Visible Light Driven Carbon Dioxide Conversion into Methanol Using Metal Doped Titanium Dioxide

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by

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CERTIFICATION OF APPROVAL

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May 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except specified in the references and acknowledgement, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MUHAMMAD OZZAL BIN IDERIS

ABSTRACT

Increasing energy crisis and declining climate caused by the excessive utilization of fossil fuel have increase exponentially on the research activities about Carbon Dioxide (CO_2) capture, storage and utilization. Artificial photosynthesis that uses Ultraviolet light (UV-light) and solar light energy to convert CO_2 to form value added chemical and renewable fuels such as methanol and methane has drawn the attention worldwide. It not only reduces the greenhouse effects caused by CO_2 emission but as well produce value added chemicals for renewable energy. Titanium dioxide, (TiO_2) nanoparticles were synthesized using Triton X-100 as surfactant. Copper (Cu) was doped into the TiO_2 nanoparticles via wet impregnation method in order for the photocatalyst to absorb the light from UV region to visible region. In this experiment, 0-5wt% Cu was used to determine the optimum amount of Cu with 40ml of distilled water. From the result, 3wt% Cu/TiO_2 shows significant result on the formation of methanol which give 2.574 ml. This report provides a brief information about the principles of artificial photosynthesis of CO_2, method and materials needed for preparing the photocatalyst as well as the progress in exploring more efficient photocatalyst for the photoreduction process.

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Greenhouse gases (GHG) consist of among other carbon dioxide (CO_2), water vapour (H_2O), methane (CH_4) and nitrous oxide (N_2O). These gases occur naturally in atmosphere but the rate which CO_2 being added into the air by human activity is of increasing concern. In the meantime, the energy demand is exponentially increasing due to rapid growth of human and industrial population. Continuous activity by human utilizing the energy resource from non-renewable fossil fuels directly interfere the environmental impairment due to the release of CO_2 into the atmosphere. If these emission keep on happening, it could bring serious problem to the human being as well as other living things. For instance, the increase in CO_2 emission could bring the global temperature up to a certain level where it can cause drought to a certain area where food is being produced and consumed by human.

Optimum conversion and utilization of the harmful CO_2 gases into valuable products could be the remedy for the depletion of fossil fuel reserves as well as the continuous rise of CO_2 concentration in the air. With the aid of UV-light or mercury lamp as well as catalyst, a method called photocatalytic reduction of CO_2 into methanol and methane can be used to achieve desired product. These result can only be achieved when a suitable catalyst is used and in a research work, $AgTiO_2$ was used in the methanol and methane making (Ma *et al.*, 2014).

In details, the reduction of CO_2 can be performed with the help of catalyst and UV-light to give the energy to break the CO_2 bonds and lead to the production of methanol or methane. This process is called photocatalytic reduction of CO_2. In previous work, photocatalytic reduction of CO_2 focused on TiO_2 and the absorption of UV light irradiation. Unfortunately, the UV light region in sunlight spectrum is limited to 5% only while the rest is in the visible region (ʎ>400nm) (Abd Aziz, Yong, Ibrahim, & Pichiah, 2012). Hence, the most promising catalyst are those that can be excited by visible light. In an effort to enhance the photoactivity of TiO_2 in visible region, several modification methods of TiO_2 have been studied including the synthesis of nano sized TiO_2, doping TiO_2 with zeolites, TiO_2 based binary catalyst and metal ion doping (Zhou *et al*., 2009). Previously, TiO_2 is used in the making of paints and coatings due to UV resistance that help to prevent the discolouration. The demand for TiO_2 is increasing rapidly when new technology called photocatalyst is introduces to make use of it due to oxidative and hydrolysis properties.

The demand on fossil fuel is increasing each year but the amount reserve is not enough to balance the needs of each year. In this project, it is very important to have a good result because it can lead to a new renewable resource than depending on the fossil fuels. Without realizing, abundance of CO_2 release in atmosphere should be studied where new technology should be developed to use this resources for the betterment. If this type of resources is left without being use, it could lead to a catastrophic such as flooding, increase in global warming and many more that can harm the existence of life.

Based on the statistic report in 2011, the most contribution factor is from the combustion of fossil fuel that contribute to 87% CO_2 emission. From that amount, 43% is from coal, 36% from oil and 20% from natural gas (Le Quéré, 2012). The current concentration reported in January 2015 is about 399.85 ppm (Observatory, 2015) while the limit of CO_2 in atmosphere is 350 ppm. The amount will keep on increasing each year because of rapid development, clearing the land and the need of the resources. If these activities keep on continuing without understanding the long term consequences, the amount of CO_2 will increase rapidly. Therefore, effective photocatalytic reduction of CO_2 employing inexhaustible sunlight energy should be studied.

1.2 Problem Statement

Emission of CO_2 is increasing each year due to heavy activities as well as the combustion of fossil fuel. Due to these activities, it is difficult to control CO_2 in the environment. Thus, to treat this problem, photocatalytic reduction of CO_2 is one of the method to convert CO_2 to valuable product.

In long term, the effect of treating CO_2 on the environment is very important as the new generation will take our place. Due to that reason, photocatalytic reduction process with the aid of catalyst is a good method to be considered to treat CO_2 without causing another problems.

1.3 Research Objectives

The objectives of this study are:

- To develop TiO_2 based photocatalyst with enhanced activity under visible light.
- To investigate the efficiency of the developed photocatalyst for photo reduction of CO_2.

1.4 Scope of Study

With or without metal doped, titanium dioxide, (TiO_2) was selected as catalyst in photoreduction process due to its redox efficiency , availability, photostability and non-toxicity (Ibhadon & Fitzpatrick, 2013). In this process, highly efficient and selective photocatalyst that could work under sunlight are the most important for solar hydrocarbon production. Among the different semiconductor materials, TiO_2 as a photocatalyst has numerous advantages. Some attractive features include powerful oxidation properties, good charge transfer potentials, low cost and corrosion resistance (Tahir & Amin, 2013a). However, this type of catalyst displays the activity when it is irradiated with UV-light (wavelength less than 380 nm) due to its higher band gap. Thus in this study, the research work will be started with the synthesis on TiO_2 and modification with Cu ion to enhance its light absorption toward visible region. For photocatalyst preparation, the parameters that will investigated are concentration of Cu dopant, calcination temperature and calcination duration. The performance of the prepared photocatalyst will be evaluated in photocatalytic reduction of CO_2 under visible light radiation.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Carbon Dioxide (CO_2)

Naturally, CO_2 is emitted when human is breathing and during the combustion of fossil fuels. Ideally, this gas eventually will be removed from the environment by photosynthesis. Photosynthesis is the process where the conversion of CO_2 into glucose by the energy obtained from the sunlight. Nevertheless, the ecosystem balance has been disturbed by human activities which causes photosynthesis process alone is insufficient to convert the accumulated CO_2 in atmosphere despite the huge amount of sunlight energy reached the earth surface daily. Therefore, it is important to find a new way to overcome the problem by introducing photo-reduction of CO_2 to produce hydrocarbons.

Solar light is the ideal energy source because it is not depleting and abundantly available. In combination with photocatalytic H_2O splitting, the solar-driven reduction of CO_2 to fuels is a very attractive approach to reduce CO_2 emission. (Evgenii, Guido, Jonas, Gaston, & Javier, 2013). It can be shown that, with the amount of energy from the sunlight, the conversion of CO_2 into methanol and hydrocarbon could be conducted and in addition to that, CO_2 content can be reduced.

2.2 Photo-Reduction of CO_2

Due to the stability of CO_2 and having low energy, it is easier for the molecule to exist and maintain their shape. When CO_2 is formed, one carbon atom forms double covalent bonds with two oxygen atoms. Carbon dioxide is considered more stable than individual atoms as now the outer energy levels of all atoms are filled. Thus, to excite the molecule, it requires an energy to break the bonds. Below is the equations of CO_2 conversion into value-added product.

$$CO_2(g) + H_2O(l) \overset{hv}{\rightarrow} CH_3OH(l) + \frac{3}{2}O_2(g) \quad \frac{\Delta H(298K)KJ}{mol} = 726.7\ KJ/mol \tag{1}$$

$$CO_2(g) + H_2O(l) \overset{hv}{\rightarrow} CH_4(g) + 2O_2(g) \quad \frac{\Delta H(298K)KJ}{mol} = 890.9\ KJ/mol \tag{2}$$

This process is highly unfavourable from the thermodynamic and kinetic point of view. Based on the equation above, one mole of CO_2 requires 726.7 KJ of energy to form one mole of methanol showing that it is highly energy consumed reaction. For the elctro or photo-catalytic conversion of CO_2, additional energy input is required, which is obviously the solar energy that one likes to directly (photocatalysis), or indirectly (electrocatalysis) store in the process (Evgenii *et al.*, 2013).

