Development and Characterization of Modified Carbon Nanotubes For CO_2 Capture Adsorption Application

By

Hasifi Bin Hasnan

Dissertation submitted in partial fulfillment
of the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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Approved by,

(Dr. Suriati Sufian)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2012

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 as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

HASIFI BIN HASNAN

ACKNOWLEDGEMENT

First and foremost, I would like to express my gratitude of Dr. Suriati Sufian, my supervisor for my Final year Project (FYP). She had been a very supportive during the entire period of the project. She had spent much time and energy to guide us throughout the 2 semesters despite her other commitments and packed schedule as lecture in Universiti Teknologi PETRONAS (UTP). Under her constant supervision, we manage to start our project with a proper planning and proceed until completion according to the timeframe scheduled.

We would like to acknowledge to other Chemical Engineering lectures and all Chemical Engineering lab technicians who had give a lot of advices, solutions, teachings and opinions regarding on the problems which I had encountered throughout this Final Year Project period. Their advice and knowledge were very helpful and insightful. Once again, thanks to all lectures from UTP who had provided invaluable input and untiring guidance throughout the project period. With this great opportunities, me as a students are able to deepen the knowledge remarkably both in the theory and practical basis of a research project.

Apart from these, I also would like to express my sincere thanks to the FYP II coordinators Dr. Norhayati Melon in handling the entire undergraduate final year project successfully.

Lastly, my sincere to my family and friends for their full support and encouragement for me to finish this Final Year Project successfully.

ABSTRACT

Adsorption of CO_2 via carbon nanotube (CNTs) recently has been investigated and various studies have been gone through especially between the temperature range of 0–200°C have been made in order to observe its performance as a CO_2 adsorbent. It is proven that CNTs can absorbed nearly twice of the volume of CO_2 as compared to activated carbon (Cinke *et al*, 2003).

The physicochemical properties of CNTs ware changed after the modification, which makes CNTs, adsorb more CO_2 gases. The adsorption capacities of CO_2 via CNTs and modified CNTs (APTS) decreased with temperature indicating the exothermic nature of adsorption process and increased with water content in air at 0–7%. The mechanism of CO_2 adsorption on CNTs and modified CNTs (APTS) appears mainly attributable to physical force regardless of temperature change, which makes regeneration of spent CNTs at a relatively low temperature become feasible. The modified CNTs (APTS) have good adsorption performance of CO_2 at 20°C as compared to many types of modified carbon or silica adsorbents (Lu *et al*, 2008).

Throughout the project, the performance of CNTs towards the CO_2 adsorption will be enhanced due to the difference in the acid treatment which leads to the attachment of different functional group.

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CHAPTER 1: INTRODUCTION

1.1 Background Project

Recently, global warming always is a big issue to all people in this world. In simple words, global warming can be known as an alteration in the climate and natural environment of our planet which all of us rely on and this can be seen through its effect and the effect totally is not good. Scientists always reported that most of it is caused by increasing concentrations of greenhouse gases produced by human activities such as deforestation and burning fossil fuels. The combustion of fossil fuels normally will lead to the production of such as carbon dioxide, carbon oxide and nitrogen which will be harmful for both our environment and the human health.

Carbon dioxide (CO_2) always is being the main factor for greenhouse gas (GHG) due to our dependant on fossil fuel as our main energy sources, which lead to a increasing of CO_2 emission. Generally, this problem should be resolved and one of the simplest ways is by stabilization of GHG concentrations in atmosphere which can be achieved by using non-carbon energy sources such as biomass, solar and wind energy. However, these method always been delayed as need high cost, skills and time in order to prepare and doing some research or study on related issue (Pires *et al*, 2011).

China is one of the countries which is undergoing a great development and growth in the industrial field and becoming greater from year to year. This leads to increase in energy consumption as well as quantity of carbon produced globally and this problem had been increased since 1978. Energy consumed normally coming from a few sources which always act as global sources of energy such as coal, oil and gas. These three sources always being used as a car fuel and also being used as generator fuel for a certain model of generator. Carbon emission growth is about 0.28% and this explains how heavy industrialization's formation and development of China increase carbon emission. Thus, heavy industry development is not advisable as it is not dealing with an environment and it will cause a strong accumulation effect on country (Wang *et al*, 2011).

