# CERTIFICATION OF APPROVAL

**Synthesis of Mesoporous Titanium Dioxide by Using Different pH**

By

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Approved

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TRONOH, PERAK

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# CERTIFICATION OF ORIGINALITY

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

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# ABSTRACT

anium Dioxide is an oxide metal which is widely used as catalyst or catalyst support. The
:us in this project is to study the characteristics of mesoporous titanium dioxide, and also to
:ntify the method on synthesizing the material. Various researches have been conducted
;arding the porous material, identifying the factors that influencing the size of the pore for the
iterial and also the suitable method to synthesize porous material, specifically, mesoporous
anium Dioxide. In this study, too, size of the pore would also be manipulated until it reaches
: desired pore size by conducting series of experiment.

ere are two parameters that need to be investigated in this project. The first and most
portant parameter is the pH of the solution. For this project, base pH is chosen (pH 8, 9, 10, 11
l 12). The pore size can certainly be affected by the pH of the solution. The pH provides a
dium for the Titanium Chloride to react with water and HCL. Therefore, it is crucial for this
earch to find the most optimum pH in synthesizing $TiO_2$. The second parameter is the calcined
iperature which comes after the drying process. Three calcined temperature is suggested (450,
) and 550°C) and, still, the optimum calcined temperature also needs to be found.

amples consist of pH 8, 9, 10, 11 and 12 respectively have been synthesized for the
)eriment. However, the results for the pore size and the crystalline structure still could not be
ained due to time constraint. Perhaps during the final presentation of this project, the results
all of the samples could be obtained.

## ACKNOWLEDGEMENT

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# CHAPTER 1: INTRODUCTION

## 1.1 Background

cording to the IUPAC (The International Union ofPure and Applied Chemistry) ssification, porous solid can be arranged in three main categories, depending on their pore e: micropore (<2nm), mesopore (2~50nm), and macropore (>50nm). Mesopore sizes are in nanometer region; therefore, the term "nanoporous" also frequently used in this area of dy. Note that the pore sizes discussed represent the diameter or the width of the pore, not the ius.

porous materials are extensively applied as catalysts (or catalyst support) and adsorbents to their open structure and huge surface area. Zeolite for example, is a member of stalline microporous materials and is already in used in various applications: catalysis, orption, separation, environmental protection, biological technology, functional material, l etc. But since the diameter of the pore for zeolite is small (<~1.3nm) it limits their lication to small molecules, not larger organic or biological molecules. Mesoporous terials with pore sizes range in between 1.5-30 nm overcome the pore-size limitation of lites. The mesopores allow many reactions on ordered porous materials to be possible, such modification by utilizing larger organic or biological molecules. Mesoporous materials also vide new opportunities for both fundamental research (e.g., gas adsorption modelling, molecular catalysis) and practical application (e.g., adsorption, separation, purification of and liquid, catalyst, biological material, semiconductor, optics component, sensors, drug-ivery carrier, material for environmental protection, energy-storage host and etc).

ne of mesoporous materials possess some exclusive outstanding properties which other ous materials do not have. They are:

- well defined pore sizes and shape, narrow pore-size distribution
- highly ordered pore structure system at the nanometer level

- adjustable pore size in the range of ~1.3 to ~ 30 nm
- various structures, wall compositions, and pore shapes
- high thermal and hydrothermal stability if properly prepared or treated
- high surface area, high porosity
- various controllable regular morphologies at different scale form nanometers to micrometers
- applications potentials (stated above)

## 1.2 Problem Statement

considering the problem of pore size as a main subject of this project, the author proposed anium Dioxide to be synthesized as a mesoporous material so that it can achieve larger pore e, within the range 1.3-30 nm in size (diameter). Limitation for the porous material is mainly cause of the pore size of the material. By using metal chloride as starting material to nthesize metal oxide porous material, hopefully larger pore size could be achieved. Larger the e size, larger in use for application purposes.

### 1.2.1 Problem Identification

search mainly conducted in studying on method for synthesizing the mesoporous material cifically $TiO_2$, not the effect of ph and calcined temperature.

### 1.2.2 Significant of the project

anium Dioxide has a very wide usage in processes which involve catalyst or catalyst support. erefore, by taking mesoporous Titanium Dioxide as main focus for this study, it opens an portunity to improve the pore size for the material, thus improving its effectiveness as catalyst catalyst support.

## 1.3 Objective

- To synthesize mesoporous $TiO_2$ by using Titanium Tetrachloride ($TiCl_4$) as a starting material.
- To study the effects of ph to the size of the pore while performing the autocleave sol-gel process in synthesizing $TiO_2$.
- To investigate the effects of calcined temperature for the size of the pore.

