CHAPTER 1: INTRODUCTION

1.1 Background

Methanol is an increasingly popular chemical nowadays. This is due to its increasingly diverse usage in base chemical industry such as chemical feedstock, antifreeze and as a promising transportation fuel. The latter application has grown in importance due to increasing awareness towards the climate change and the greenhouse effect **due to the fact that the production requires CO_2 and CO as syngas. This will give the alternatives for the industries to recycle the gases instead of releasing them to the atmosphere. Methanol possess hydrogen-carbon ratio of 4, which further support the usage as an alternative fuel.** Although the suitability of methanol to replace the conventional fossil fuel is still under debate, **current research holds promising understanding that this could be made possible**. Methanol is also harmless to the environment, although it is harmful to human**.** Affects including temporary or permanent blindness, even death, is to be expected from intake of methanol**.** Proper **handling method is still to be found in order to cater the problem in order to make it a potent fuel alternative.**

1.2 Problem statements

As stated before, the importance of the methanol is derived from its multiple uses in base chemical industry and as emerging environment friendly transportation fuel. Research to increase the productivity will benefit many parties. Presently methanol is synthesized industrially from syngas at 200-300^{o}C and at elevated pressure condition. As this reaction is exothermic the overheating is likely to occur in some zones of widely

used tube type fixed bed reactors (e.g., Lurgi process at PML currently in research). This is due to poor thermal conductivity of current Cu/ZnO based catalyst. Such localized overheating results in deterioration of mechanical strength of the catalyst pellets, progressive build up of the crumb and powder like masse. This masse blocks gas pathways in the reactor, causing the catalyst surface to lose its original activity. The production rate will go down and the plant's output will progressively decrease. In order to maintain the reactor productivity, higher inflow pressure is required. This, however, usually cause the rise of operating expenditure (OPEX), which is unfavorable in the industry. A cost effective solution to this problem is required.

Recently, researchers in UTP have found the promising solution to the problem by means of promoting the catalyst with carbon nanotubes. This approach will be further explored in given project.

1.3 Objectives and scope of study

Main objectives of this study are:

1. To synthesize the CNT-promoted Cu/ZnO/Al2O3 catalyst and conduct study on the potential increase in mechanical strength and durability of catalysts.

2. To investigate the potential of increment in catalyst activity due to the conducted experiment.

This study is to find out the optimum ratio for industry-standard CNT-promoted $Cu/ZnO/Al_2O_3$. This is to ensure optimum performance and durability for industrial usage. The research is also focusing on the analysis of the catalyst sample obtained from the industry. This is conducted in order to obtain the chemical composition of the spent industrial catalyst.

1.4 Significant of study

As been stressed out before, methanol is a potential chemical with increasing importance in the future. It is useful in many applications in industry such as antifreeze and chemical feed for various production lines. Since the optimum industrial production requires CZO catalyst, it is important to optimize the performance and durability. An important issue to be considered is the durability of catalyst which could only maintain rigidity for 4 years while turnaround occurs every 3 years, where the catalyst will be replaced even before the end usage period. Hopefully, promoting the catalyst with carbon nanotube will increase the durability and solve the issue.

1.5 Feasibility of study

There will be four phases of work focus along this study:

i. *Research for understanding the process, the catalyst, the importance of carbon nanotube and any conducted research on the issue or methodology:* This is done through reading and reviewing journals, literature, articles, books, internet surfing and exploring many other possible media.
ii. *Conducting proposed experimental methods for CNT-promoted catalyst synthesis:* Catalyst will be produced through electrodeposition method. Different amount of catalyst ratio will be mixed in each sample to obtain the best ratio for the catalyst.
iii. *Report and propose the findings of experiment and analysis:* This will be done after the experiment is conducted and analysis is done thoroughly to ensure validity and reliability. Comparison and study will be done on the results obtained. Finally, best combination/result could be reported and proposed.

CHAPTER 2: LITERATURE REVIEW AND THEORY

2.1 Methanol

2.1.1 Properties, characteristics and issues

Methanol is a solution of hydrocarbon group, of the alcoholic type. The formula is CH_3OH, with the OH group acting as functional group. It is an important base chemical with multiple usages as feedstock in chemical productions such as formaldehyde, methyl-tert-butyl-ether and acetic acid. The structure allows H:C ratio of 4, making it a potent hydrogen storage chemical for possible fuel cell applications.

Completely colourless, miscible in water and organic solvent is another properties of methanol. As mixing with air occurs, methanol forms explosive mixtures and it burns in nonluminous flames, which reduce visibility, should fire occurs. The key physical properties of methanol are as follows:

Formula: CH_3OH
Molecular Weight: 32.042 kg/kmol
Relative Density: 0.79
Melting Point: -97.7^{o}C
Boiling Point: 65 ^{o}C
Heat of Formation: -201.3MJ/kmol

Methanol is also ‘green’ in perspective of reducing syngas emission to air in an industry. Current methanol synthesis makes use of syngas from coal burning and other resources as feed. As increase of demand for methanol occurs, so does the demand for syngas. This will provide an alternative to the syngas-as-byproduct industry to market

the syngas to the methanol-production industry. This will reduce release of the greenhouse gases and lower the impact on the environment in the long run.

Methanol has the very high potential of becoming an alternative fuel in the future. Due to the desire around the globe to improve the environment, more specifically the air quality, the usage of methanol had long been considered, dating back to 1970s. Experimental vehicle using methanol had shown great promises. However, lack of infrastructure (refueling) had only led to development of flexible fuel vehicle, which could use methanol or gasoline as fuel, which is still an improvement. In addition, other possible potential of methanol in alternative fuel industry is in fuel cell technology. With hydrogen to carbon ratio of 4 to 1, methanol is excellent hydrogen storage chemical.

Another issue that is mingling is the fact that most alternative fuel, including methanol, possess less energy per volume as compared to gasoline. Although they are more energy efficient as compared to gasoline, as people have been 'set' to think in terms of distance per volume, the issue has became worrying. Increase volume will mean bigger tank is needed. It is suggested that the price should be based on energy basis instead of volume in order to increase demand for methanol and other alternative fuel.

Methanol is very harmful to human. This arise concerns that the usage of methanol in vast quantities (fuel for a car) will affect the health in the long run. More research is needed in terms of handling and storing method to ensure that methanol could be safely used before any commercial effort could be done.

One more concern that is worth noted is the colour of the flame. As pure methanol combust and burn, the flame is invisible under visible light. The problem this might create is the unavailability for the bare eye to detect the burning upon the occurrence, which could occur while driving a methanol-powered car and handling methanol storage tank. The problem is solvable by mixing the methanol with gasoline. However, this spoils the purpose of making methanol as a substitute for conventional fuel. More research on the matter is needed to cater the issue.

2.2 Carbon Nanotube

2.2.1 Discovery, properties and characteristics

Carbon nanotube is considered as one of the greatest finding of the era. The extraordinary properties had become debate subject of research on variety of science and technology field such as production industry, medicine, electronics, constructions, aerospace and military. The vast research had contributed to the multiple synthesis method found nowadays. The strength is formed due to its unique atomic arrangement and the *sp* bond that tie the molecules together, allowing tensile strength of 13-53GPa compared to stainless steel of 0.38-1.55GPa or Kevlar of 3.6-3.8GPa. These are only some of CNT extraordinary characteristics.