Taiwan currently emits about one percent of world CO_2 and they had been monitored this problems for since 1989. Method being used was input-output (I-O) structural decomposition to examine the changes of CO_2 in their atmospheric. In applying this method, they had been divided the investigation into three which 1989 – 1994, 1994 – 1999 and 1999 – 2004. During 1989 – 1994, the main factor of CO_2 emission was electricity emission followed by oil coal and natural gas. However, during 1994 – 1999, main cause of CO_2 emission was the rapid growth of export and followed by domestic final demand (caused by oil guzzling-industries). Last but not least, during 1999 – 2004, electrical emission was the main factor however the CO_2 emission was declined in this period as a result of using a less CO_2 emission fuel for industrial used (Chang *et al*, 2008).

From both study as which have been made by a researchers from China and Taiwan, CO_2 emission is main world disturbance and have to be reduced immediately as much as we could so that our atmospheric condition will be in the best condition and greenhouse effect can be reduced totally. Fast actions have to be taken to eliminate this CO_2 emission problem. CO_2 emission still can happen through combustions for example and we need that combustion for its energy. In the other words, CO_2 emission have to be happen and it is us to create a mechanism to eliminate or capture CO_2 in order to prevent it from released to the atmosphere. CO_2 capture can be done through a few processes, which are absorption, adsorption, gas separation membrane and cryogenic distillation. Among them, the adsorption-regeneration technology has been recognized as the most matured process so far (Lu *et al*, 2008).

Carbon nanotubes (CNTs) are very unique and one dimensional macromolecules that have thermal and chemical stability. This material have been proven that have a great potential as a adsorbents for removing many kinds of organic and inorganic pollutant which contaminated the air streams. Large adsorption capacity by CNTs is because of their pore structure and the existence of surface functional group which can be achieve by chemical modification of CNTs which expected to be the best material for CO_2 capture application from flue gas (Su *et al*, 2009).

In addition, a research also has been done from researchers in order to prove CNTs is the best adsorbent to capture CO_2 compared to other material such as activated carbon. Referring to the experimental data, the conclusion is CNTs are able to capture nearly twice CO_2 compare to activated carbon. Generally, this characteristic of CNTs is being influenced by adsorption characteristic of iron oxide which is a non-porous material and exhibit type 3 adsorption for CO_2 (Cinke *et al*, 2003).

1.2 Problem Statement

CO_2 emission becomes a major problem for a industrial sector nowadays. The more CO_2 emitted, the more it will affect the environment and not excluded also us as a human being who is really dependant on the nature to survive. The source of the CO_2 could be from the combustion of vehicle and power generation plant, oil drilling and a few more which better is taken seriously before it damage our environment in total.

It is important today when seeking ways to reduce CO_2 emission and for sure it will cost a lot of effort, knowledge, economics and skills. And one of the methods is by developing the adsorbent which can capture CO_2 and reduce CO_2 emission to our atmosphere. In addition, researches prove that CNTs can be another adsorbent to capture CO_2 because of its chemisorption and physisorption behavior which help the adsorption to be happened nicely.

1.3 Objective

This experimental study is focusing on the effect of modified (single wall/multi wall) carbon nanotube due its physicochemical properties and adsorption performance of capture CO_2. Generally carbon nanotube can be categorized into a single wall and multiwall carbon nanotube. And the modification can be done by impregnation of a few materials as an addictive which can enhance the adsorption behavior such as 3-aminopropyl-tryethoxysilane (APTS), propylethylenediamine (EDA) and polyethylenimine (PEI). However, there is no article related on affect of difference acid treatment which can affect the chemisorption and physisorption of CNTs towards CO_2

adsorption. In order to achieve this objective and throughout the study and experiment, the effect of the different in acid treatment will affected physicochemical properties which lead to the observation of the performance of CNT to capture CO_2 application can be enhanced.

1.4 Scope of Study

a) To synthesize modified CNTs with different acid treatment and testing it for CO_2 capture application.

b) To prepare modified CNTs behavior on physicochemical properties and adsorption performance of CO_2 adsorption.