## 1.4 Scope of study

ıdy about:

- Methods to synthesize mesoporous Titanium Dioxide, $TiO_2$
- Crystallization of the synthesized porous material by using X-ray Diffraction (XRD) method
- Surface area of the porous material, thus calculating the pore size, by using Brunauer-Emmet-Teller (BET) method
- Chemical compound exist in the sample by using Fourier Transform Infrared Spectroscopy (FT-IR)

## 1.5 Relevancy of the project

anium Dioxide has a lot of applications in catalyst industry which means it is really important a chemical student to take part in doing research and development about the material. By ɔroving the effectiveness of the porous material, it could also increase the demand for it, thus, ing up the standard for technology in synthesizing the porous material, specifically, :soporous Titanium Dioxide.

r this research, due to limitation by cost and time constraint, studying the effects of nperature and duration is sufficient enough in investigating the characteristics of mesoporous :anium Dioxide. The university itself has already taken porous material as one of its attention achieving the title of Research University.

**1.6 Feasibility**

e project research is divided into 2 semesters (8 months, 4 months per semester). For the first nester, basically is about planning the work. The related literature research study is mpleted and the literature review is wrapped up to brief on the scope of the project. Then, m the study research, the right methodology is developed to ensure all equipments are ıilable for the work execution as well as to obtain the feasible time frame for research and ies of experiments.

e second semester is about working the plan by completing the developed experimental rk. The work execution is done based on the developed methodology to ensure the good rk flow. The complete report of the work is attached with the result analysis plus crucial cussion, and related documents are attached.

# CHAPTER 2: LITERATURE REVIEW

## 2.1 Literature Review

ıe earliest synthesis of the hexagonal mesoporous silica material was reported in US patent ;56,725 by Chiola, Ritsko and Vanderpool.[1] The goal of this patent was to prepare low-bulk-nsity silica that would be one component of luminous powder (coating fluorescent-lamp ›e's). This patent claimed that high-purity silica can be prepared by conducting the ımoniacal hydrolysis of tetraalkyl orthosilicates (TEOS) in the presence of a cationic ·factant. TEOS as silica resource and cetyltrimethylammonium chloride (CTAC) as surfactant ɪre used in the process. They managed to recover fine, pure silica from the aqueous hydrolysis ethyl silicate with ammonia. The product bulk density was about 0.1g/$cm^3$. In 1997, Di-nzo [2] repeated the synthesis and found the product to be highly ordered hexagonal ;soporous silica material.

general, the synthesis mixture for mesoporous material contains four major elements: ›rganic precursors, organic template molecules, solvent, and acid or base catalyst. The mation of a material with a desired structure and morphology depends on a delicate interplay ween several basic processes, whose relative rates determine the structure and properties of final structure. These are the self-assembly technique or sol-gel process. The surfactant ybe cationic or anionic or even non-ionic, but cationic quarternary ammonium surfactant is lely used for the sol-gel process.

›cedure is simple whereby the synthesis procedure consists of three main components; rganic species for the formation of the inorganic wall, template (surfactant) and solvent. The factant molecules in the solution will self-assembly into a micelle or liquid-crystal phase. e structure of the micelle or liquid crystal will determine the structure of the mesoporous ›duct. Although it is simple, but many factors play major role in the sol-gel process such as , catalyst, organic or inorganic additives, and reaction conditions (temperature, time and etc).

Table shown below are summarized journals which reported about porous materials and what the author learnt from the journals.

| No | Name | Author | Objective | Remarks |
|---|---|---|---|---|
| 1 | A Novel Method for the Synthesis of Mesoporous Molecular Sieve[3] | Xiu Mei TAI, Hong Xia WANG, Xiu Qi SHI | To prepare a mesoporous molecular sieve MCM-41 in glycerol and ethylenediamine(EDA) at room temperature | Basic understanding on how to synthesis the mesoporous material |
| 2 | A simple, template-free route for the synthesis of mesoporous titanium dioxide materials[4] | Chunqing Liu, Lei Fu and James Economy | To prepare a mesoporous $TiO_2$ via a simple and environmentally benign template-free sol-gel process | A unique method to synthesis specifically $TiO_2$ |

**Table 1 Summary of Journals**

Most common method used in synthesizing the mesoporous (Titanium Dioxide) material is a sol-gel process which has been studied to produce multi-component oxides (glasses and ceramic). Based on cohydrolysis of molecular precursors such as metal alkolides, the reaction rates depend on the nature of the metals. [5]