The material was believed to be found early in mid-1970s by Endo. He attained a cylindrical carbon structure through HRTEM. Unfortunately, the findings was not popular due to researchers are more interested in micron-size carbon fibers. The famous finding was made by Sumio Iijima on 1991 using an arc-discharge fullerene reactor. Under the High-Resolution Transmission Electron Microscopy (HRTEM), he observes the existence of a unique helicon carbon microtubules, which was later called nanotube, in the reactor. Afterwards, research are made on the electronic properties, transport measurement and mechanical strength, many came out with the findings of the characteristic's dependency on chirality (non-superimposable molecular arrangement) and structure. Nowadays, many other applications are found in the areas of gas storage components, STM probes and field emission sources, high-power electrochemical capacitor, electronic nanoswitches, chemical sensors, magnetic data storage devices and catalyst support (Mauricio Terrones et al. 2003).

2.2.1.1 Mechanical Properties

CNT is an ideal material to be announced as the stiffest structure ever produced. This is because it is well known that carbon-carbon bond that forms CNT is one of the strongest in nature. It is observed that, under electron microscope, the tubes are very flexible that breaking is not occurring even after continuous bending. Thorough theoretical studies were able to estimate the properties. It is assumed that with decreasing radius and by varying chirality, CNT will soften in properties. Treacy et. al. had found in his research that the average Young's modulus of CNT could reach up to 1 to 1.8 TPa which is a lot higher as compared to carbon fibers which is about 800 GPa. Other group experimented on bending forces by equating as a function of displacement and found that the value of Young's Modulus oscillates between 0.32 to 1.47 TPa. Falvo et al. even observed that CNT could be bent repeatedly through large angles without having damaging failure. Another test done by Brenner et. al. shows that CNT could exhibit Young's Modulus value comparable to that of diamond.

One research pointed out a theory that the diameter of CNT determines the mechanical properties. Gao et al., the researcher, estimated that a nanotube with diameter of more than 1 nm could have a theoretical Young's modulus in the range of 0.6–0.7 TPa. Hernandez et al. further discovers that the mechanical properties approach that of planar graphite as the diameter increases. Yu et. al. procced to measure the Young's modulus and discover the values to be in the range of 320 and 1470 GPa while the breaking strength of CNTs is in between 13 to 52 GPa (mean 30 GPa).

Overall, we could conclude that the mechanical properties of CNT are generally excellent. However, it is important to note that the overall mechanical strength is not always great and is dependant to many factors. Other mechanical strength measurements tests done on CNTs revealed lower values of the Young's modulus. The factors affecting the value include the crystallinity of the material and the number of defects present within the structure.

2.2.1.2 Thermal Properties

It is generally known that the thermal conductivity of the well-known carbon allotropes (forms of the same element which exhibit different physical properties) such as diamond and graphite is extremely high. Based on that basis, it is predictable that the thermal conductivity of CNTs along the tube axis may be one of the highest ever when compared to other materials. Ruoff & Lorents were the first to discuss this possibility in 1995. It is important to note that CNT is dominated by phonon that is a quasiparticle or group of particle with influence on the system that is characterized by quantization of modes of lattice vibrations.

For a graphite that is phonon-dominated, the specific heat achieve is around 20 K, while in CNTs, all temperature ranges are controlled by phonon contribution. Yi et al. did thermal conductivity measurements on MWNTs and discover that the property changes linearly in the temperature range of 4 to 300 K. It is understood that as the diameter of MWNTs are observed to be larger than SWNTs, the behaviors are predicted to be similar to two-dimensional graphite and the result shows that thermal conductivity do increases similarly as graphite.

Kim et al. confirmed that thermal conductivity for singular MWNTs is higher than graphite (3000 W/K) at room temperature and of those found from bulk MWNTs. The research shows that the thermal conductivity is temperature dependence with exhibition of a peak at 320 K.

Smalley and coworkers conducted thermal conductivity measurements on bundles of SWNTs. The findings display different in temperature dependence for thermal conductivity. This indicates the presence of smaller crystalline inside the graphitic domains as compared to the MWNTs. Hone et. al. measured the thermal conductivity of randomly oriented SWNTs to be 35 W/m K and for aligned SWNTs to be more than 200 W/m K. They also tests the thermal conductivity for SWNTs at low temperatures and discovered that the thermal conductivity is linearly dependence as a function of temperature (linear acoustic bands contribute to the thermal transport at the lowest temperatures and optical subbands contributes at higher temperatures).

For the specific heat (Cv) of SWNTs and MWNTs, studies had been conducted in theory and experiments. Benedict et. al. suggested that the Specific heat for SWNTs is directly proportional to Temperature in low temperature conditions. Yi et al. discovered experimentally that the specific heat of MWNTs changes linearly in a temperature ranging between 10 and 300 K. Mizel et al. afterwards found that specific heat for MWNTs from arc-discharge technique is identical to the theoretical curve for a nanotube.

The phonon quantization for CNTs has been documented experimentally during heat capacity and thermal conductivity measurements. However, further thermal properties measurements on MWNTs and SWNTs produced using different methods need to be carried out in the near future.

2.2.2 Carbon Nanotube as Catalyst Support

2.2.2.1 Structural Features

Carbon nanotube possesses unique structural features that provide its properties. Carbon nanotubes could be classified into Single-walled carbon nanotube (SWNT), which are made of a perfect graphine sheet (a polyaromatic, mono-atomic layer of hexagonal formed carbon atom rolled into cylinder closed with two gaps) and Multi-walled carbon nanotube (MWNT), with multiple layers of carbon nanotube, concentric and with more diameter than SWNT. Diameter could vary between 0.4 to 2.5 nm with length between few microns to several millimeters for SWNT. For MWNT, number of walls present varied from two to several tens, reaching 100 nm for diameter. There are notes proving that some residual metallic particles from production process is found in the inner cavity of MWNT, showing the ability to hold particle in becoming a support for catalyst.

2.2.2.2 Adsorption Properties

For SWNT found in bundles, the adsorption properties should be considered by focusing on the external and internal part of the bundle itself while avoiding consideration single nanotubes. As for MWNT, similar case is observed as adsorption is occurring on the tube, in the inside or in between the MWNT. Studies show that curvature of graphene sheet produce lower heat of adsorption compared to planar graphite sheet. This is due to rehybridization of carbon orbital from the rolling up of the sheet to form tube, leading to modification of density of the sheet.

Carbon nanotube is a porous structure as different studies on adsorption of nitrogen on SWNT and MWNT had shown. The pores in MWCN can be divided into two that is the small diameter, inner hollow cavities (narrowly distributed, mainly with 3–6 nm in diameter) and aggregated pores (widely distributed, 20–40 nm of diameter) formed by interaction of isolated MWNT. For SWNT, the evidence of microporous nature is shown with adsorption of nitrogen on as-prepared and acid-treated SWNT, contrary to the MWNT mesoporous nature. The specific surface area of SWNT is found to be larger than in MWNT. For SWNT, the BET value will be affected by the tube diameter and the number of tubes in the bundle.