CHAPTER 2: LITERATURE REVIEW

2.1 Carbon Nanotubes (CNT)

A single wall carbon nanotube is basically defined as a cylindrical shape which made up of rolled up sheet of grapheme which can clearly be described in the Figure 1 and Figure 2 (Chandra *et al*, 2009):

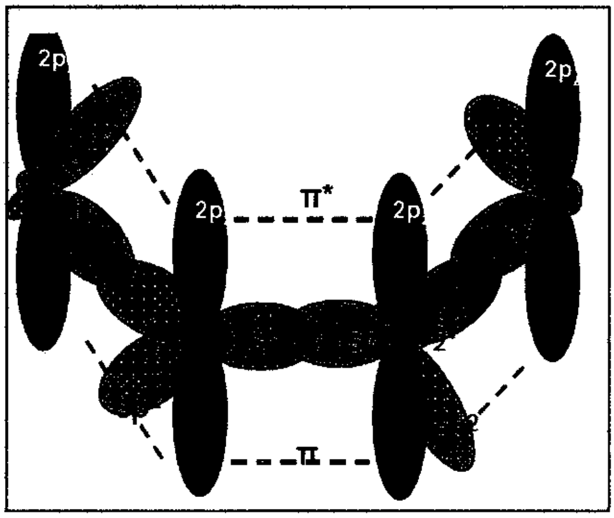


Figure 1: The three sp^2 hybridized orbital are in-plane (Chandra *et al*, 2009)

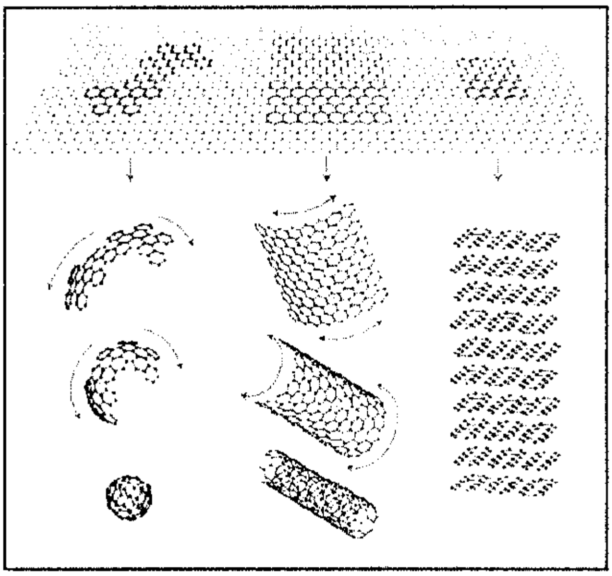


Figure 2: Graphene as the source of Fullerene (left), carbon nanotubes (Center) and bulk graphite (right) (Chandra *et al*, 2009)

Figure 1 is about three sp^2 hybridized orbital are in-plane, with 2p orbital orthogonal to the plane, π and π^* denotes the bonding and anti bonding orbital. However Figure 2 is about graphene as the source of three different materials- Fullerene (left), carbon nanotube (Center) and bulk graphite (right). These different materials only have differences in how the graphene itself being shaped and structured. Generally, Graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice (Novoselov *et al.*, 2005). Referring to Figure 3, several graphene layer stacked over each other gives bulk graphite. These layers are loosely bonded to each other and hence can slip freely, making the extraction of graphene possible from graphite crystal through mechanical/chemical exfoliation (Zhang *et al.*, 2005).The diameter of CNTs typically varies from 0.7-3.0 nm depending on the purpose of it being synthesized. Due to such small diameters, nanotubes become quasi one dimensional. They can posses as a single shell or multiple shells, as shown in Figure 3. Tubes with single shell are called single wall carbon nanotubes (SWNT) while if it is more than one shell it is known as multiwall carbon nanotubes (MWNT). Generally said, SWNT and MWNT are similar except the number of walls. The length of nanotubes can be up to centimeters, giving them an astonishing length/diameter ratio of 10^7(Chandra *et al.*, 2009).