2.3 CO_2 recycling for hydrocarbon production

Currently, human activities highly depending on fossil fuels is not favourable since it is depleting and causes serious CO_2 emission. Therefore, renewable energy should be research and put into development. For example the harmful CO_2 emitted from the industrial or naturally should be recycled to produce renewable energy. The current energy infrastructure is mostly dependent on fossil fuels. Combustion of these fossil fuels generates greenhouse gases especially carbon dioxide, the main cause of global warming (Tahir & Amin, 2013a). New technology such as photochemical conversion of CO_2 into value-added chemicals shows a promising future for sustainable energy and to supply energy demand in this world. In addition, hydrocarbons from CO_2 reduction using solar energy could be potential source since it is abundant and inexpensive feedstock.

Recycling of the CO_2 via reduction process with the water to produce hydrocarbons offers a viable new permanent alternative. As world primary source of energy is depleting, the uses of CO_2 reduction would continue to support production and the uses of hydrocarbon for a longer time. By using this approach, there will be no drastic change of the nature that the energy we currently use. As CO_2 is available to everybody on earth, it would constrain us from the reliance on non-renewable fossil fuels frequently present only in geopolitically unstable areas (Radin, 2013).

2.4 Introduction to photocatalyst

Catalyst is a substance that can cause and accelerate a chemical reaction without being affected by the reaction. It is usually used in small amounts relative to the reactants that increase the rate of reaction without being consumed in the process. In this research, the types of catalyst to be used is photocatalyst. Photocatalyst helps to convert the sunlight energy into chemical energy. During the process, photocatalyst will help to increase the wavelength absorption from the UV light to visible light. By adding the photocatalyst, the ability to use visible light can be achieved.

2.4.1 Titanium Dioxide (TiO_2)

Titanium dioxide has received wide attention due to its properties of chemical stability, non-toxicity, and photo-catalytic characteristics concerning environmental pollution (Tabaei, Kazemeini, & Fattahi, 2012). TiO_2 is a fine white powder. It is widely use in the whitening product such as paints and plastic industry.

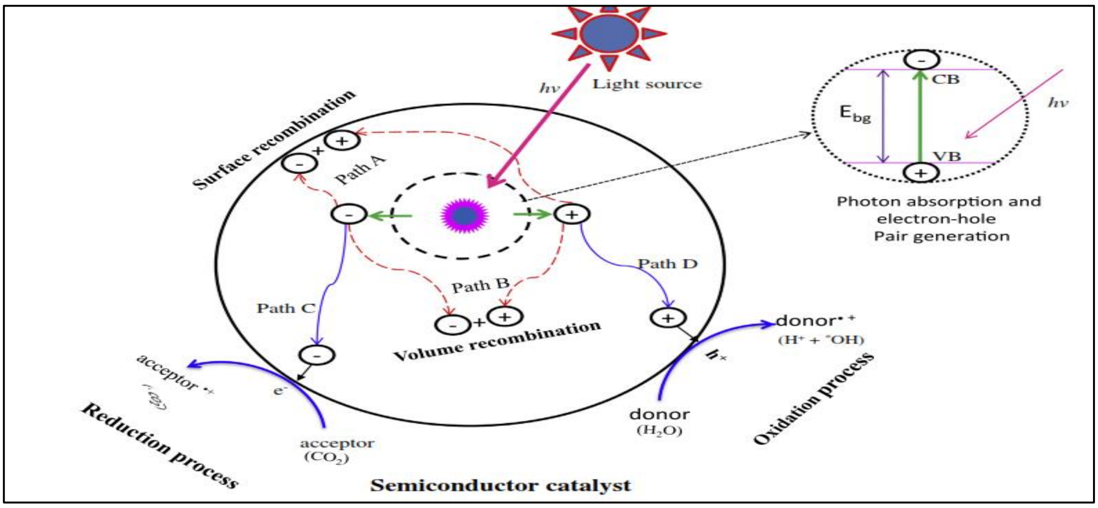
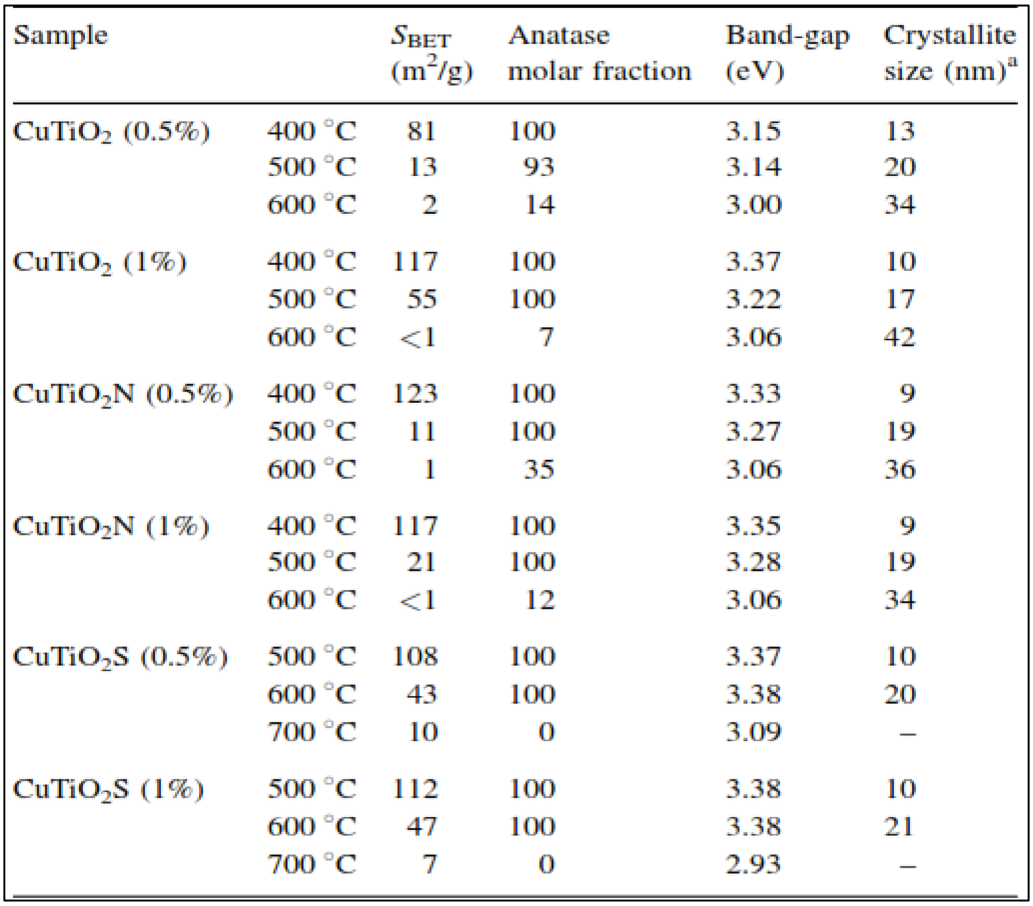


FIGURE 2.1 Mechanism and pathways for photocatalytic oxidation and reduction processes on the surface of heterogeneous photocatalyst (Tahir & Amin, 2013a)

The absorption of ultraviolet (UV) radiation by the photo-catalyst TiO_2 from the sunlight cause pairs of electrons and holes to produce. Figure 2.1 show the stage is referred as the semiconductor's "photo-excitation" state. The band gap (E_{bg}), shows the energy difference between the valence band (VB) and the conduction band (CB). The function of TiO_2 is to create a band gap between the negative electron (e^-) and the positive hole (h^+) when is excited by UV-light. However, if the electrons fail to find any trapped species (e.g. CO_2) on the semiconductor surface or their energy band gap is too small, then they recombine immediately and release unproductive energy as heat (Tahir & Amin, 2013a). In addition, TiO_2 is considered as a good photocatalyst for hydrogen generation because of its activity towards both light and water as well as excellent resistance to chemical and photochemical corrosion in aggressive aqueous environments. It is also less expensive than many other photo-sensitive materials (Yoong, Chong, & Dutta, 2009)

However, the disadvantage of application of TiO_2 as a photo-catalyst for visible light-induced chemical reactions has been hampered by its large band-gap energy (3.2eV for anatase TiO_2), which requires ultraviolet (UV) light to activate thus leads to the lower energy efficiency. Widening the absorption edge of TiO_2 from the UV to the visible spectral range could provide the groundwork to develop TiO_2 catalysts with visible light activity (Thuy, Van, & Hai, 2012).