Adsorption sites of a SWNT bundle is located in either of these locations; the inside of the tubes (pore), the outer surface of the bundle, at interstitial triangular channels between the tubes or the grooves of contact between adjacent tubes outside of the bundle. For MWNTs, the location is either in the aggregated pores, inside the tube or on the external walls.

In summary, it appears that carbon nanotubes present specific adsorption properties, mainly due to their peculiar morphology, the role of defects, opening/closing of the tubes, chemical purification or the presence of impurities as catalyst particles that can govern the adsorption properties has not been yet examined in detail

2.2.3 Reasons for Selection of Carbon Nanotube.

In order to get thorough analysis on effects of introducing CNT as support in catalyst, reviews were done on previous effort in the same field. There are several attempts done in the field of methanol processing in which CNT was either doped or totally substitutes the conventional support. The results obtained are promising in regards to the project.

CNT is chemically inert without any functional group on it. Therefore, it is safe to assume that CNT does not affect a chemical process negatively. The review of structural features shows that the tubes have well-defined structure. No amorphous carbon is seen in and around the periphery of the tubes. The CNT are straight and hollow. The open end structure provide extra bonus in selection as a catalyst support, which means that the surface area is increased. This is shown by BET surface area obtained that is $310 m^2/g$ [Eswaramoorthi et.al. (2006)]. It is also shown that CNT is capable to induce a metal/support interaction which makes it a potential candidate for a catalyst support. However, more thorough research are needed to clear the remaining inquiry on the statement [J.M. Planeix et. al. (1994)].

Another important improvement of CNT introductions is increased ability to adsorb hydrogen towards the catalyst. The CNT-supported Pd–ZnO catalysts could reversibly adsorb a greater amount of hydrogen, which would be in favor of generating a micro-environment with higher concentration of active H-ad species at the surface of the functioning catalyst, thus increasing the rate of surface hydrogenation reactions. It is also best to note that introduction of CNT in the place of Alumina as support does not alter the main reaction pathway in CO_2 hydrogenation. Most research found that CNT promote the catalyst. The promoting action was determined by the structural arrangement of carbon in CNT. These are some of the promising properties in addition to high mechanical strength, nanosize channel and graphite-like wall tube [Hong-Bin Zhang et. al. (2008)].

Shijun Liao et. al. had conducted an experiment which put CNT as support for a PtRuIr metal catalyst. From the research, he found out that the metal nanoparticles of the

catalyst are uniformly coated on the surface of CNT. The reason is due to the high surface area available on the CNT. This excellent dispersion had provided increment of the catalyst's activity as compared to the conventional method. As the catalyst in the experiment is also metal, one could deduce that CNT is a capable support for support in catalyst.

2.2.4 Method of Depositing Catalyst onto CNT

There are researches on ways to deposit catalyst onto the surface of CNT. The first one composed of traditional co-precipitation of catalyst solution together with the CNT in desired ratio [Saidakhrorov S. (2010)]. The method incorporates preparing the aqueous solution containing the desired elements and then the CNT is introduced into the solution. The solution is then continuously stirred and aged until precipitate is formed. The solution is then filtered and washed with de-ionized water to remove residue, baked in oven and then mashed into fine powder.

The second method is through electrodepositing of elements onto metal plate with CNT deposited on the surface [YI Golovin et. al. (2010), Susumu Arai et. al. (2003)]. The method involves dispersing the CNT uniformly inside a solution upon deposition onto metal surface. The CNT is suspended using sonicator in de-ionized water to reach uniform dispersion [YI Golovin et. al. (2010)] or placed in plating bath together with the metal plate with addition of acid with stirring to allow uniform dispersion of CNT [Susumu Arai et. al. (2003)].

Both methods provide different results upon testing under Scanning Electron Microscopy (SEM). The elements are merged with the CNT, forming small particles along the surface of CNT. The differences are that for the first method, the sizes between the particles are not uniform, ranging from 100 nm to 5 microns as can be viewed in Figure 2(a). For the second method, the sizes are uniform as well as the distance between beads.

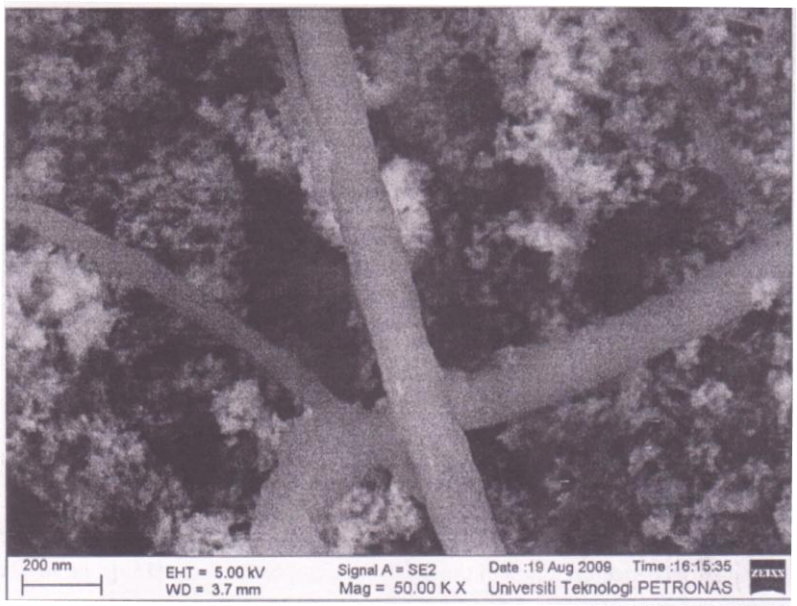

Figure 2(a): Catalyst formed around the CNT under FESEM by co-precipitation of CNT with catalyst solution

The first method is tested using Copper-Zinc-Alumina (CZA) catalyst. For the second method, the experiment involves nickel elements only and had never been tested on systems with multiple elements. It is desired to use the optimum ratio of chemicals from the first method together with the methodology of the second method. The results obtained using the second method are desired compared to the former, as uniform-small-sized particles are important in maximizing the performance of the catalyst.

CHAPTER 3: METHODOLOGY

3.1 Research Methodologies and Project Activities

3.1.1 Preparation of catalyst

Catalyst is prepared through an electrodeposition method [YI Golovin et. al. (2010), Susumu Arai et. al. (2003)]. The method is applied to two different ratio of catalyst obtained from the previous research [Saidakhrorov S. (2010)] to obtain the optimum catalyst in terms of durability and efficiency.

The experiment is devised into two phase. The first one is the preparation of the catalyst itself while the second one is the in-depth analysis of the sample. For the experiment, methods employed are liquid suspension and electrodeposition while for analysis, hi-tech equipment from central laboratory are used.

1. **Preparation of electrode**

   Two copper plates are first polished using fine-grade sand paper to ensure purity of the surface from other elements (e.g. carbonate verdigris due to presence of air and water [http://www.chemicool.com/elements/copper.html]). The plates are then degreased in an 80% aqueous solution of Sodium Hydroxide (NaOH) for 5 minutes. The purpose of degreasing is to ensure that the process will proceed without any adherence. For electroplating process, oil layer on the metal surface can prevent adhesion of the metal ions in the process. This might disturbed the process from achieving desired results. After degreasing, the plates are rinsed with de-ionized water to remove the basic solutions from the metal surface.