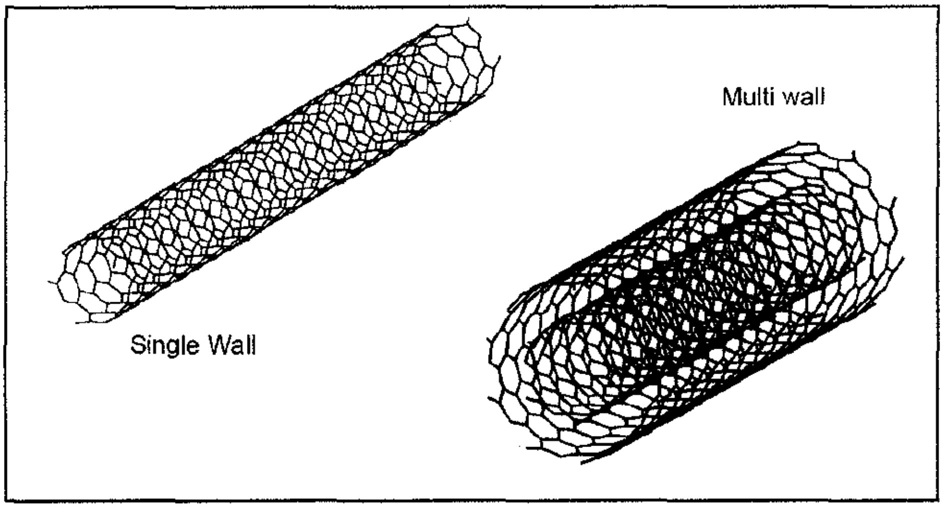


Figure 3: Single and multiwall carbon nanotubes (Chandra *et al.*, 2009)

One of the methods to produce CNTs is by Chemical Vapor Deposition (CVD) process (Iijima *et al*, 1993), (Iijima, 1991). In the last 10 years, tremendous researches have been made in order to synthesis both SWCNTs and MWCNTs (Dai *et al*, 2001), and also their potential use such as in electronic circuit (Ouyang *et al*, 2002), thin film (Gruner *et al*, 2006), composite, and also an adsorbent (Su *et al*, 2009). On the industrial front, normally carbon nanotubes have found use in making composites and gas sensors. This is because of their extraordinary mechanical properties and high surface area which allow the adsorption to happen. With this behavior, enable the CNTs to be used as adsorbent for a various gasses such as N_2, CH_4, CO and CO_2 (Lithoxoos *et al*, 2010). Referring to the properties of CNTs that stated in the previous paragraph, this nanomaterial also have been proven to possess a good potential as superior adsorbent to removing many organic and inorganic pollutants in air streams (Long RQ, 2001) or from an aqueous environment (Li *et al*, 2002). Another behavior that lead CNTs towards the stated behavior is mainly attributable to their pore structure and the existence of a wide spectrum of surface functional group which can be achieved by chemical modification on the CNTs itself which enhancing its performance for particular purposes.

One of the methods to do CO_2 capture test is via magnetic suspension balance. Magnetic suspension balance can be used to observe the performance of CNTs in capturing CO_2 especially to characterize the sorption capacity and adsorption rate. It is one of the gravimetric instruments and it is extremely accurate as a measuring method for scientific research. Examples of CO_2 capturing using Magnetic suspension balance (Maciej, 2007):

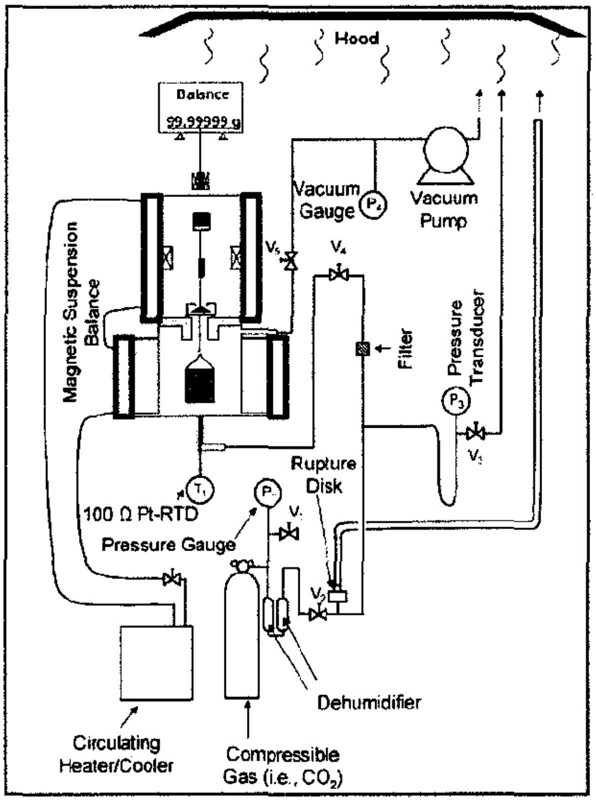


Figure 4: CO_2 adsorption equipment (Maciej, 2007)