2.4.2 Modification of TiO_2 for Enhanced Photocatalytic Activity



Sample		S_{BET} (m^2/g)	Anatase molar fraction	Band-gap (eV)	Crystallite size (nm)[a]
$CuTiO_2$ (0.5%)	400 °C	81	100	3.15	13
	500 °C	13	93	3.14	20
	600 °C	2	14	3.00	34
$CuTiO_2$ (1%)	400 °C	117	100	3.37	10
	500 °C	55	100	3.22	17
	600 °C	<1	7	3.06	42
$CuTiO_2N$ (0.5%)	400 °C	123	100	3.33	9
	500 °C	11	100	3.27	19
	600 °C	1	35	3.06	36
$CuTiO_2N$ (1%)	400 °C	117	100	3.35	9
	500 °C	21	100	3.28	19
	600 °C	<1	12	3.06	34
$CuTiO_2S$ (0.5%)	500 °C	108	100	3.37	10
	600 °C	43	100	3.38	20
	700 °C	10	0	3.09	–
$CuTiO_2S$ (1%)	500 °C	112	100	3.38	10
	600 °C	47	100	3.38	21
	700 °C	7	0	2.93	–

FIGURE 2.2 Surface and structural properties of Cu-TiO2 system (Colón, Maicu, Hidalgo, & Navío, 2006)

Figure 2.2, shows the surface and structural properties of the metal doped TiO_2. The surface and structural properties of different Cu–TiO_2 systems are summarised. Brunauer, Emmett and Teller (BET) surface areas for all series progressively decrease as calcination temperature increases, following a similar trend than undoped series.

However, incorporation of Cu significantly increases the surface area with respect to the former ones. This higher surface area values might be attributed to the effect of nitrate coming from Cu precursor that thermally decompose during calcination at temperature lower than 400^{o}C, increasing the porosity of surface (Colón, Maicu, Hidalgo, & Navío, 2006).

2.4.3 Modification with Metal Dopants

Another important achievement in photocatalysis is modification of TiO_2 by incorporating noble and transition metal ions onto the surface and into TiO_2 lattice. Due to high cost of noble metals, it restricts its application as a dopant causing limited number of acceptance. As an alternative, transition metals provide the option as more promising metal dopants.

For example, addition of metal can enhance the separation and transfering of photogenerated charge carriers to minimize the recombination of electron-hole pairs resulting from the formation of Schottky barrier. An optimal 3wt% CuO loaded TiO_2 shows higher CO_2 reduction than TiO_2 (Wenguang Tu, 2014). It effectively lower the barrier for CO_2 activation. The activation energy,E_a of TiO_2 and 3wt% CuO loaded TiO_2 is +26 and +12 KJ/mol respectively. The resulting result of lower activation energy will improve the efficiency of CO_2 reduction.

In other aspect, metal dopant can affect the selectivity of the products in view of many different products during the activity of CO_2 reduction. Addition of TiO_2 with Pt or Pd mainly produced CH_4, but some amount of acid such as acetic acid was produced when using other metal. For example, NiO was added into TiO_2 with band gap of 2.6 eV for reduction of CO_2 into methanol under visible light irradiation (Wenguang Tu, 2014).

(Tahir & Amin, 2013a) stated that Ag doped with TiO_2 has excellent photocatalytic properties that can reduce the band gap with 0-5,2wt% of Ag will shifted the band gap into the visible region. The conventional method can also be enhanced by using metal nanoparticle doped TiO_2 through plasmon effect such as gold nanoparticle doped with TiO_2 will easily be transferred under visible light irradiation. Impregnation of nano–sized iron was carried out to further the light absorption of TiO towards visible region. Upon successful impregnation with Fe (2 at.%), the band gap of TiO_2 was reduced to 2.07 eV (λ = 600nm), (Satishkumar, 2011).

2.5 Factors influencing Photocatalytic Degradation

Operating parameter that could affect the photocatalytic degradation of organic compound such as catalyst concentration, pH of the reaction media, calcination temperature and duration, dopant content and dopant composition were studied.

2.5.1 Metal Content

One of the important factor that affect the efficiency of the metal corporated with photocatalyst is the metal content. The amount of metal content varies with respect to preparation method and the application. The study conducted by (Nguyen & Wu, 2008), the effects of Cu-Fe on VLR of TiO_2-SiO_2 under solar irradiation for photoreduction of CO_2, the band edge of TiO_2-SiO_2 was shifted from 3.30eV to 2.95eV by doping 0.5wt% of Cu and Fe. It means that, it allowed the light source from the UV region to be shifted to the visible region. Table 2.1 show several metal doped TiO_2.

TABLE 2.1 The influence of metal loading on the photocatalyst

Application	Light Source	Photocatalyst	Doping (wt%)	Ref
Methanol	UV	CuO/TiO_2	3.0	(Slamet, Nasution, Purnama, Kosela, & Gunlazuardi, 2005)
Methane & Methanol	UV	Ag/TiO_2	7.0	(Kočí *et al.*, 2010)
H_2 Production	Visible	Cu/TiO_2	10	(Yoong *et al.*, 2009)
Degradation of paranitrophemol	Visible	Fe/TiO_2	3.0	(Sood, Umar, Mehta, & Kansal, 2015)

From table 2.1, we could observed that with incorporation with some amount of metal dopant into TiO_2, the efficiency of the catalyst can be improved. Some photocatalytic activity increased with the appropriate amount of the metal dopant which could be attribute to the creation of surface barrier on the TiO_2. The improvement in photocatalytic performance is attributed to the enhanced light adsorption in UV−Vis range and the decrease of the recombination rate of photoinduced electron−hole pair (Xi-jia YANG, 2014). In addition, metal dopant reduced the band gap energy of TiO_2 by making the photocatalyst more suitable under visible light irradiation. However, other report mention that outside the optimum amount, the metal doped TiO_2 could accumulate during activation process, thus lessing the photocatalyst surface area and showing lower photocatalytic activity (Adán, 2007).

2.5.2 pH of mixture

The photocatalytic reduction of CO_2 is favourable under basic pH values and carbonates and bicarbonates may be produced during its reduction. Carbonates and bicarbonates are good holes quenchers and more stable compounds than CO_2 and it is harder to reduce them. Lower pH could shift the conduction band edge towards more positive and would be favourable to reduce CO_2 to methanol (Tahir & Amin, 2013b). The ionization state of photocatalyst surface varies based on the pH value of the solution, corresponding to the reaction on equations 3 and 4 (Ramli, Chong, Omar, & Murugesan, 2013).

$$TiOH + H^+ \leftrightarrow TiOH_2^+ \tag{3}$$

$$TiOH + OH^- \leftrightarrow TiO^- + H_2O \tag{4}$$

Other than that, the solution could also affect the charges of the reactant. Thus, adsorptivity of the reactant molecules will be prompt onto the surface of TiO_2, a significant procedure for photocatalytic reaction to occur (Lu, 2009).

CHAPTER 3

METHODOLOGY

3.1 Photocatalyst preparation

The research work will be started with the synthesis and preparation of Cu/TiO_2 followed by characterisation. Further, performance of the prepared Cu/TiO_2 will be assessed in photocatalytic CO_2 reduction system under simulated solar light. Figure 3.1 depicts the work flow of this research.