2. **Suspension of Carbon Nanotube**

   Carbon Nanotubes (L-MWNT-4060 from Shenzhen Nanotech Port Co.) are applied onto the surface of the copper plate by means of aqueous suspension

(1.0g/l) prepared in de-ionized water inside a 250 ml beaker using ultrasonic dispersion using Sonicator (Sonicor Model SC-420TH). The frequency is fixed at 55 Hz and lasts for 1 hour. Upon drying off the water from the surface of the cathode, the CNT particles were deposited onto the surface of the copper using dropper. In theory, the suspended CNT are uniformly dispersed inside the liquid. After the surface of metal is polished and degreased, most of the impurities on the metal surface are removed. By dropping the liquid on the metal surface, the suspended CNT is transferred together with the liquid. Upon drying, the CNT will remain evenly scattered on the metal surface. The copper piece is then baked inside a baking oven at 65 ^{o}C temperatures for 30 minutes to dry. The dropping-baking process is repeated three times to attain maximum concentration of CNT on the surface.

3. Electrodeposition of catalyst

The Electrodeposition method requires electrolyte consisting of the catalyst ions. Chemicals used are:

Chemicals	Formula	Purpose
Copper nitrate trihydrate	$Cu(NO_3)_2.3H_2O$	Catalyst Reagent – Acid solution
Zinc nitrate hexahydrate	$Zn(NO_3)_2.6H_2O$	Catalyst Reagent – Acid solution
Aluminium nitrate nonahydrate	$Al(NO_3)_3.9H_2O$	Catalyst Reagent – Acid solution
Carbon nanotube	C	Catalyst Reagent

Table 3 (a): Chemicals used in electrolyte

The solutions (electrolyte) were prepared in these ratios:

Mass, g		
Copper Nitrate.$3H_2O$	Zinc Nitrate. $6H_2O$	Aluminium Nitrate.9 H_2O
0.636	0.527	0.220

Table 3 (b): Ratio (in mass) of chemicals used for 300 ml solution

An aqueous solution of the desired ratio was prepared by dissolving the metals in 300 ml of de-ionized water. Electrolysis was then conducted onto the solution as can be viewed under Figure 3(a). The CNT-doped copper plate acts as the cathode. Another copper plate was placed as anode and the experiment was run under 1.0 Volt and 1.0 Ampere current for 10 seconds. Upon completing, the electrode was baked under 65 ^{o}C to remove excess water and the copper was prepared for analysis. The actual setup could be viewed under appendices.

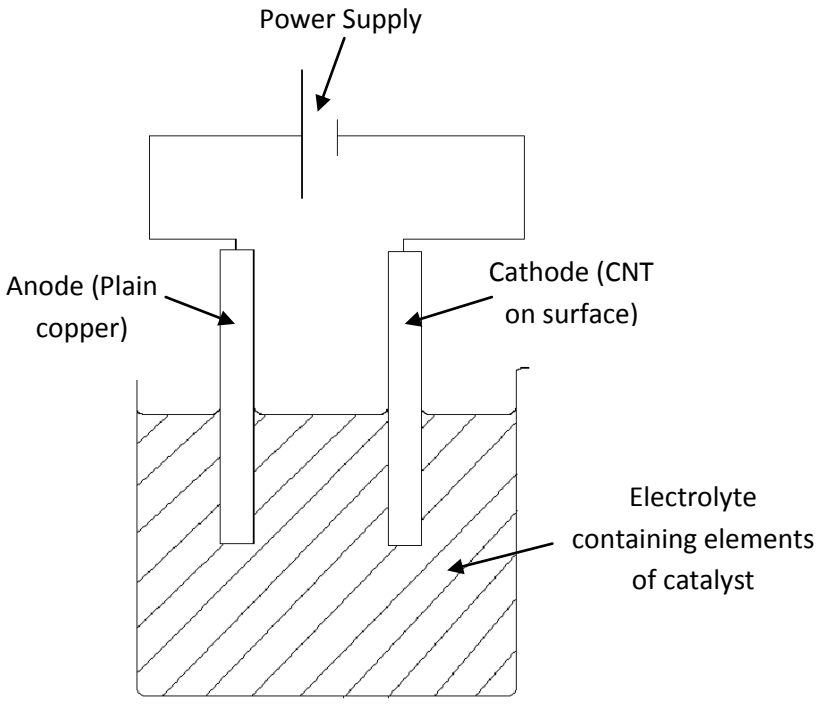

Figure 3(a): Electrodeposition Setup

3.2 Analytical procedures

3.2.1 Field Emission Scanning Electron Microscopy (FESEM) with Energy Dispersive X-Ray Spectroscopy (EDX)

Figure 3(b): Variable Pressure FESEM with EDX

FESEM is one of the important equipment in analyzing the catalyst. The equipment will capture the image of a solid sample. This could be further advance to determining the elemental composition and the distribution of the elements of the surface.

There are generally two groups of microscopy instrument available that is Scanning (SEM) and Transmission Electron Microscope (TEM). The Transmission could provide surface resolution until 0.2 nm while the Scanning could only reach 10 nm. This is the reason for the generally low cost of a Scanning Electron Microscope. FESEM is included in Scanning Electron Microscope group.

There are seven major parts in the operation system. The parts are: vacuum, beam generation, beam manipulation, beam interaction, detection, signal processing and display & record. The combined part will determine results and qualities of a micrograph that is the magnification, resolution, field depth, contrast and brightness.

In SEM, electrons are ejected by thermostat after heating. The electron is then focused into fine beam through magnetic lens. In FESEM, electrons are ejected after passing through a strong magnetic field which provides the electron with sufficient energy to overcome atomic forces of the atom. The electron is focused by an electrostatic lens as compared to magnetic lens in usual SEM. This gives FESEM higher resolution and better imaging of trenches and deep hole as compared to conventional SEM.

The electron beam will bombarded the surface of the sample. There will be backscattered/secondary electron emitted by the surface in response to the bombardment. These will determine the composition of the material for the sample. These electrons will be detected by BSE (backscattered electron) and SE (scattered electron) for analysis.

Integrated with FESEM are EDX. The equipment is used to elemental analysis and chemical characterization of the sample. It apply the principle of exciting electron in the atom using high-energy beam of charged particles (X-ray) to stimulate emission of characteristics X-ray from a sample. An electron from the ground state, inner shell is excited by the beam to exit the inner shell of the atom while an electron from the outer, higher energy shell will fill the area. The difference in energy between the outer and inner shell will release X-ray which is measured by EDX to obtain the elemental composition data.