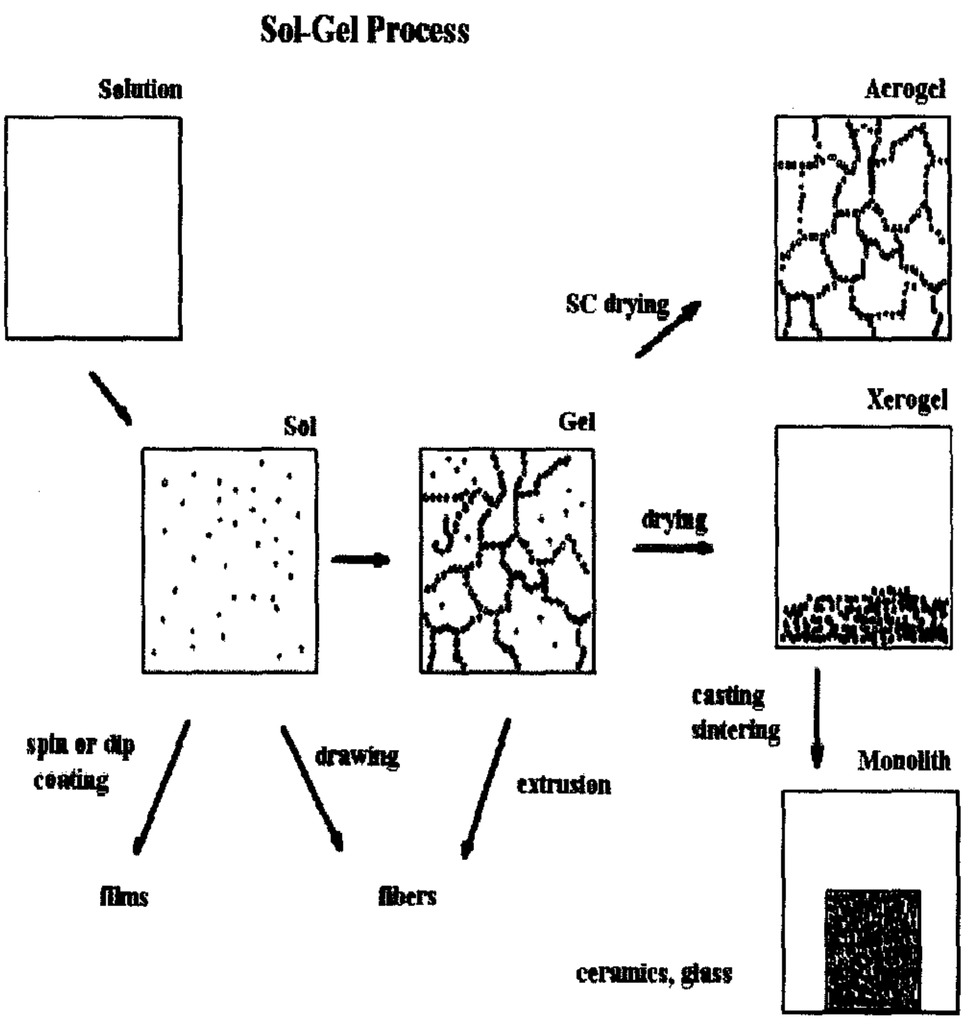


Figure 1 Illustration of Sol-Gel Process

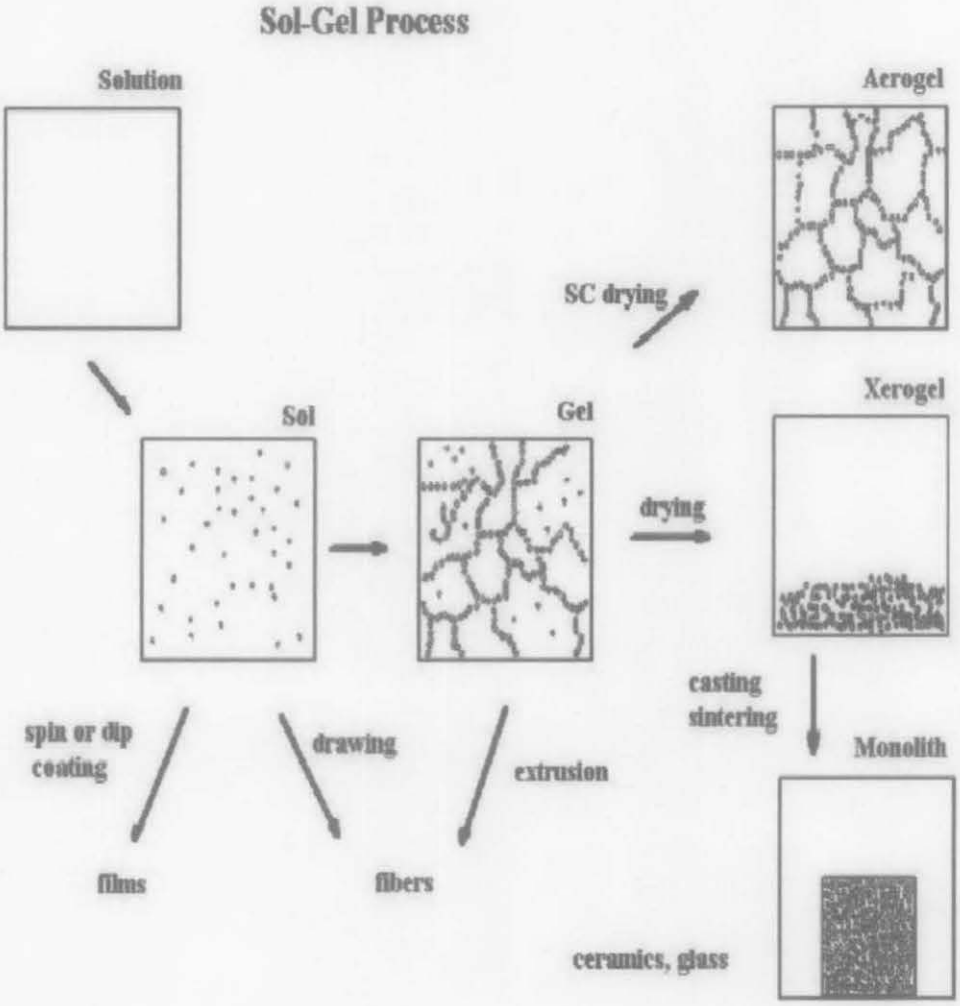


Figure 1 Illustration of Sol-Gel Process

# CHAPTER 3: METHODOLOGY

## 3.1 Research Methodology

### 3.1.1 Equipments


Figure 2 Hot plate magnetic Stirrer

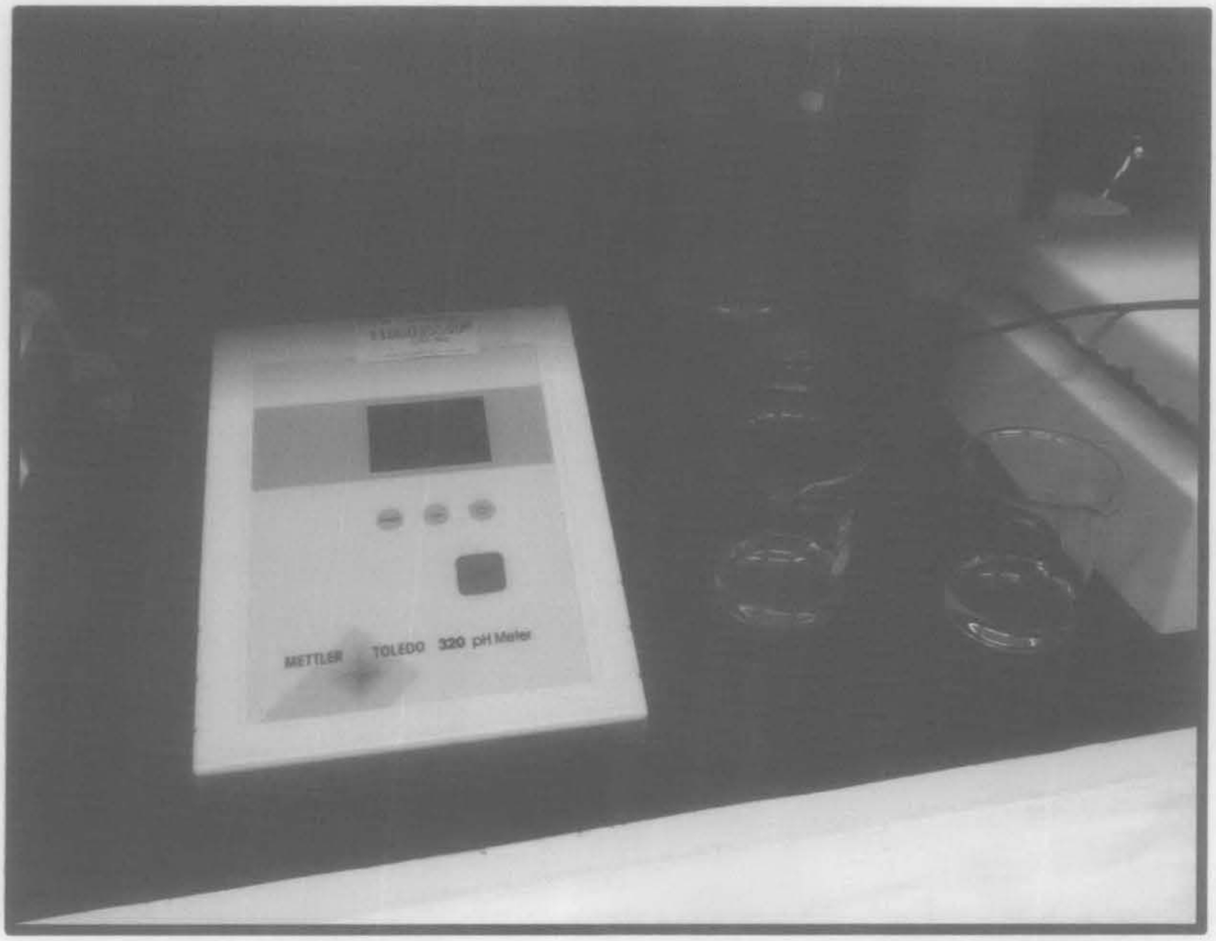


Figure 3 pH meter

### 3.1.2 Preparation of Sodium Hydroxide (NaOH)

In order to maintain the desired pH for the solution, a required amount of NaOH will be added dropwise to the $HCl + H_2O + TiO_2$ solution later on. The NaOH is diluted to achieve the desired concentration. The calculations are as follows:

$$Molarity = \frac{Number\ of\ Moles\ x\ 1000}{Volume\,(ml)}$$

$$Number\ of\ moles = \frac{Mass}{Molecular\ Weight}$$

The required molarity for NaOH is 5.0M and the volume is 500ml. This gives the number of moles of 2.5. By using the second formula, which NaOH has the molecular weight of 40g/mole, the amount required for NaOH to be diluted is 100g.