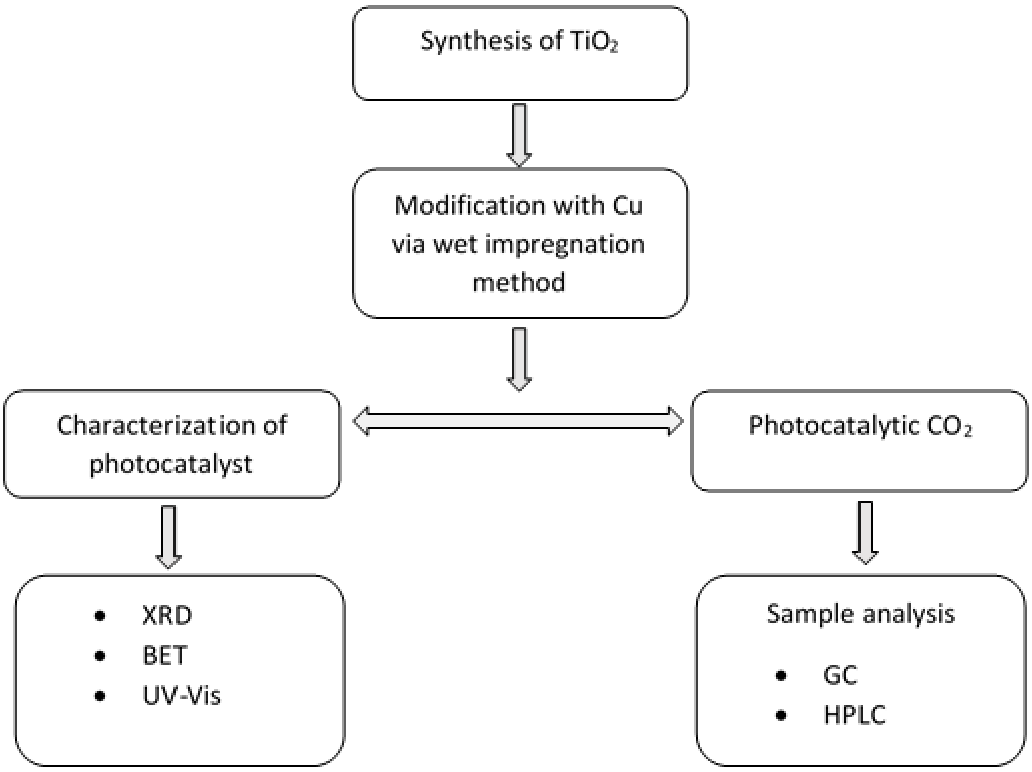


FIGURE 3.1 Work Flow of the preparation and conducting the experiment

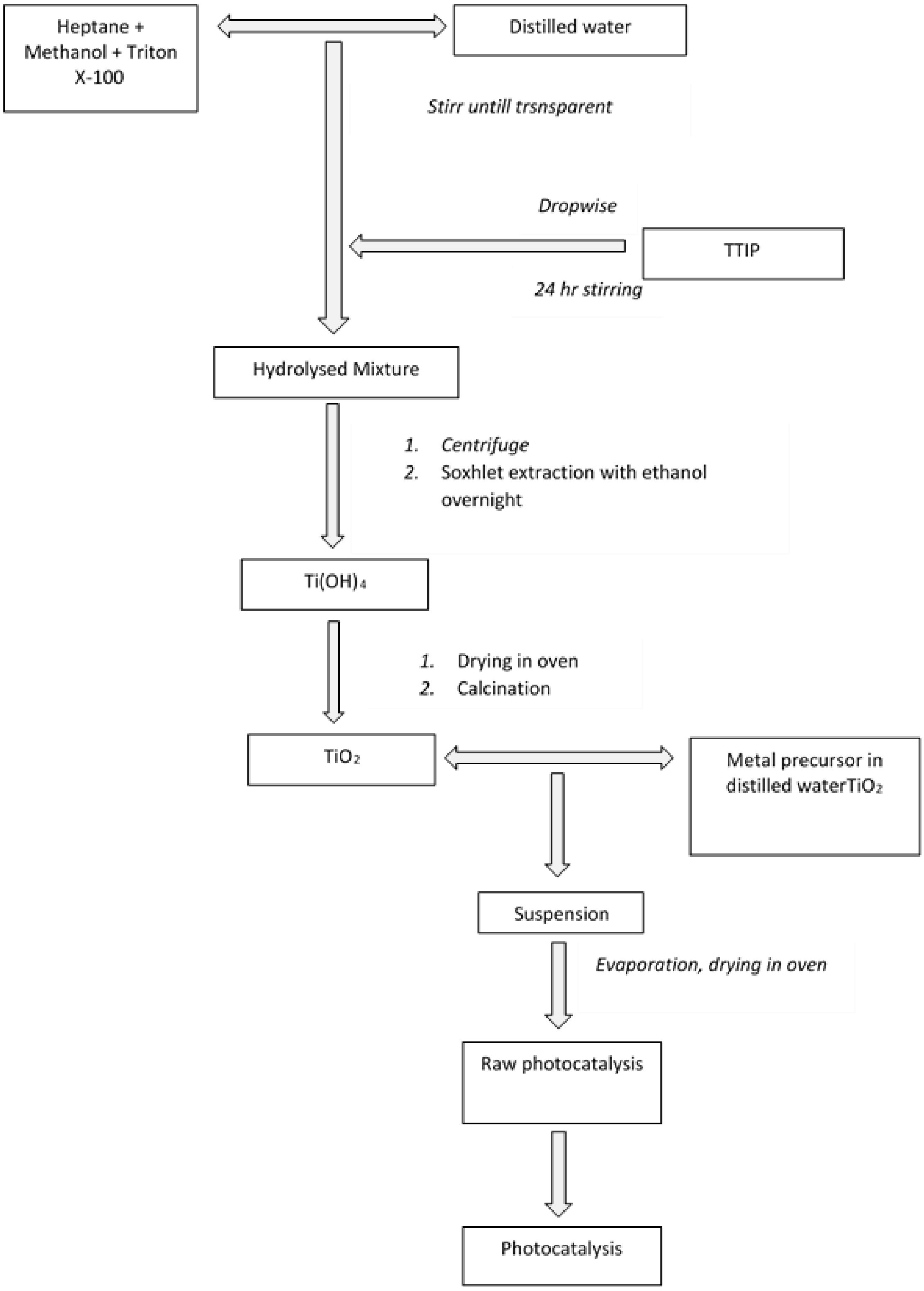


FIGURE 3.2 Photocatalyst synthesis and preparation process flow

Chemicals

The details of the chemicals used in the present research are summarized in Table 3.1. All chemicals were used as purchased without further purification.

TABLE 3.1 Chemical used in the present research work.

Chemicals	**MW g/mol**	**T_m, ^oC**	**T_b, ^oC**	**ρ(T=25 ^oC), g/cm^3**	**Purity (%)**
Heptane(C_7H_{16})	100.21	-91	98.4	0.68	>98.0
Triton X-100 ($C_{14}H_{22}O(C_2H_4O)$	646.85	6	270	1.06	>98.0
Hexanol	102.17	-52	158	0.81	>99.9
Titanium Isopropoxide (TTIP)	284.26	15	240	0.95	>98.0
Ethanol (C_2H_5OH)	46.07	-114	78.3	0.79	100
Copper Sulphate ($CuSO_4.5H_2O$)	249.685	110	150	2.284	99

3.2 TiO_2 Synthesis

The TiO_2 nanoparticles was prepare by using n-heptane, Triton X-100 and hexanol following the procedure reported by (Ramli *et al*., 2013). The molar ratio of the mixture was 5:3:1. In a 250 ml round bottom flask, 18.3 ml of n-heptane was added followed by 13.6 ml of Triton X-100 (TX-100) and finally 9.4 ml hexanol. The mixture was then stirred for 10 minutes after the addition of 12.0 ml of distilled water. The mixture is continuously stir until became transparent indicating the formation of micro-emulsion.

Then, titanium tetraisopropoxide (TTIP) will be added drop wise with the stirring continue for 24 hours to ensure complete hydrolysis of TTIP. After that, 15.0 ml of ethanol was added into the mixture to break the microemulsion and the mixture was centrifuged at 6000 rpm for 10 minutes to retrieve the solid. The solid was transfered into a thimble and place in the soxhlet setup. Residual organic compounds will be removed from the solid through soxhlet extraction using methanol as solvent. This procedure was conducted overnight (~14 h). The white solid was dried in an oven at 80^oC for 5 hours follow by grinding into very light and fine white powder.

The titanium hydroxide, $Ti(OH)_4$ is dispersed in a flat crucible to get thin layer of the powder and calcined at 400^oC for 1 hour. Afterwards, Cu ions (1-2wt. %) was doped to the TiO_2 via wet impregnation method. The resulting powder will be subject to heat treatment in a furnace. Prior to the heat treatment, the powder was analysed using Thermagravimatric Analyser (TGA) to determine the temperature range for heat treatment. Once the photocatalyst ready, it will be characterized with X-Ray Diffraction (XRD), Ultraviolet Light (UV-Vis) and Brunauer, Emmett and Teller (BET) to determine its properties. The process flow for the photocatalyst preparation is summarized in Figure 3.2.