2.2 CO_2 Adsorption in Carbon Nanotubes (CNTs)

By comparing the adsorption behavior between raw SWCNTs and high purity SWCNTs, the adsorptive capacity of high purified SWCNTs are slightly higher compared to raw SWCNTs due to the influence of Fe_2O_3 on the adsorption characteristic. Raw SWCNTs from HiPCo process consist of 22wt% of Fe (Cinke *et al*, 2003). Fe is normally the catalyst which being used for the catalyst in the CNTs growth. However, after purification the percentage of Fe has been reduced to 0.4wt% and the purified material exhibits a total BET area of $1587m^2/g$ and total pore volume is $1.55cm^3/g$. However, if we are comparing the adsorptive capacity between purified SWCNTs and activated carbon, the adsorption of CO_2 will be twice in purified SWCNTs as the site in the activated carbon are not uniform and the number of sites with affinity for CO_2 maybe lower than the total area [1]. TEM image of raw SWCNTs can be referred as in the Figure 4 and Figure 5;

Figure 5: TEM image of CNTs 1 (Lu *et al*, 2008)

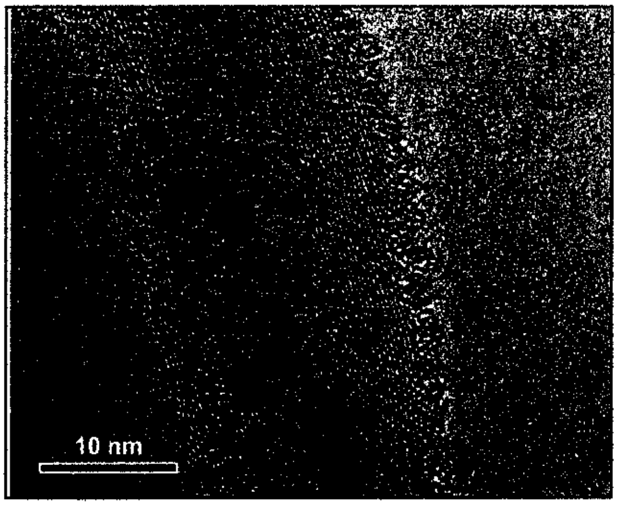


Figure 6: TEM image of CNTs 2 (Lu *et al*, 2008)

2.3 Modification of Carbon Nanotubes (CNTs) for CO_2 Capture Application

In general, CNTs were fabricated by Chemical Vapor Deposition (CVD) process and being modified with 3-aminopropyl-tryethoxysilane ($C_9H_{23}NO_3Si$, abbreviated as APTS) in order to increase their physicochemical properties and adsorption performance of CO_2. After the synthesis of CNTs, it will undergo the purification process in order to remove the organic substances and remaining catalyst attached in the CNTs wall. CNTs then are being dispersed in the flask containing modification material which is APTS which then being filtered and dehydrated via oven. Figure 6 shows how APTS is attached to the surface of CNTs and also mechanism on how CO_2 is attached to CNTs (APTS) (Su *et al*, 2009).