3.3 Tools and Equipments

In general, the tools and equipments involved are used according to the experiment run:

1. **Preparation of Electrode:** 2 piece of copper plate, 500 ml Beaker, NaOH pellet.
2. **Suspension of Carbon Nanotubes:** 250 ml beaker, digital weighting scales, plate, 1 unit Sonicator.
3. **Electrodeposition of Catalyst:** 1 unit of Power Supply, 2 piece of Wire with alligator clip end, 500 ml beaker, 1 unit Sonicator
4. **Analytical Procedure:** Variable Pressure Field Emission Scanning Electron Microscope (Zeiss Supra55 VP)

3.3 Project Timeline

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic	■	■													
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															●

Mid-semester break

● Suggested milestone

■ Process

3.4 Key Milestone

1. Progress Report Submission	13 July 2011
2. Pre-EDX	4 August 2011
3. Dissertation Submission	22 August 2011
4. Oral Presentation (viva)	14 September 2011

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Results Under FESEM

Under FESEM, these images are captured and analyzed later using EDX:

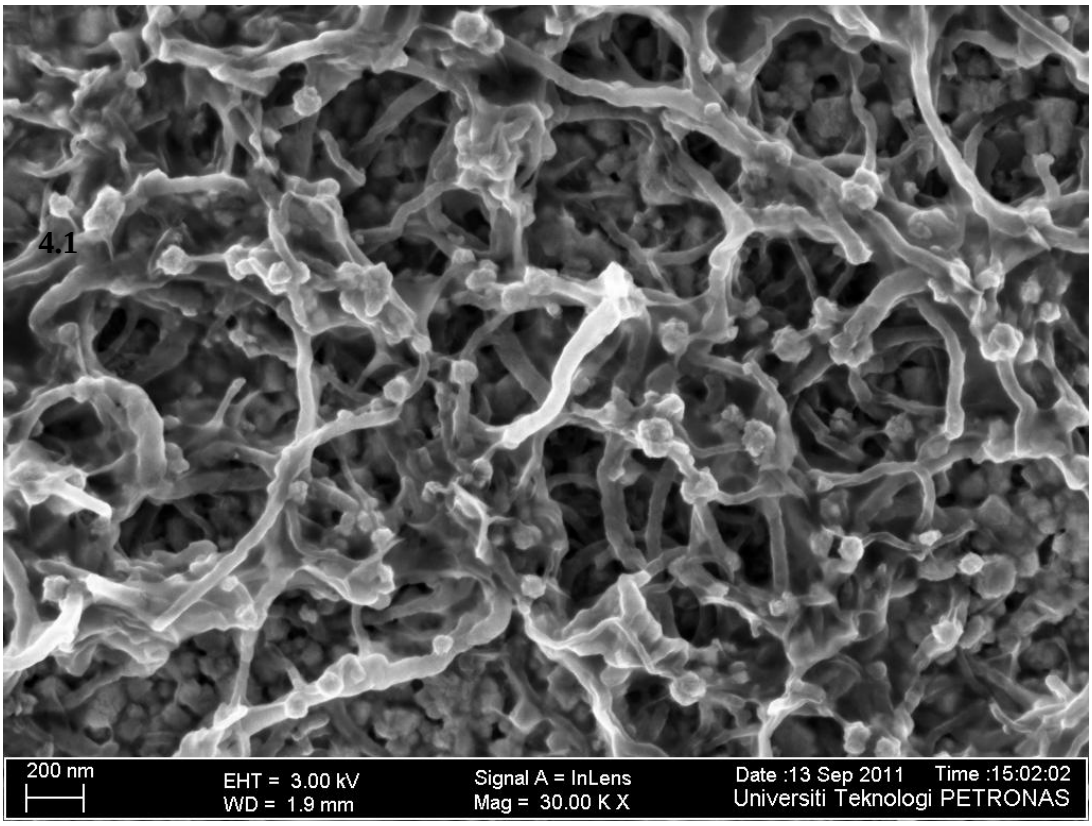

Figure 4(a): Image of Catalyst under FESEM

The image shows the formation of bead-like structure at the end and the surface of CNT. The distribution patterns are random and well-distributed on the CNT. Other images could be viewed in the appendices.

The reasons for formation of particles at the end and on the surface of CNT are due to selective deposition [Susumu Arai et. al. (2003)]. The CNT possess high electrical conductivity in the axis direction due to the structure. The end of CNT has lower resistance than along the structure, favoring the electron to accumulate and attract positive ions for deposition to occur. There are also defects of carbon atom vacancy on

the outer surface of CNT. These sites are active and may possess lower resistivity than others. The positive ions are easily deposited on the site.

The sizes of several particles are measured by the FESEM and the results are shown in the figure below:

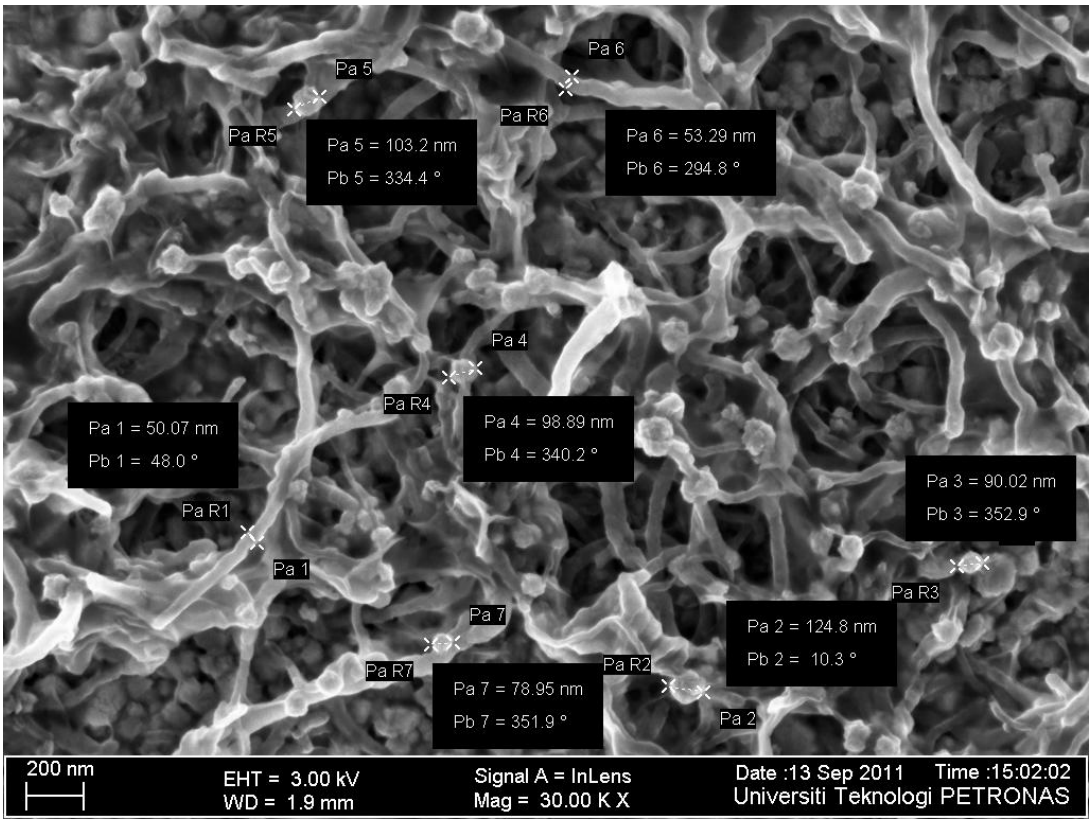

Figure 4(b): Measurement of particles formed during Electrodeposition under FESEM

The image shows that the particles are all in nanosize range. The smallest are 78.95 nm while the largest one is 128.4 nm, indicating that the sizes are uniformly in nanoscales. It is undeniable that the sizes could be made constant in the future.