Calculation method

For 1wt% of Cu dopped with TiO_2, taking basis of 1g TiO_2:

$$CuSO_4.5H_2O = 0.01g\ Cu\ x\ \frac{1\ mol\ Cu}{63.54\ g\ Cu}\ x\ \frac{1mol\ CuSO_4.5H_2O}{1\ mol\ Cu}\ x\ \frac{249.685\ g\ CuSO_4.5H_2O}{1\ mol\ CuSO_4.5H_2O}$$

$$CuSO_4.5H_2O = 0.0393\ g$$

For 2wt% of Cu dopped with TiO_2, taking basis of 1 g TiO_2

$$CuSO_4.5H_2O = 0.02g\ Cu\ x\ \frac{1\ mol\ Cu}{63.54\ g\ Cu}\ x\ \frac{1mol\ CuSO_4.5H_2O}{1\ mol\ Cu}\ x\ \frac{249.685\ g\ CuSO_4.5H_2O}{1\ mol\ CuSO_4.5H_2O}$$

$$CuSO_4.5H_2O = 0.0786\ g$$

3.3 Characterization

After preparing Cu/TiO_2 sample with range 0-5wt% for the photocatalytic reduction of CO_2, the sample will be analyse with XRD, BET and UV-Vis for characterization. The sample will be classified and will be tested for functionality.

TABLE 3.2 Equipment used for characterization

Equipment	Description
XRD	Identifies the molecular and atomic structure of a crystal.
BET	Provides accurate specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser
UV-Vis	A radiation source for spectroscopy must generate a beam with enough power, wavelength range and stability for detectable and reproducible results

1. X-Ray Diffraction (XRD)

X-ray crystallography is a device used for identifying the molecular and atomic structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By identifying the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information. XRD measurements were carried out on a pristine film and on films annealed at temperatures T_a ranging from 470–1320 K. These measurements have been used for the structural investigation and for the determination of the average crystallite size in the nanocrystalline films. XRD spectra of the samples exhibit the characteristic diffraction peaks if annealed up to T_a = 1220 K due to the anatase phase, but no peaks of rutile (Orendorz *et al*., 2007).

2. Brunauer, Emmett and Teller (BET)

BET analysis provides accurate specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in m2/g yielding important information in studying the effects of surface porosity and particle size in many applications. Below is the calculation on BET:

$$S = \frac{Vm\ x\ Na}{m\ x\ 22400} \tag{5}$$

$$S = Va(1 - \frac{P}{Po}) \tag{6}$$

Vm = volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, in millilitres.

Na = Avogadro constant (6.022 × 1023 mol−1)

M = mass of test powder, in grams

Va = volume of gas adsorbed at standard temperature and pressure (STP) [273.15 K and atmospheric pressure (1.013 × 105 Pa)], in millilitres.

P = partial vapour pressure of adsorbate gas in equilibrium with the surface at 77.4 K (b.p. of liquid nitrogen), in pascals

Po = Saturated pressure of adsorbate gas, in pascals

3. Ultra Violet -Visible test (UV-Vis)

This test is conducted using spectrophotometers. Spectrophotometers are made up of stable source of radiant energy, a transparent sample called container, a equipment for isolating specific wavelength, a radiation detector which changes transmitted radiation to a usable signal, and a signal processor and readout. A radiation source for spectroscopy must generate a beam with enough power, wavelength range and stability for detectable and reproducible results. Deuterium lamp is used to generate the UV range and switch to a tungsten filament lamp at 350 nm for the visible range. The electrical excitation of deuterium at low pressure results in a continuous spectrum of emitted radiation from 160 nm to the beginning of the visible (375 nm). An arc is formed between a heated, oxide-coated filament and a metal electrode. When about 40 Volts is applied to the heated filament, a direct current is produced resulting in an intense ball of radiation. At around 350 nm, spectrophotometer will switches its radiation source to a tungsten filament. The radiant energy emitted from a heated tungsten filament approaches that of a black body and thus, is temperature dependent. The operating temperature is usually 2597^{o}C (2870 K) which results in radiation in the 350-2500 nm range. The lower limit is due to absorption at 350 nm by the glass container housing the filament.

3.4 UV-light photocatalysis reactors

The photocatalyst will be used for photoreduction of CO_2 under visible light radiation. Figure 3.3 shows the experimental setup for photocatalytic reduction of CO_2.

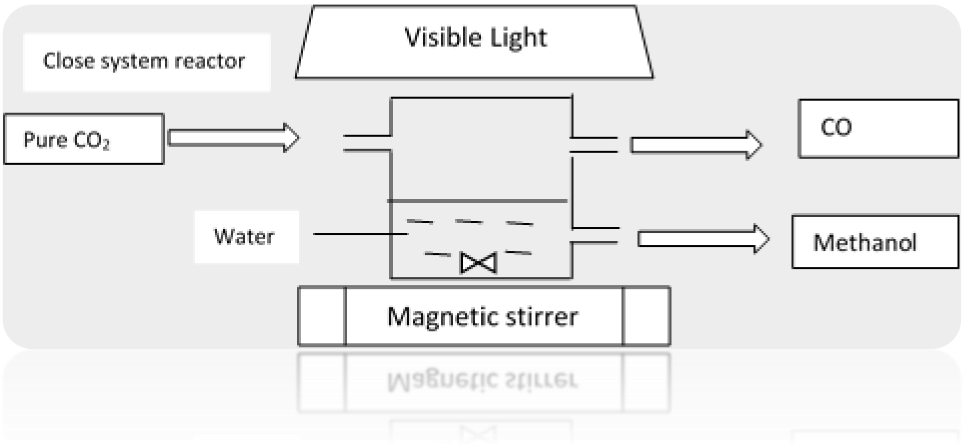


FIGURE 3.3 Experimental Setup for the photocatalytic reduction of CO2

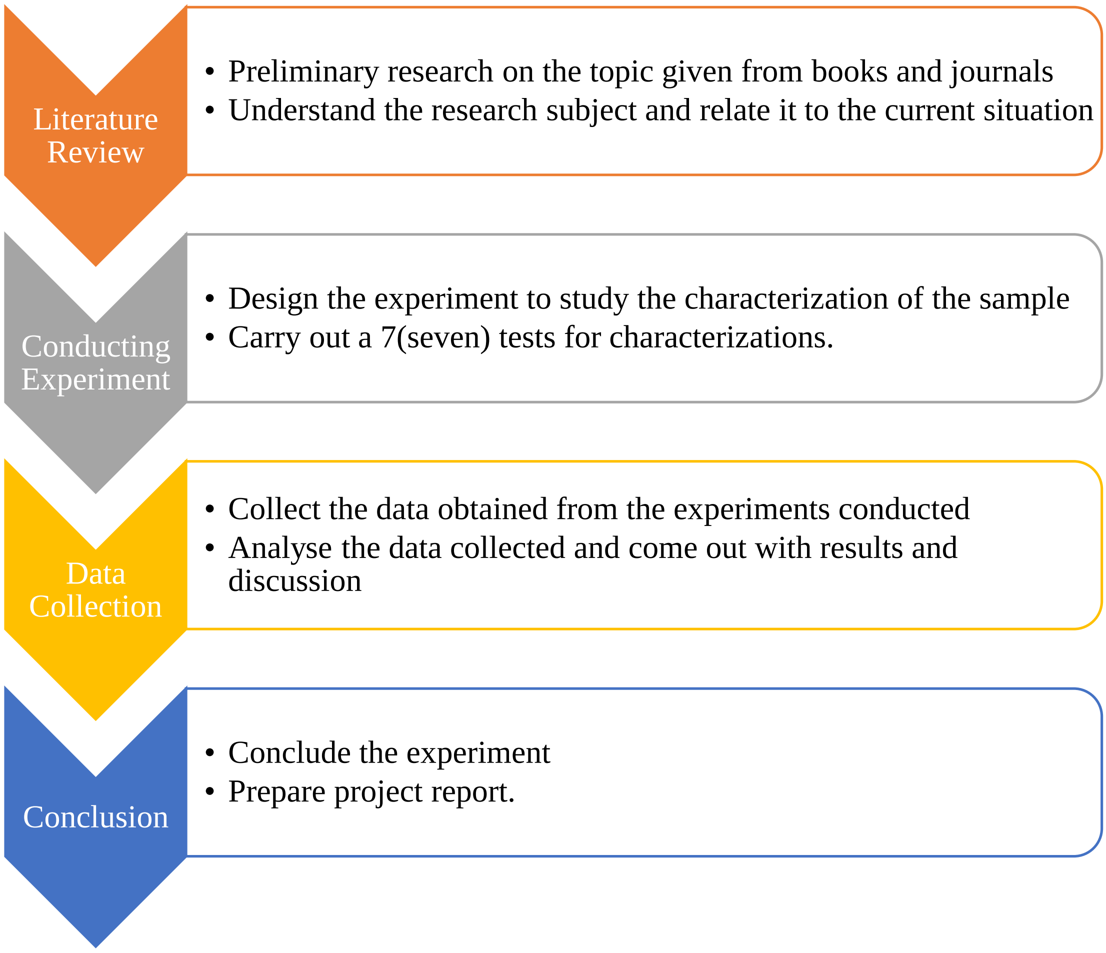
The sample will be collected and analysed using gas chromatography (GC) for gas sample and high performance liquid chromatography (HPLC) for liquid sample. The gas collected from the experiment will be injected in the injector port and it is carried by carrier gas. Characteristic of carrier gas should be chemically inert for example nitrogen, helium, argon and carbon dioxide.