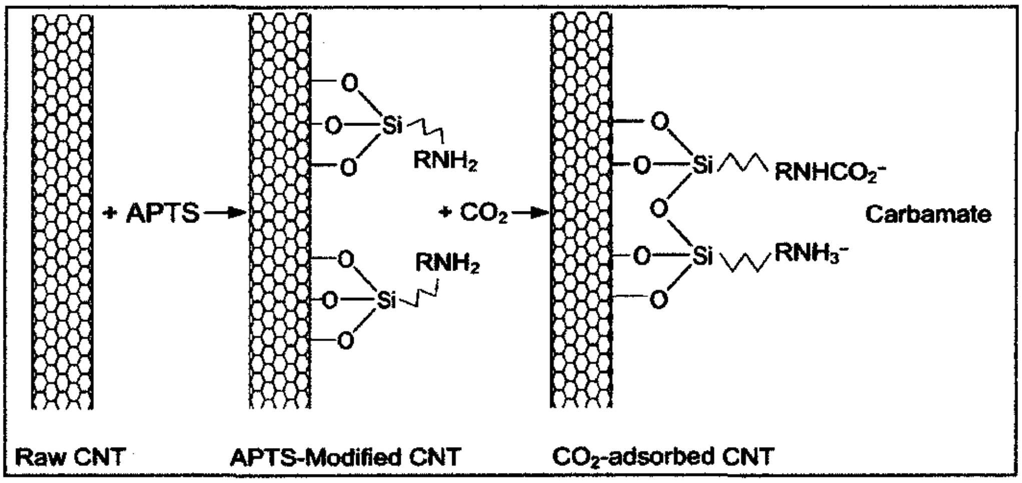


Figure 7: Mechanism for chemical adsorption of CO_2 on APTS-modified CNT

The nature on CNTs were improved after the modification including the increase in affinity between CO_2 and CNTs surface due to the attachment of amine functional groups in which can be simplify as the more amine functional group, the more CO_2 gas can be adsorbed. However, the adsorptive capacity of CNTs (APTS) will decrease with temperature increment thus will label it as a low-temperature CO_2 adsorbent. Although the CNTs (APTS) show good performance, the unit cost of employed CNTs is slightly higher compare to Granular Activated Carbon (GAC), however it is expected to further reduced in future (Su *et al*, 2009).

Previously, for CO_2 adsorption process, one of its adsorbent is by using a granular activated carbon (GAC). Modified CNTs and GAC are being prepared by using the same method which being dispersed in the flask containing modifying material which APTS. Referring to the data provided by BET analyzer, CNTs (APTS) are having an average pore diameter and pore volume which in the range of 5-20nm size and $0.63cm^3/g$ while for GAC (APTS) are in the range of 1.7-5nm size and $0.2563cm^3/g$. So that, modified CNTs are showing greater enhancement in adsorption capacity compared to modified GAC (Lu *et al*, 2008).

2.3.1 Study 1: Comparative Study of CO_2 Capture by Carbon Nanotubes, Activated Carbons and Zeolites

The study had been made by Chungsying Lu in order to observe the comparative behavior for capturing CO_2 application by adsorbents of CNTs (MWCNTs), granular activated carbon (GAC) and Zeolites. The comparison also had been made for a modified adsorbent such as CNTs (APTS), GAC (APTS) and Zeo (APTS). In this study, APTS had been chosen as it has ability to be the best functional group which enhances the capturing of CO_2. Details on APTS can be referred in the Appendix 1(Lu *et al*, 2008).

Table 1: Comparative study of CNTs, GAC and Zeolites

Title: Comparative study of CO_2 capture by carbon nanotubes, activated carbons and zeolites.				
Author: Chungsying Lu, Hsunling Bai, Bilen Wu, Fengsheng Su and Jyh Feng Hwang.				
Type of CNT or adsorbent	Properties of CNT or adsorbent	Adsorption Condition	Adsorption uptake	Remark
Before modification 1. CNTs (MWCNTs) 2. Zeolites (Zeo) 3. Granular Activated Carbon (GAC) After modification 1. CNTs(APTS) 2. Zeo (APTS) 3. GAC (APTS)	Size and internal diameter 1. CNTs: <10nm 2. Zeo: 24.7Å (2.47nm) 3. GAC: 0.55-0.75mm 4. (550-750nm)	1. Temperature: 25°C 2. Pressure : 1 atm 3. Influence CO_2 concentration: 5-50% 4. System flowrates controlled: 0.08 L/min	Chemisorption (mg/g) 1. CNTs : 3.9 2. Zeo : 1.4 3. GAC : 1.9 4. CNTs(APTS): 22.4 5. Zeo (APTS) : 12.5 6. GAC (APTS) : 8.0 Physisorption (mg/g) 1. CNTs : 65.3 2. Zeo : 62.1 3. GAC : 71.0 4. CNTs(APTS): 73.9 5. Zeo (APTS) : 69.9 6. GAC (APTS) : 71.5	Adsorption behavior CNTs>Zeo>GAC for modified adsorbents

A few characterizations had been made in order to observe its properties. One of them is by Raman Spectrometer which shows in Figure 7.

