, cosmetic, leather and others for coloring purposes. Table 2.2 shows several types of dyes. The effluent from the industries that content dyes will introduce potential danger to the marine ecosystem. There are various methods used to eliminate the dyes from the waste water system such as chemical methods and biological method, flocculation, adsorption, reverse osmosis and ultrafiltration. However, dyes with the complex structure cannot be eliminated with the conventional method such as biological method for decolorization. In addition, some of the dyes are not degraded and adsorbed on the sludge. Toxic organic compound will release to the aquatic system without proper treatment. Improper waste management will lead to various health hazards.

In this experiment, methyl orange will be act as an organic compound and used to test the ability of rutile-phased TiO_2 for photocatalytic activity. Methyl orange is an azo dye which is mostly used in dyeing, printing textile, leather industries and paper. Unfortunately, the improper management of waste in the industries could contribute a serious pollution to the environment. Azo dye is known as a toxic waste and potential carcinogenic substance. Table 2.2 shows the types of the dyes exist in the industries. Conventional treatments available are nondestructive. Thus, the new improved treatment which is rutile phase TiO_2 microsize rods/flowers film may solve the problem.

Table 2.2: List of dyes

No	Dyes	Chromophoric groups	Example
1	Acridine dyes	Acridine ring 	Acridine orange 
2	Anthraquinone dyes	Anthraquinone ring 	Alzarin 
3	Arylmethane dyes	Methine group, C=N	Auramine 
4	Azo dyes	Azo group 	Methyl orange 
5	Nitro dyes	Nitro groups, NO2	Picric acid 

6	Nitroso dyes	Nitro groups, NO2	Nephthol yellow S 
7	Quinone-imine dyes	Methine group, C=N	Indophenol 
8	Azin dyes	Methine group, C=N	Safranin O 
9	Xanthene dyes	Xanthene ring 	Erythrosin B 
10	Oxazin dyes	Oxazine group 	Nile bue 

2.6 Working principles of devices used for characterization

2.6.1 X-ray Diffraction (XRD)

XRD is a rapid analytical technique often used for phased analysis for crystalline material. The operation begins when the cathode X-ray generates the X-ray and filtered to produce monochromatic radiation, collimated to concentrate and directed toward the sample. The production of constructive interference is from the interaction between the sample and the incident rays when the condition follows the Bragg's Law as shown in equation (2.6).

$$n\lambda = 2d \sin \theta \tag{2.6}$$

Where d is the d-spacing, perpendicular distance between pairs of adjacent planes in the crystal, θ is the incident angle, n is the layer of planes, and λ is the wavelength of the X-rays.

The XRD system consists of three basic elements which are an X-ray tube sample holder and the x-ray detector. The process of X-Ray diffraction starts by heating the filament in the cathode ray tube to produce electrons. Then, the electrons will be accelerated toward the target by applying a voltage and bombarding the target material with electrons. When the electrons have sufficient energy to jump from the inner shell electrons of the target material, characteristic of X-ray spectra are produced.

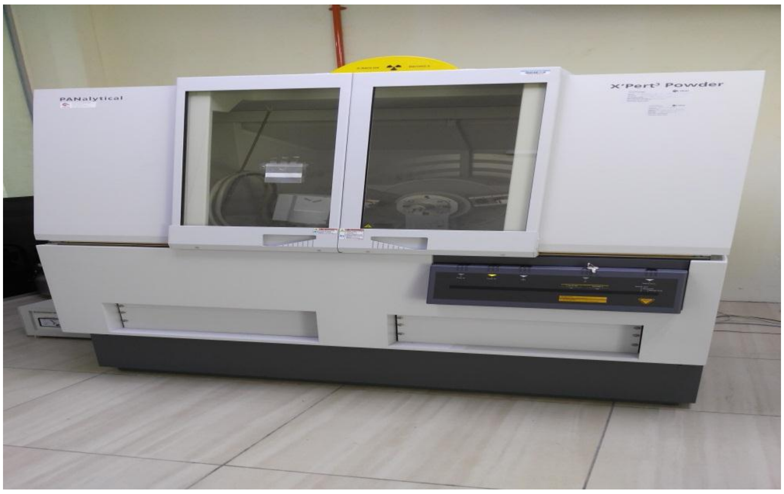


Figure 2.7: XRD Machine

In this experiment, the XRD is used to determine the crystal structure of the TiO_2 nanorods/nanoflowers film. The intensity and quantization at certain angle, XRD spectra will be recorded by scanning 2θ in the range of 20-80.