Sample analysis

Gas sample will be analysed using A carlo Erba, model HRGC 5300 gas chromatography equipped with a flame ionization detector (FID) system. The chromatograph was equipped with a split/splitless injector (used in a splitless mode), a 3 m×3.3 mm I.D. stainless steel column packed with Porapak Q, a 3 cm×3.3 mm I.D. stainless steel column packed with molecular sieve 5A, a 4 cm×3.3 mm I.D. glass tube packed with Ni catalyst plugged with glass wool, a manual needle valve for controlling the hydrogen flow through the methanizer, two four-port UW type electromagnetic switching valves of 0.40 mm I.D. for by-passing the molecular sieve 5A column and/or the methanizer. A 0.5 mm I.D. stainless steel tubing was used throughout. The length of tubing used to connect any two units of the modified GC system did not exceed 10–15 cm (Kamiński, Kartanowicz, Jastrzębski, & Kamiński, 2003).

Meanwhile, the liquid sample will be examined using HPLC. A LiChrospher diol column (250X4.0 mm I.D., 5 um) (Merck) and a mixture of n-hexane-dichloromethane (9:1, v/v) as the mobile phase at a flow-rate of 1.2 ml/min at room temperature was used. The column eluate was monitored at 350 nm wavelength. The solvent was filtered with filter (Milipore, HV, 0.45 um) under vacuum for degassing before use.

3.5 Project Flowchart



- Preliminary research on the topic given from books and journals
- Understand the research subject and relate it to the current situation

- Design the experiment to study the characterization of the sample
- Carry out a 7(seven) tests for characterizations.

- Collect the data obtained from the experiments conducted
- Analyse the data collected and come out with results and discussion

- Conclude the experiment
- Prepare project report.

FIGURE 3.4 Project Methodology

3.6 Gantt Chart for FYP I

Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Date	14/1							4/3		18/3		1/4	8/4	
Selection of Final Year Project title	X													
Preliminary research work: Perform literature review related to the research project.		■	■	■	■									
Catalyst preparation presented by research assistance					■									
Prepare the methodology of the experimental work.						■	■							
Identify the equipment to be used in the project							■	■						
Submission of Extended Proposal to the SV and Coordinator.								X						
Prepare the presentation slide for Project Proposal Defence.								■	■	■				
Project Proposal Defence										X				
Interim report writing.										■	■	■	■	
Submission of Draft Interim Report to SV.												X		
Submission of Final Interim Report (after correction).													X	

3.7 Gantt Chart for FYP II

Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Date														
Synthesis TiO_2 catalyst preparation and setup the equipment	■	■	■	■										
TiO_2 catalyst doped with Copper preparatiion		■	■	■										
Cu/TiO_2 catalyst undergone characterization process: 1) XRD 2) BET 3) UV-Vis					■	■	■							
Reduction of CO_2 with water experimental process							■	■	■	■				
Submission of progress report.							X							
Pre-SEDEX										X				
Submission of Draft Final Report.														
Submission of Dissertation (soft bound)														
Submission of Technical Paper.											X			
Viva												X		
Submission of Project Dissertation (hard bound)														X

3.8 Key Milestones

FYP	Date Start	Date End	Period	Milestones
FYP I	20/1/2015	20/1/2015	1 day	Selected the title for the research project.
	30/1/2015	27/1/2015	4 week	Completed writing the extended proposal report and submitted to the supervisor to be reviewed.
	2/3/2015	4/3/2015	3 days	Made correction to the extended proposal report and submitted to the supervisor to be evaluated.
	3/3/2015	18/3/2015	2 weeks	Completed and presented Proposal Defence.
	2/3/2015	20/4/2015	7 weeks	Completed preliminary experimental work (experimental setup)
	11/3/2015	8/4/2015	4 weeks	Completed the interim report writing.
FYP II	18/5/201	15/6/2015	4 weeks	Completed synthesis for catalyst doped with Copper
	15/6/2015	6/7/2015	3 weeks	Characterization procedure for catalyst
	29/6/2015	27/7/2015	4 weeks	Completed experiment for reduction of CO_2.
	24/7/2015	21/8/2015	4 weeks	Completed and submission of project dissertation.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 X-Ray Diffraction

The XRD patterns of Cu-doped TiO_2 are shown in Figure 4.1. The diffraction peaks were indexed to (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) planes of anatase phase of TiO_2 (JCPDS No. 78-2486). The XRD pattern shows the crystal structure of Cu doped TiO2 was similar to the bare TiO_2. There is no Copper peaks observed, showing that Cu was doped into TiO_2 lattice or due to low concentrations in TiO_2 matrix (Xi-jia YANG, 2014).

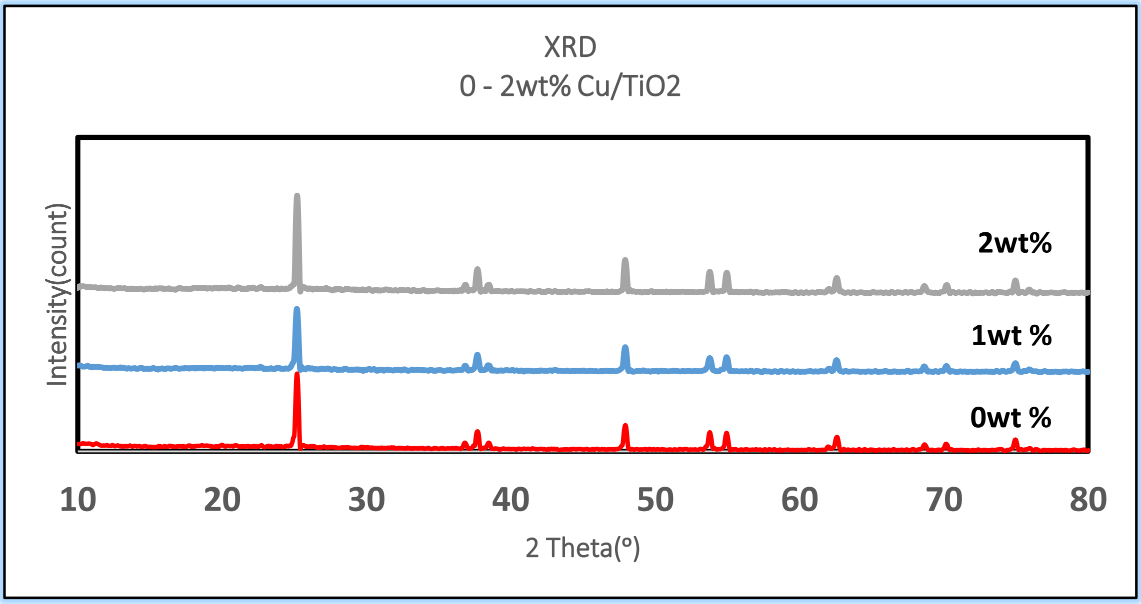


FIGURE 4.1 XRD pattern 0-2wt% $CuTiO_2$

The diffraction pattern of undoped TiO_s sample is similar but not as sharp as doped samples showing that the crystalline structure was not formed for the plain titania catalyst during the heat treatment procedure. The crystallite sizes of the samples were determined from XRD patterns using Scherrer equation:

$$D = \frac{k\lambda}{FWHM cos\theta}$$

Where k is a constant for Cu/TiO_2, λ is the wavelength of X-rays, FWHM is the pure full width of the diffraction line at half of the maximum intensity and θ is the Bragg angle. The results showed that the mean grain size is about 32.73 nm.