Figure 4 Preparation of NaOH

### 3.1.3 Preparation of Hydrochloric Acid (HCl) and deionized water ($H_2O$)

Objective is to give volume of HCl: $TiCl_4$:$H_2O$ at ration of 1:2:12. Therefore, using HCl as basis, which has 10ml in volume, is then added with 120ml deionized water.

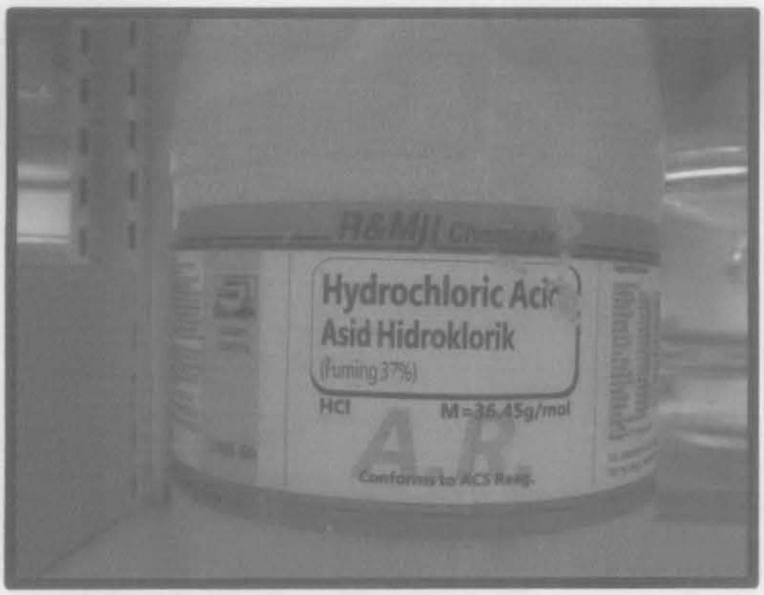


Figure 5 Hydrochloric Acid

Figure 6 Titanium Tetrachloride

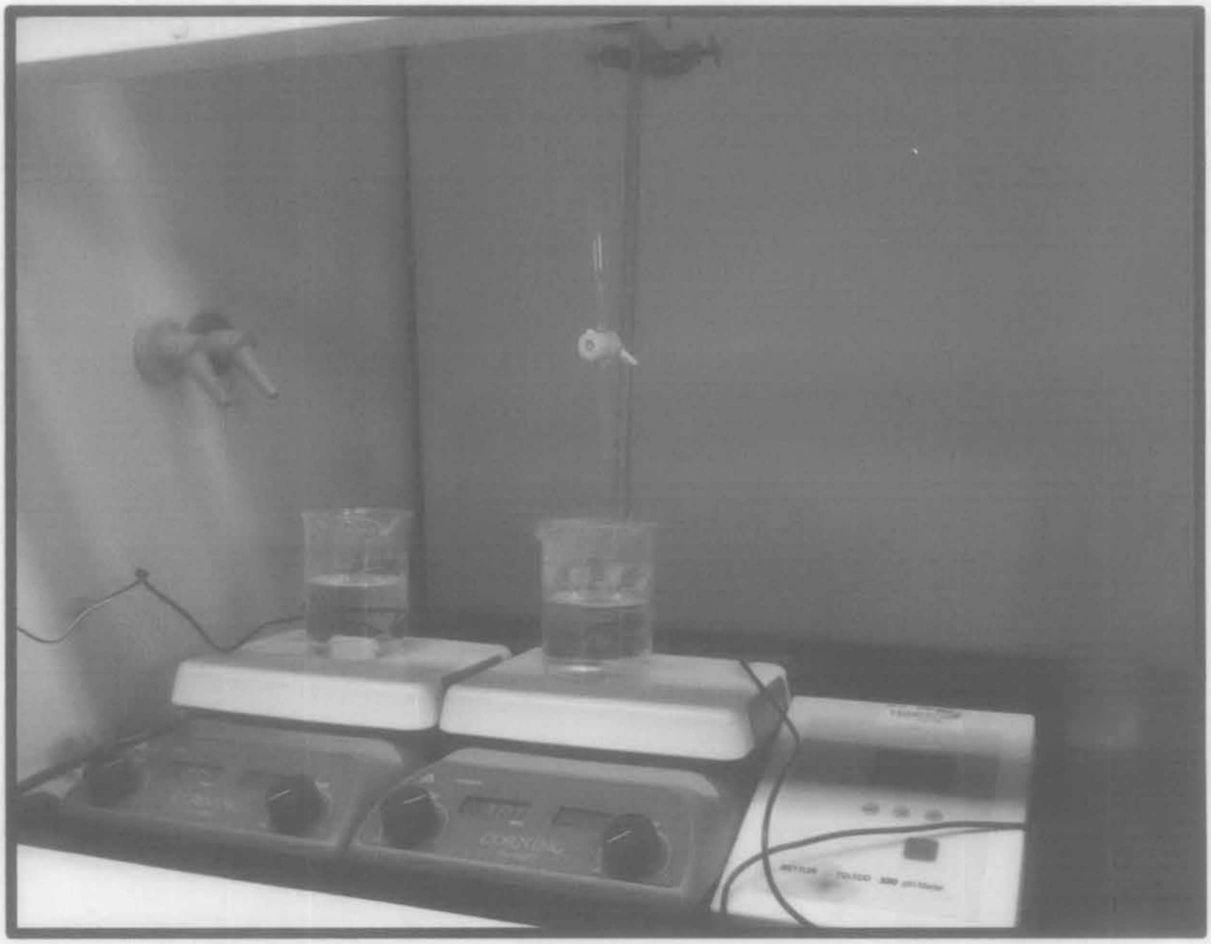

Figure 7 Solution under continuous stirring while maintaining the pH

Since the autoclave equipment has not arrived yet, slight change has been made. Instead of transferring the gel into the Teflon, the solution is continuously stirred at room temperature for 24 hours.

### 3.2 Project Activities

The project activities are divided to 2 semesters (8 months, 4 months per semester). Throughout the project, there are 3 different work scope, including literature research study, documentation and practical work.

### 3.2.1 Semester 1

Under literature research, the related research and study are performed and the necessary documents are listed. The critical analysis of the research included the comparison of the related literature review and the findings are attached for the understanding towards the objective achievement of the particular project. This reviews on the importance of literature review and remarks on the research objective. The extended proposal is about the review on the future research. The research is determined the feasibility in this stage and necessary improvement and adjustment is conducted to make certain on obtaining the suggested result in the research. Interim report is prepared for the wrap up on the chosen project title. It consists of the research steps from the preparation till the necessary results are obtained. The preparation is the method of synthesizing and equipment preparation such as FT-IR, XRD and BET.

### 3.2.2 Semester 2

For the semester 2 research planning, it is divided into two sections which are documentation and practical work. The research study begins with synthesizing mesoporous Titanium Dioxide using Sol-Gel method. The test will be repeated over by different ph and calcined temperature. Next, for the characterization of the mesoporous Titanium Dioxide, X-ray diffraction (XRD) measurements will