2.6.2 Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscopy or FESEM is used to analyze the surface morphology, cross sectional area and uniformity of the film sample. FESEM is a microscope that uses the field emission cathode in the electron gun which provides narrower probing beam at low and high electro energy thus resulting in both improved spatial resolution and minimized sampling charging and damage on the sample. Figure 2.8 shows the FESEM used for characterization of the samples.

The specialty of FESEM which are combination of higher magnification, larger depth of focus, greater resolution and simple observation on the sample make FESEM machine usually used by the researcher to characterize their sample. FESEM has a wider range in magnification which can produce image 100 times to 10 million times of the normal size. FESEM can produce clearer image, less electrostatically distorted images with spatial resolution down to 1 nm which six times better compared to Scanning Electron Microscopy (SEM).

Figure 2.8 : FESEM machine

2.6.3 Energy dispersive X-ray analysis (EDX)

Energy dispersive X-ray analysis (EDX) is used to analyze the elemental or chemical properties of the samples. It depends on the interaction of some source of X-ray excitation and a sample. The capabilities to characterize the sample are due to the large part to the fundamental principle for each element and unique atomic structure allows a unique set of peak on its X-ray spectrum. A high energy beam of charge particles for example electrons and protons or beams of X-ray is focused into the sample being analyzed to stimulate the emission of characteristic X-ray from the specimen.

An atom within the sample contains unexcited electrons in discrete energy levels or electron shell bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDX allows the elemental composition of the specimen to be measured.

2.6.4 Ultraviolet visible (UV-Vis) Spectrophotometer

Ultraviolet visible (UV-Vis) spectrospotometer is spectrometer measurements which refer to the absorption of spectroscopy reflectance or transmittance in the ultraviolet visible spectral region. The wavelength of the ultraviolet region is in between the range of 190-380 nm while the visible region is in between 380-750 nm. In the measurement process, it uses the light in the visible and adjacent ranges from near ultraviolet (UV) until near infrared (NIR) ranges in order to indicate the intensity of absorbance and transmittance of the film sample. In this experiment, UV-Vis is used to measure the absorbance value of TiO_2 film and determining the percentage degradation concentration of methyl orange. Figure 2.9 shows the UV-Vis that used for characterization of the samples.

Figure 2.9 : UV-Vis Spectrophotometer

2.7 Application of TiO_2

Nowadays, a nanotechnology of TiO_2 has received a great attention from the worldwide. This is because the strength of the technologies distributes numerous benefits to the society. TiO_2 has been used for Dye Sensitized Solar cell (DSSC) [48-49]. Malaysia has an abundant solar energy since it has a hot climate all year round. Thus, DSSC can be replaced as a new source of electrical energy because the natural source has been depleted. Then, TiO_2 was found to have an ability in killing bacteria [50–53]. This was an interesting area and could help in medication field. For gas sensor application, TiO_2 has an ability to sense various types of gas such as oxygen and ammonia [54-55]. In addition,it is found that the TiO_2 has an ability in self-cleaning for the building which make a cost effective technology for the industries [56-57]. Furthermore, TiO_2 has a greater of photocatalytic activity than other semiconductors. This advantage can be implemented to the current waste water treatment technology to improve the system before releasing to the environment. TiO_2 has a huge ability to destruct a various types of polluted water such as dyes, palm oil mill effluent (POME) and paper mill effluent [28], [58–63]. The aim of this study is to improve the photocatalytic activity of rutile phased TiO_2 film towards degradation of MO before applying to the real waste water.

CHAPTER 3

METHODOLOGY

In this chapter, the experimental procedure is divided into three main stages. Detailed information about the process of the experimental procedure is reported in this chapter. Figure 3.1 shows the flow chart of the research methodology.

3.1 Overview of the experimental process

The overall experimental work was summarized in a flow chart shown in Figure 3.1. The experimental work was conducted in three main stages which is the cleaning substrates process. Then, the cleaned FTO was used to fabricate rutile phased TiO_2 by varying parameter and characterize the fabricated TiO_2 samples. Finally, the optimized samples will undergo verification stage with photocatalytic analysis.

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