Taking the average, the size from the image is:

$$\boldsymbol{Avg\ Size} = \frac{\mathbf{103.2 + 98.89 + 90.02 + 78.95 + 124.8}}{\mathbf{5}}$$

$$= \mathbf{99.172}$$

Based on the average, the particles formed are nanoparticles with the size of around 100 nanometer [Paul Holister et.al. (2003)]. Nanoparticle size automatically increases the activity of catalyst due to increase in surface-area-to-volume which is a prime indicator to catalyst activity. Copper nanoparticles are also proven to exhibit better catalytic activity as compared to copper powder even without activation [N. Arul Dhas et.al (1998)].

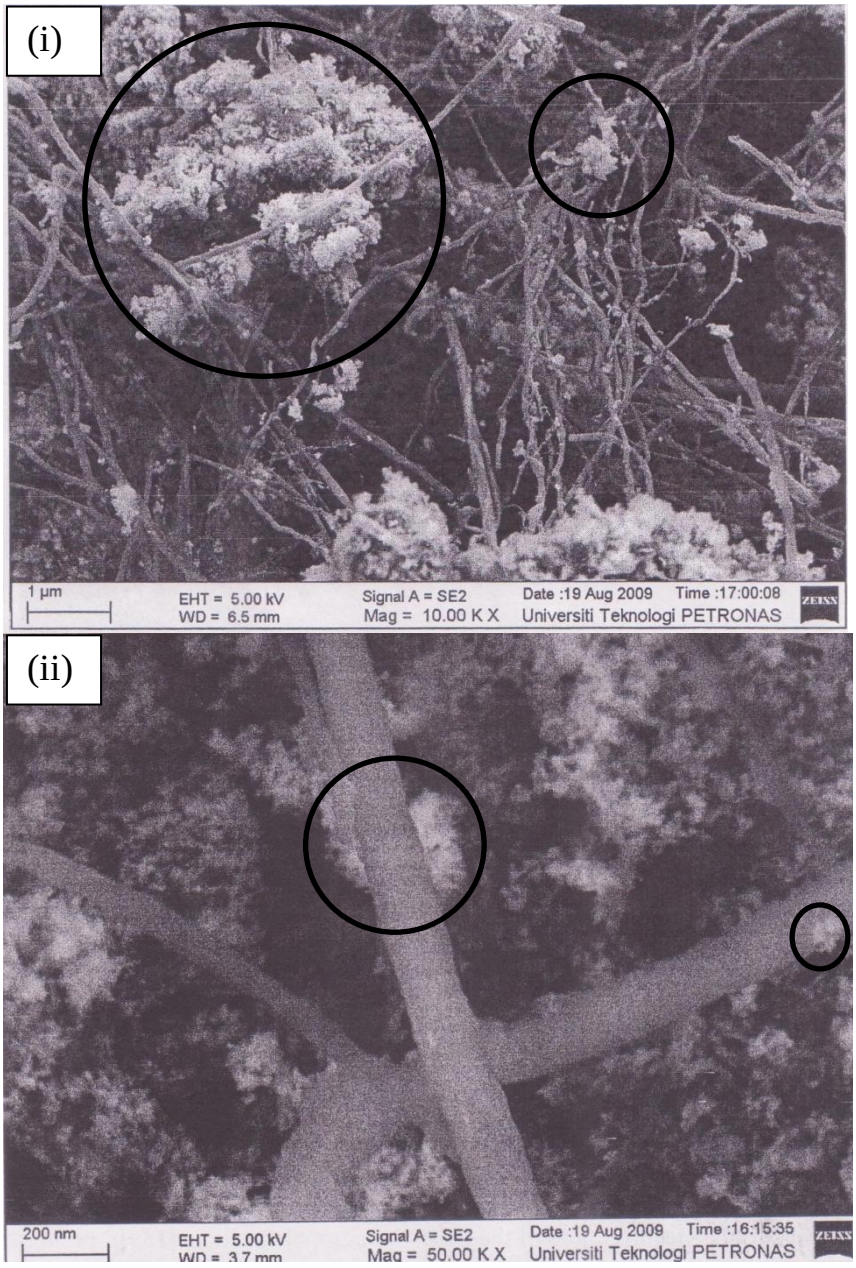

Figure 4(c): Images from Previous Research by Saidakhrorov S. (i) The particles are not uniform in size (ii) The particle are not spherical in shape

By comparing the image from the preceding work [Saidakhrorov S. (2010)], we could see that the particle size had improve dramatically. In the previous work, the catalyst particles formed are large and not uniform in size. The particle also does not cover the CNT as the one in this experiment. The improvement is expected to increase catalyst activity as well as durability [Paul Holister et.al. (2003)][J.M. Planeix et.al (1994)].

4.2 Results of EDX

The sample was analyzed under EDX to obtain data on the elements composition inside the nanoparticle. The results are shown in figure below:

Element	Weight%	Atomic%
C K	61.42	83.54
O K	8.38	8.56
Al K	0.40	0.24
Cu K	29.80	7.66
Totals	100.0	

Figure 4(d): EDX Analysis on Particle Site 1

The relevant data to be taken are Weight Percent as this shows the mass of elements that are in the interest site. From the first site, the main composition element is Carbon. However, this is expected as CNT are the majority in the volume. Copper elements are in second. The results shows that copper are the one of the main elements

in the particles. In the methanol production, copper is the main catalyst which interact with zinc oxide and alumina to form the current catalyst [Saidakhrorov S. (2010)]. Copper provide the active site for the process. Having copper-based nanoparticle is a good indication that this catalyst will function in methanol production. However, without sufficient data on the behavior of the copper-based nanoparticle, study of thermal behaviors is not possible to be conducted.

The analysis was also conducted on another location:

Element	Weight%	Atomic%
C K	63.12	84.04
O K	8.76	8.75
Al K	0.42	0.25
Cu K	26.44	6.65
Zn K	1.26	0.31
Totals	100.00	

Figure 4(e): EDX Analysis on Particle Site 2

The second location shows the same pattern where Carbon made the main elements and Copper are the second majority. The composition of the particles is uniform. Uniform formations of particles in terms of compositions are possible to be done.

4.3 Comparison With Other Experiments

There had been previous attempt to create a uniformly distributed catalyst around CNT. With that structure, the catalyst will attain maximum possible strength from the CNT. One research had applied CNT in a conventional method of catalyst preparation. The FESEM image shows that the catalyst crumbled together around the CNT with random sizes. Although the objective of strengthening the catalyst is achieved, the sizing could be improved so that the particles are evenly distributed with minimum size to maximize catalyst surface area [Saidakhrorov S. (2010)].