be conducted. The equipment will assist in determining the position of the atoms or solid structure. The SEM also will take into measure to be used in preparing SEM images of mesoporous Titanium Dioxide for different ph and calcined temperature. The documentation part included the progress report to measure the research progress over time and achievement. Final task would be preparing the full interim report and also submission of technical paper.

## 3.3 Project Timeline

Final Year Project 1

| No. | Detail/ Week | 1 | 2 | 3 | 4 | 5 | 6 | 7 | | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Selection of Project Topic | ■ | ■ | | | | | | Mid-semester break | | | | | | | |
| 2 | Preliminary Research Work | | ■ | ■ | ■ | ■ | | | | | | | | | | |
| 3 | Submission of Extended Proposal Defence | | | | | | ● | | | | | | | | | |
| 4 | Proposal Defence | | | | | | | | | ■ | ■ | | | | | |
| 5 | Project work continues | | | | | | | | | | | ■ | ■ | ■ | | |
| 6 | Submission of Interim Draft Report | | | | | | | | | | | | | | ● | |
| 10 | Submission of Interim Report | | | | | | | | | | | | | | | ● |

Table 3.1 FYP 1 Project Timeline

The important key milestones of this semester project are submission of Submission of extended proposal defence, proposal defence and Interim Report.

<u>Final Year Project 2</u>

| No. | Detail/ Week | 1 | 2 | 3 | 4 | 5 | 6 | 7 | | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Project Work Continues | ■ | ■ | ■ | ■ | ■ | ■ | ■ | Mid-Semester Break | | | | | | | | |
| 2 | Submission of Progress Report | | | | | | | | | ● | | | | | | | |
| 3 | Project Work Continues | | | | | | | | | ■ | ■ | ■ | ■ | ■ | | | |
| 4 | Pre-EDX | | | | | | | | | | | | ● | | | | |
| 5 | Submission of Draft Report | | | | | | | | | | | | | ● | | | |
| 6 | Submission of Dissertation (soft bound) | | | | | | | | | | | | | | ● | | |
| 7 | Submission of Technical Paper | | | | | | | | | | | | | | ● | | |
| 8 | Oral Presentation | | | | | | | | | | | | | | | ● | |
| 9 | Submission of Project Dissertation (Hard Bound) | | | | | | | | | | | | | | | | ● |

Table 3.3 FYP 2 Project Timeline

The Key milestone for FYP 2 will be performing the experimental work and achieve the data for pore size of $TiO_2$ and to submit the project dissertation at the end of week 15.