TABLE 4.1 Particle size

Sample	**Particle size (nm)**
0wt% Cu/TiO_2	32.2
1wt% Cu/TiO_2	33.8
2wt% Cu/TiO_2	32.2

It is observed that by addition of some amount of metal dopant in the preparation of TiO_2 photocatalyst resulted in small increase in the crystallite size of TiO_2. This indicate that the doping procedure resulted in a slightly larger nano-sized titania crystallite particles.

4.2 Brunauer Emmett-Teller

TABLE 4.2 BET surface area

Sample	**Temperature (°C)**	**BET surface area(m^2/g)**	**Total pore volume (cm^3/g)**	**Average pore diameter (A)**
0wt% Cu/TiO_2	120	9.6828	0.055542	232.051
3wt% Cu/TiO_2	120	8.3739	0.0053299	263.824
5wt% Cu/TiO_2	120	8.0019	0.050244	253.593

Based on table 4.2, surface area of the materials after calculated according to the Brunauer Emmett-Teller (BET) method was 9.6828 m^2/g. The larger the surface area the higher the photoactivities (Yuan & Xu).

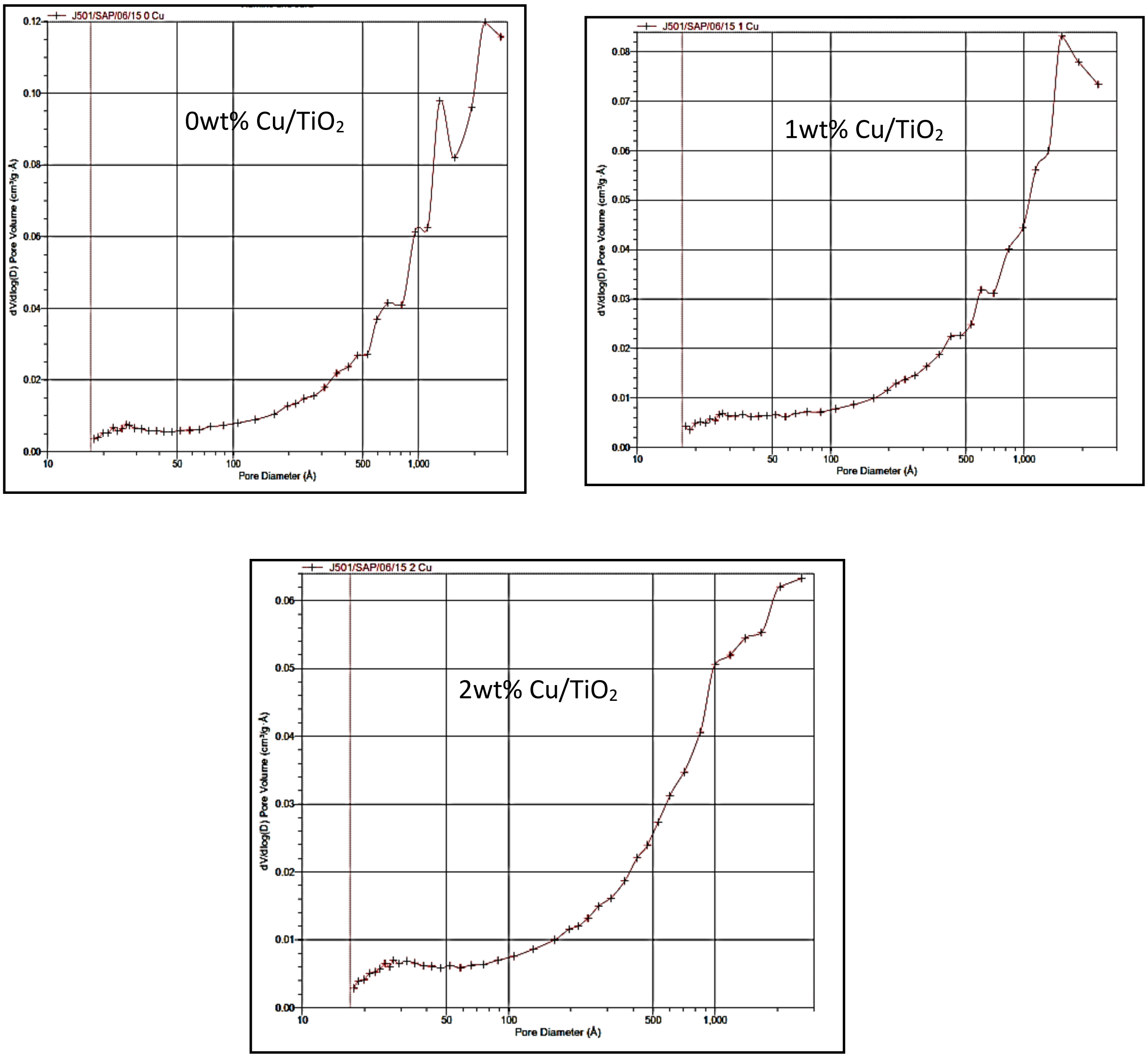


FIGURE 4.2 BJH pore size distribution

In figure 4.2, pore-size distributions calculated by BJH method for three (3) samples are presented. The graphs demonstrate that the investigated photocatalysts possessed broad pore size distributions in the mesoporous region, revealing the variable-sized mesopores in the photocatalyst structure.

4.3 UV-Visible

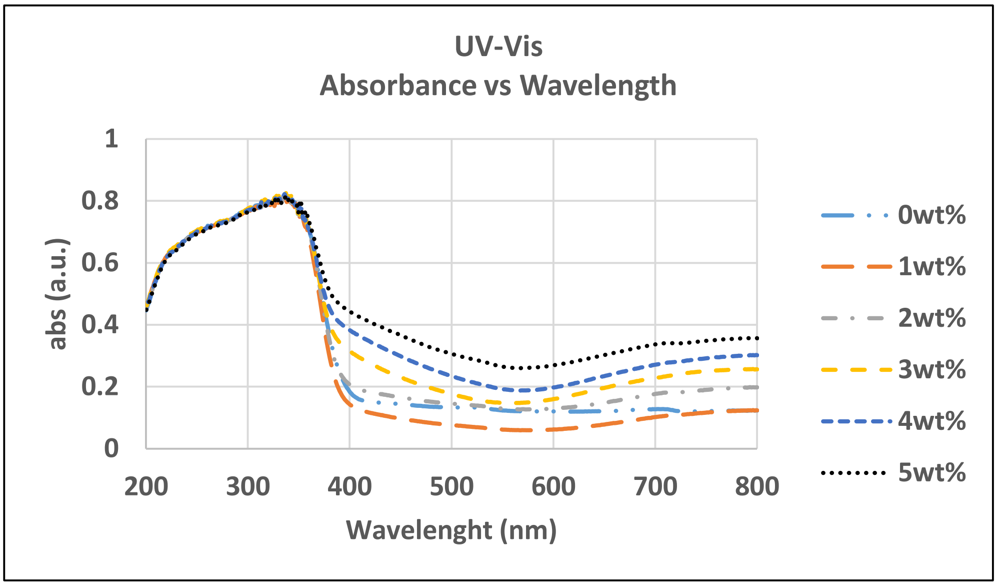


FIGURE 4.3 UV-Vis absorbance of the photocatalyst

Figure 4.3 shows that the UV–vis of the 0-5wt% Cu/TiO2 samples. Results indicated that the absorbance was obviously shifted to the visible light range with the transition metal additives. The undoped TiO2 has low absorption in the visible region (>400 nm), while the photocatalysts with copper additives showed that visible light photoresponse of the doped samples was increased.