Researchers from Russia had found a procedure to optimize the particle distribution around CNT [YI Golovin (2010)]. The experiment involves Nickel to be embedded onto CNT by means of electrodeposition method. The results are promising as could be viewed below:

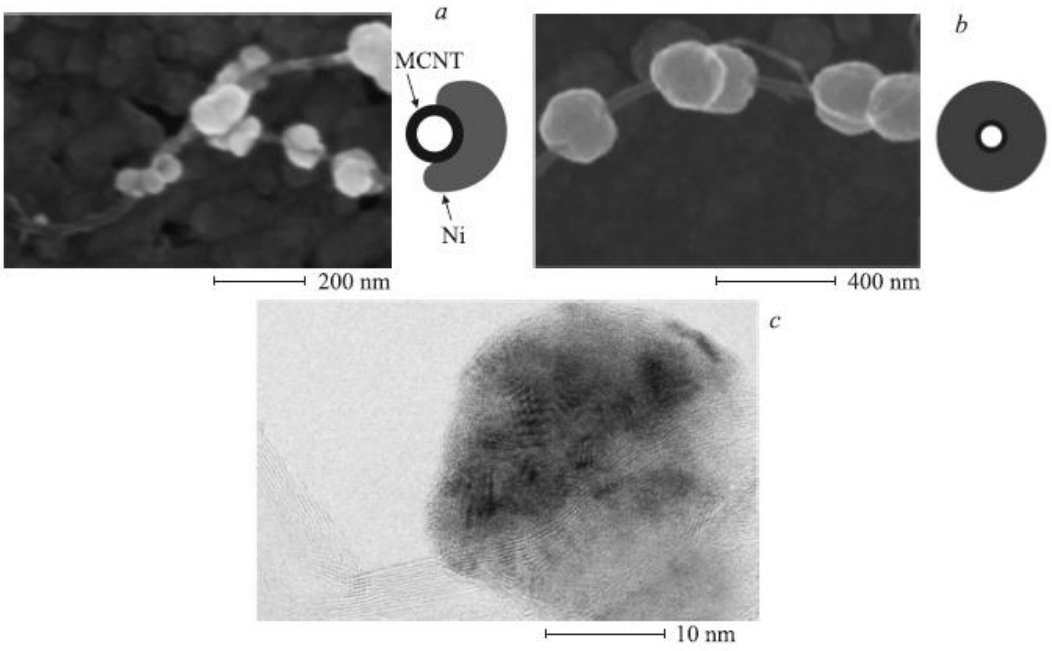

Figure 4(f): The CNT under SEM (a) The bead does not surround the CNT (b) Spherical shape is obtained with the particle surrounding the CNT (c) Overall view

It is observable that in figure *b*, the Nickel particle covers the CNT, forming bead-like structure similar to the one found in this research that surround the CNT. These provide maximum strength due to even force distribution towards the CNT and maximize surface areas that will results with optimum effectiveness.

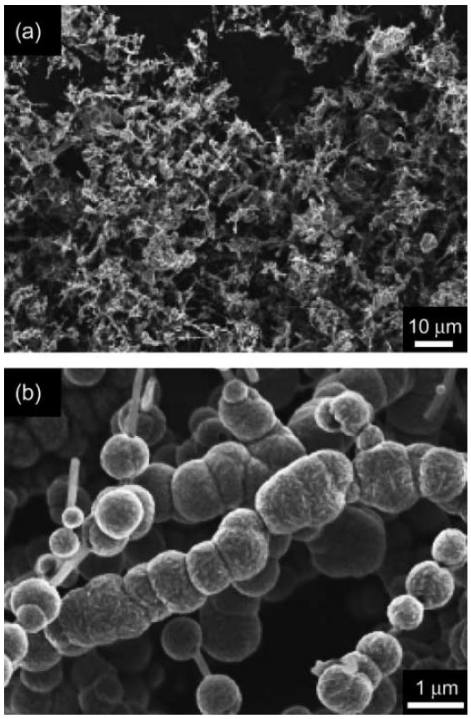

Figure 4(g): Formation of beads particles along the CNT (a) The overall view (b) Under high magnification

Similar with the other experiment [Susumu Arai et. al. (2003)], it is observable that the beads formed are uniform in shapes and sizes. The differences are that the distance between the particles is shorter and the beads merged between them, unlike the previous which have the bead exclusive between them. However, the desired characteristics in the particle formation are met which is to have small uniform-sized particles distributed along CNT.

It is understood that catalyst generally requires large surface area in order to achieve maximum efficiency. This purpose is achieved through being smaller in size with constant mass. As shown, the catalysts particles formed are universally small and evenly distributed across the CNT. As the numbers of particles formed are estimated to be high across the CNT, the maximum surface area could be achieved.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

Conclusion

The objective is to synthesize the catalyst involved in methanol production and analyze the catalyst to investigate possible properties. From results of the research conducted, the catalyst is possible to be made. The characteristics are similar to the one intended and this show promising future potential as the nanoparticle form of copper allows increase in catalyst activity due to the increment in surface-area-to-volume of the catalyst and the Carbon Nanotube provides the needed strength and durability for the catalyst.

From the literature reviews, one could see that the methanol itself is an ever growing chemical in the future, thus increasing the importance of the project itself. The catalyst is also seems to have issues that require more improvement. Overall, carbon nanotube is applicable and is one of the best candidates to be used as catalyst support in methanol production, either to be doped with the current Al_2O_3 support or to replace the support completely.

Recommendation

There are several suggestions to be made. The first one is to improve the process, specifically on equipments. One of the main hurdles in this project is the lack of capabilities of equipments. In sonication process to suspend the CNT, the sonicator used does not have the required frequency as needed. The provided frequency are 55-60 Hz while the required frequency are 22 kHz. For the power supply, it is favored to use lower voltage in order to control the formation of nanoparticle better. However, the voltage used in the experiment is lowest that the device could manage. By doing improvements, the process could be managed further and better results could be achieved.

The second suggestions are to conduct studies in ways to increase the number of particles per volume of catalyst embedded with CNT. The reasons are increasing the number of particles will increase the specific surface area. This will lead to increment in catalyst activity. From the current research, the number of particles formed could be further increased to equal the particle number found in the journal.

The third suggestions are to explore the method in removing the catalyst composite from the copper plate. In order to use the catalyst, the catalyst needs to be removed from the copper plate. The method suggested [Susumu Arai et.al (2004)] is to conduct Ultrasonic Irradiation using Sonicator. The method is tested during the project period. However, it is found that the method is inefficient due to the low frequency provided by the sonicator. It is hoped that the method could be further explored in the future.

The fifth suggestions are to focus study on thermal behavior of the copper-based nanoparticle found in this project. One worrying findings is that the melting point of nanoparticle decreases as the size goes lower. On record, melting point of gold nanoparticle is 250 ^{o}C [Ph. Buffat et.al (1975)]. Without sufficient data, the study could not be conducted. Research is needed in the topic to further investigate the potential of this factor.

The final suggestions are to study on possibilities of increasing the productivity. Catalyst will only be feasible if it could be produced in sufficient quantity in affordable price. The price of Carbon Nanotube is still high and the process is yet to be optimized. Addition of Zinc Oxide is another possibility to improve the activity. With so much potential, study on productivity could be conducted to see the actual potential of the catalyst.