## 3.4 Gantt Chart

### 3.4.1 Semester 1

| | FINAL YEAR PROJECT 1/ WEEK NUMBER | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Activities** | | | | | | | | | | | **0** | **1** | **2** | **3** | **4** |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Topic Selection** | ■ | | | | | | | MIDSEM BREAK | | | | | | | |
| **Research related topic** | | ■ | ■ | ■ | ■ | ■ | | | | | | | | | |
| **Complete literature review** | | | | | ■ | ■ | ■ | | | | | | | | |
| **Submission of extended proposal** | | | | | | | ■ | | | | | | | | |
| **Proposal Defense** | | | | | | | | | ■ | ■ | | | | | |
| **Study of method** | | | | | | | | | | ■ | ■ | ■ | | | |
| **Study of characterization method** | | | | | | | | | | ■ | ■ | ■ | | | |
| **Development on methodology** | | | | | | | | | | | ■ | ■ | ■ | | |
| **Submission of Interim Draft Report** | | | | | | | | | | | | | | ■ | |
| **Submission of Interim Report** | | | | | | | | | | | | | | | ■ |

Table 3.41 Gantt chart for Semester 1

### 3.4.2 Semester 2

| **Activities** | **FINAL YEAR PROJECT 2/ WEEK NUMBER** | | | | | | | | | | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Initial study on synthesizing $TiO_2$** | ■ | ■ | | | | | | MIDSEM BREAK | | | | | | | | |
| **Execute synthesing $TiO_2$** | | ■ | ■ | ■ | ■ | ■ | | | | | | | | | | |
| **Characteriztion study on $TiO_2$** | | | ■ | ■ | ■ | ■ | ■ | | | | | | | | | |
| **Submission of Progress Report** | | | | | | | | | ■ | | | | | | | |
| **Data Analysis and Report** | | | | | | | | | | ■ | ■ | | | | | |
| **Pre-SEDEX** | | | | | | | | | | | | ■ | | | | |
| **Submission of Draft Report** | | | | | | | | | | | | | ■ | | | |
| **Submission of Dissertation and Technical Paper** | | | | | | | | | | | | | | ■ | | |
| **Oral presentation** | | | | | | | | | | | | | | | ■ | |
| **Submission of Project Dissertation (Hardbound)** | | | | | | | | | | | | | | | | ■ |