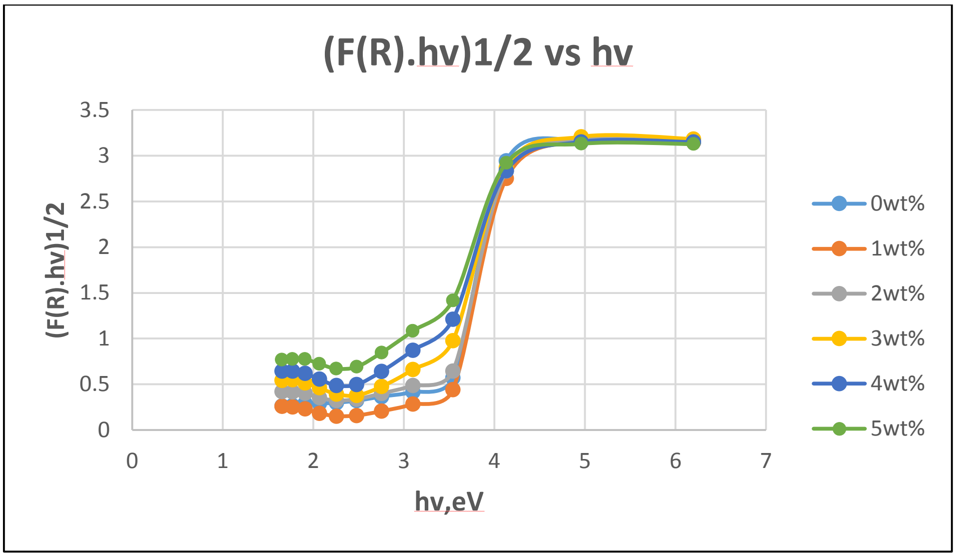


FIGURE 4.4 Photocatalyst (Cu/TiO2) Band gap energy

TABLE 4.3 Band gap energy

Photocatalyst (Cu/TiO2)	**Band gap energy (eV)**
0 wt%	3.40
1.0 wt%	3.43
2.0 wt%	3.36
3.0 wt%	3.23
4.0 wt%	3.10
5.0 wt%	2.99

Based on the figure 4.4, the amount of doped material can really affected the band gap energy of the photocatalyst. When the amount of doped is increase the band gap energy will be decrease. The decreasing in band gap energy can be benefits to the experiment where less amount of energy required to overcome the band gap energy. As you can see in the table 4.3, it shows each of the band gap energy for the photocatalyst. The highr amount of doped photocatalyst shows the lowest band gap energy.

4.4 Methanol Yield

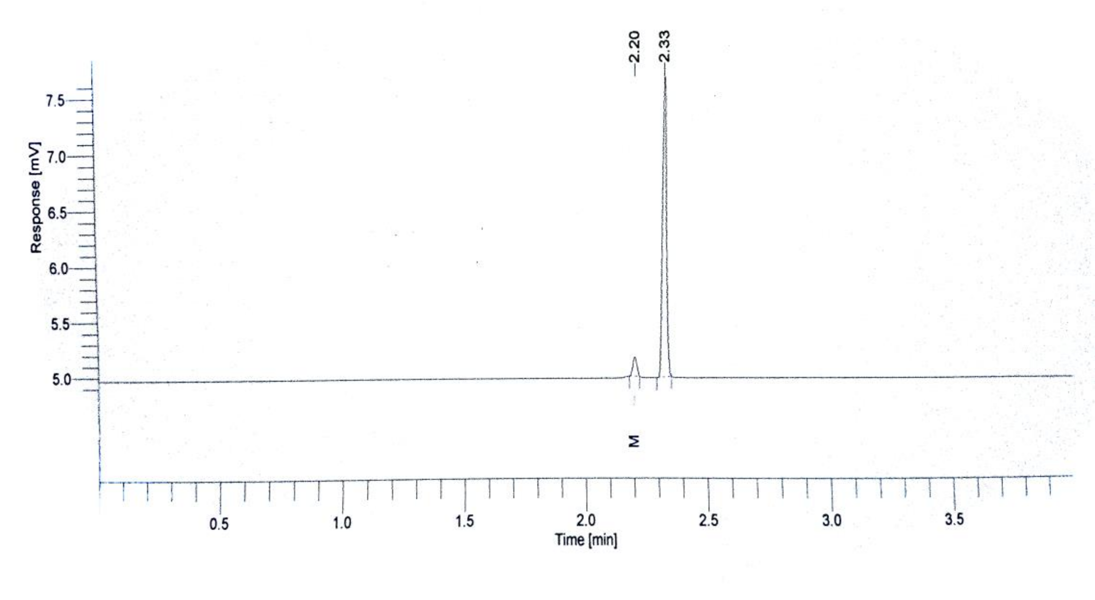


FIGURE 4.5 Gas Chromatography

TABLE 4.4 Methanol formation

Sample	**Methanol (g methanol/ g catalyst)**
0 wt% Cu/TiO_2	-
1 wt% Cu/TiO_2	-
2 wt% Cu/TiO_2	-
3 wt% Cu/TiO_2	32.51
4 wt% Cu/TiO_2	-
5 wt% Cu/TiO_2	-

Figure 4.5 shows, the formation of methanol was tested by using gas chromatography (GC). All the sample was tested but only 3wt% Cu/TiO_2 shows the significance reading compare to the rest. Table 4.4 show the methanol formation for each sample. Based from figure above, the initial peak was measured to be the peak for methanol while the bigger peak shows the by-product further reactions during the experiment. It can possibly happen due to less pure CO_2 supply to the reactor or the reaction was carried out longer than it should be.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Based on the research objectives, the conclusion can be made from the present research work on CO_2 conversion using water as solution and Cu/TiO_2 as photocatalyst:

TiO_2 was synthesized using microemulsion procedure and the modifications were conducted under wet impregnation method to produce doped Cu with TiO_2. From the characterization analysis, the synthesized Cu/TiO_2 was found to be smaller when the calcination temperature is increase. The sample was tested using BET and the surface area of the sample has proved that the size was below average due to high degassing temperature.

Based on the UV-Visible light test, it shows that the reading move toward the visible light region when the amount of copper doped in TiO_2 increase. There is a possibility for the photocatalyst to be increase on the efficiency towards the visible light region. Besides, from the XRD test, the pattern shows that all the samples was in anatase form.

The amount of methanol produce using 3wt% Cu/TiO_2 shows that, not all the photocatalyst can be used for photoreduction process. In this experiment, 32.51 (g/g) methanol was formed. Thus, it is important to develop a photocatalyst with enhanced activity under visible light as well as knowing the efficiency of the photocatalyst itself.

5.2 Recommendation

For future work, some of the recommendations could be taken into consideration as per below:

1. This experiment was conducted in very small scale of aqueous solution (40ml). Bigger scale may shows different result and may produce more accurate data.
2. In actual practical, the presence of other compounds could affect the reaction mechanisms and the efficiency of the photoreduction of the process.
3. The current experiment was conducted under visible light, thus in order to measure the efficiency of the system under solar light, the experiment should be held using direct sunlight which can bring variation in result.

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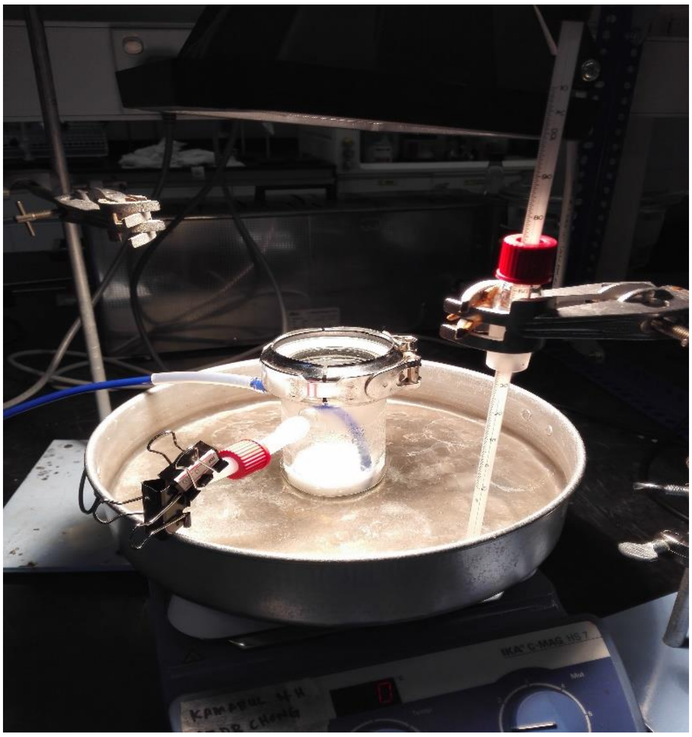
APPENDICES

APPENDIX 7.1 Setup of the Experimental



APPENDIX 7.2 Carbon dioxide tank supply

APPENDIX 7.3 Outside Frame of experimental setup

APPENDIX 7.4 Sample of photocatalystCu/TiO_2