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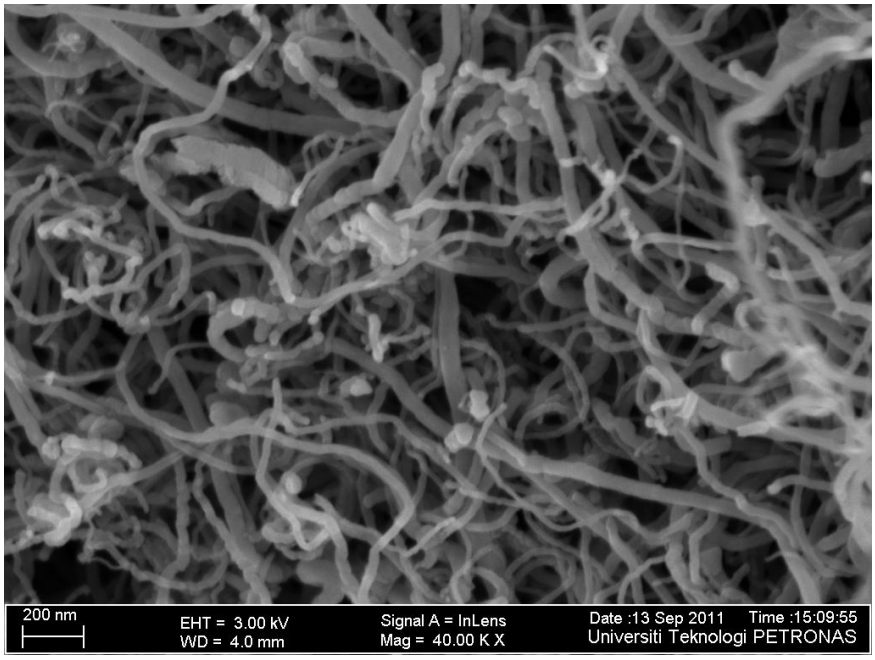
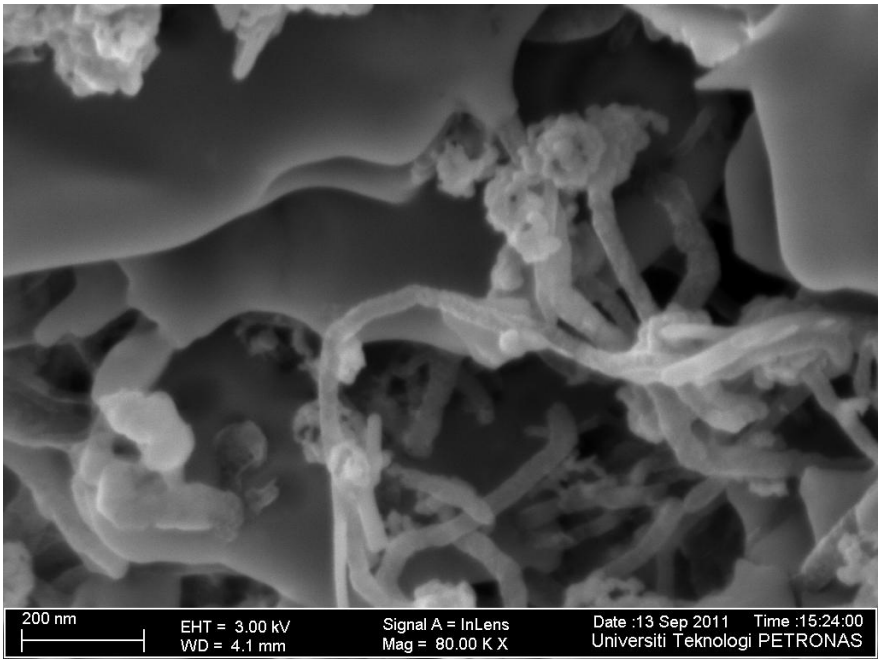
APPENDICES





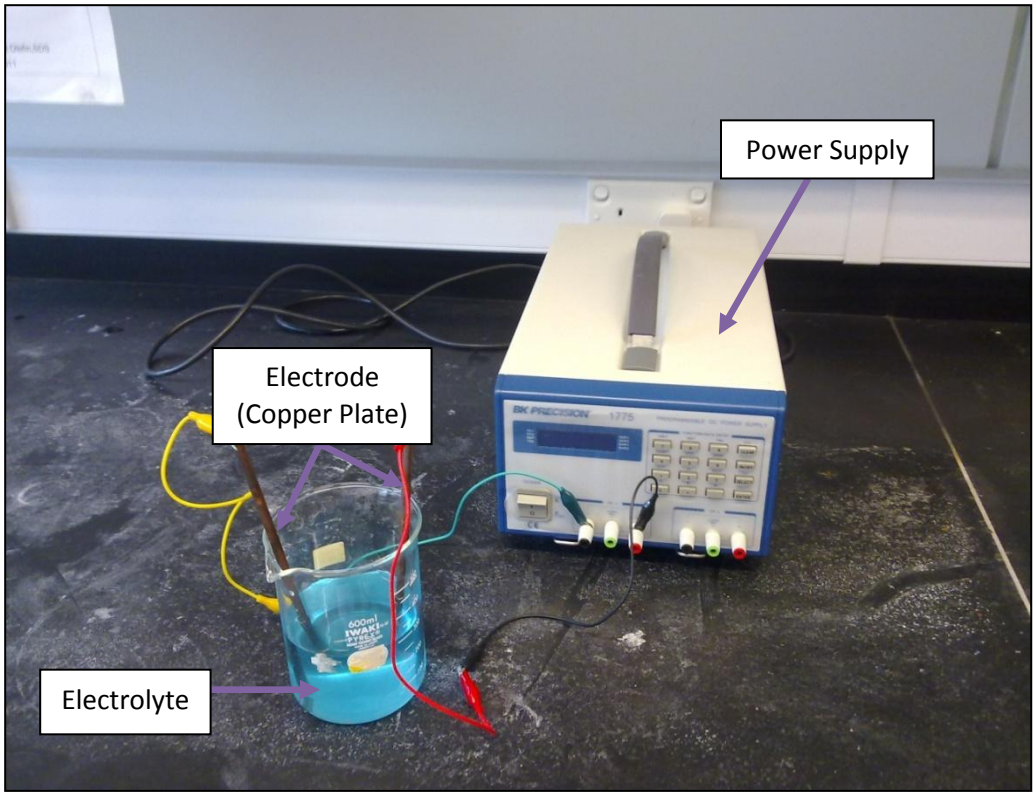
Images from other locations in the sample under FESEM

深圳市纳米港有限公司
ShenzhenNanotechPortCo.,Ltd.

CERTIFICATE OF ANALYSIS

Product	L-MWNT-4060		
Items	Test methods	Nominal	Results
Appearance		Black Powders	Black Powders
Diameter	**TEM**	40-60nm	40-60nm
CNTs content (%)	**TEM, TPO**	>95	>95
Length	**TEM**	5-15μm	5-15μm
SSA	**BET**	40-300m2/g	40-300m2/g
Ash	**EDS, TGA**	< 2%	

Certificate of analysis for Carbon Nanotube used in the project



Electrodeposition Setup

Sonication Process of CNT in de-ionized water

Sonicator (Sonicor Model SC-420TH)