Table 3.42 Gantt chart for Semester 2

# CHAPTER 4: RESULTS AND DISCUSSION

## 4.1 Results

Figure 8 sample of pH 8 $TiO_2$

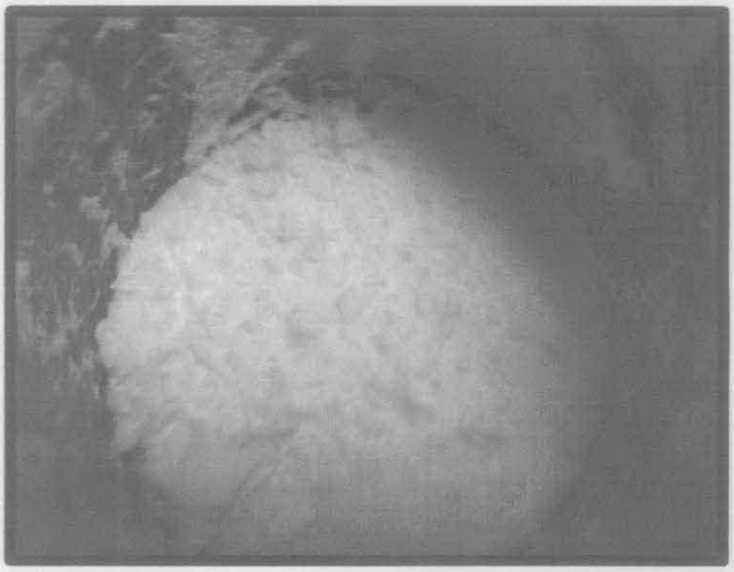

Figure 9 sample of pH 9 $TiO_2$

Figure 10 sample of pH 10 TiO2

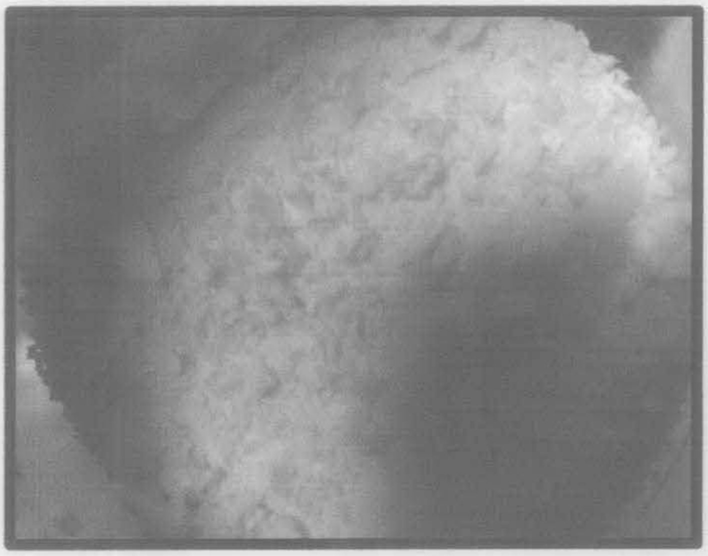

Figure 11 sample of pH 11 TiO2

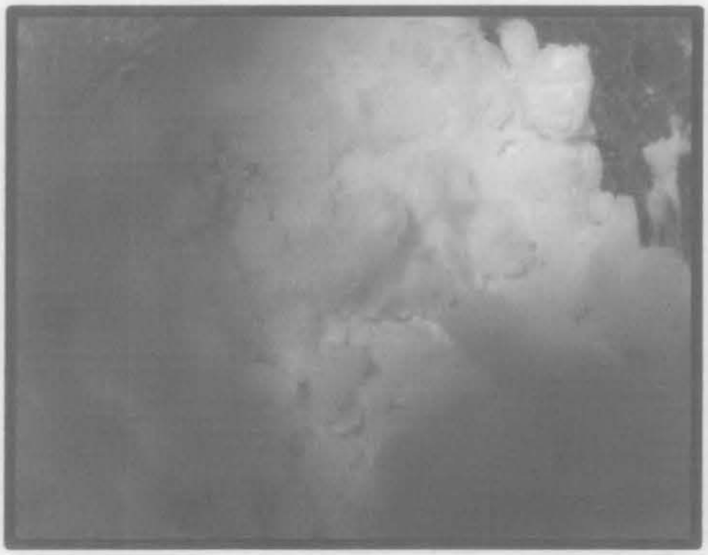

Figure 12 sample of pH 12 $TiO_2$

| pH | Mass (g) |
|---|---|
| 8 | 9.45 |
| 9 | 9.93 |
| 10 | 15.13 |
| 11 | 25.56 |
| 12 | 24.82 |

Table 4.1 Mass of TiO2 acquired

| pH | Time taken (hours) |
|---|---|
| 8 | 4 |
| 9 | 5 |
| 10 | 0.5 |
| 11 | 3 |
| 12 | 4 |

Table 4.2 Hours spent in synthesizing $TiO_2$ gel

## 4.2 Discussions

As for now, the research is still in progress. Therefore, all the samples have yet undergone to check for the result in terms of crystalline structure (XRD) pore size (BET) and chemical compound (FT-IR).

During experimenting, lots of failures have occurred. For sample of pH8, the solution was stirred continuously for 24 hours under room temperature inside the fume chamber; ever, gel still did not form. I tried to leave for 3 days and waited for the gel to form but still same. I decided to halve the volume of HCL, $H_2O$ and $TiCl_4$ but still maintaining the ratio of : $TiCL_4$:$H_2O$ at ration of 1:2:12 (First attempt, HCl 10ml, $TiCl_4$ 20ml, $H_2O$ 120ml; Second npt, HCL 5ml, $TiCl_4$ 10ml, $H_2O$ 60 ml). Redoing the experiment but keeping it under room erature and set the RPM (rev per minutes) to 300. Still, after 24 hours, the gel did not form ell. The final attempt was to put a thermometer inside the solution and heat the solution up 70°C and set the RPM to 1000. Finally the gel has formed for ph 8after continuous 8 hours ing. I repeat the same procedure for pH 9, 10, 11 and 12 which consumes roughly 5 days. failure before really put me behind schedule.

After the gel have undergone for drying and calcination process, I have come to final stage e experiment which is checking the result for XRD, BET, and FT-IR. Due to time traint, I highly regret that, I could not show the result for those three tests in this report.

## CHAPTER 5: CONCLUSION AND RECOMMENDATION

As a conclusion, Sol-gel process has been proved as the way to synthesize mesoporous 2. The experiment has been conducted with different pH and calcinaton temperature which ›H 8, 9, 10, 11 and 12 and 450°C, 500°C and 550°C. Due to some technical issues, the mum pH and calcination temperature could not be found. Hopefully after checking the lt, we may find which is the most optimum ones.

In the future, titanium dioxide that has been produced in this project may be tested for its lytic ability. The product may also be used for another project. This topic can be widen to ›nly titanium dioxides but other metal oxides

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