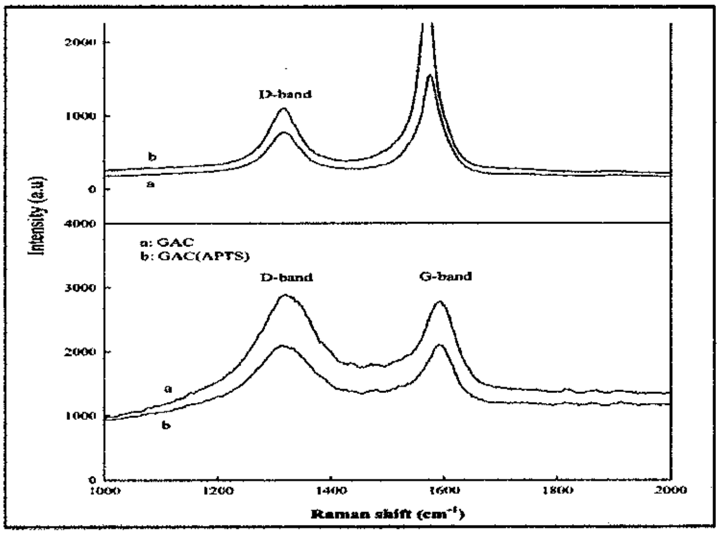


Figure 8: Raman spectra of raw and modified CNTs and GAC (Lu *et al*, 2008)

The result of the study shows in Figure 8 which showing for the raw adsorbents, CNTs is the best adsorbent and CNTs (APTS) is the best for modified adsorbent.

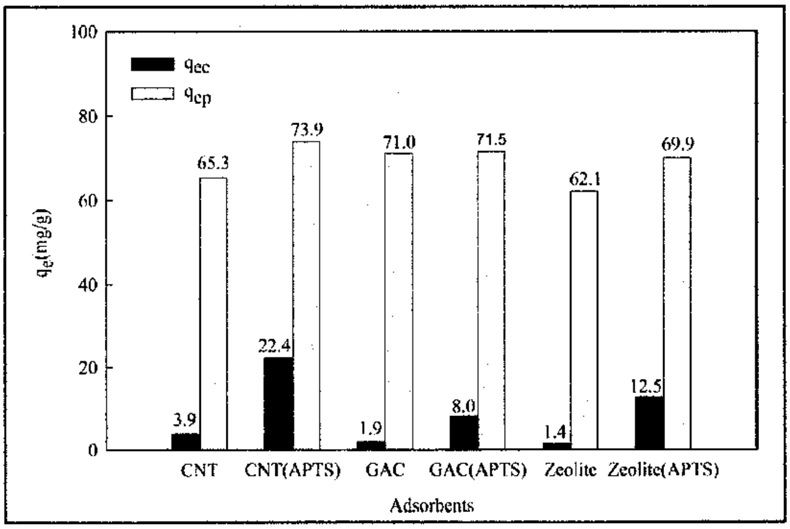


Figure 9: Physisorption (q_{ep}) and chemisorption (q_{ec}) capacities of CO_2 via raw and modified adsorbents with a C_{in} of 50% (Lu *et al*, 2008)

2.3.2 Study 2: Capture CO_2 from flue gas via multiwall carbon nanotubes

Another study which also had been done by Chungsying Lu was the study of Capture CO2 from flue gas via multiwall carbon nanotubes, which observing the modified adsorbent performance in capturing CO_2 which is in specific the performances of CNTs (APTS) and raw CNTs. Same as in Study 1, type of CNTs being used was multiwall carbon nanotubes. In this study also, the author observe the performance of both raw CNTs and CNTs (APTS) towards the increment of temperature which started from 20°C, 40°C, 60°C, 80°C and 100°C (Su et al, 2009).

Table 2: Study of Capture of CO_2 from flue gas via multiwall carbon nanotubes

Title: Capture of CO_2 from flue gas via multiwall carbon nanotubes				
Author: Fengsheng Su, Chungsying Lu, Wenfa Cnen, Hsunling Bai, Jyh Feng Hwang				
Type of CNT or adsorbent	Properties of CNT or adsorbent	Adsorption Condition	Adsorption uptake	Remark
1.CNTs (MWCNTs) 2.CNTs (APTS)	Physical properties 1. Surface area: 1458 m^2g^{-1} 2. Pore volume: 0.332 cm^3g^{-1} 3. Pore diameter:0.23 nm	1. Temperature: 20, 40, 60, 80, 100 °C 2. Pressure : 1 atm 3. Influence CO_2 concentration: 50% 4. System flowrates controlled: 0.08 L/min	Ratio of q_{ec} and q_{ep} 1. CNTs q_{ec}: 2-17% 2. CNTs q_{ep}: 83-98% 3. CNTs (APTS) q_{ec}: 11-29% 4. CNTs (APTS) q_{ep}: 71-89% q_e at C_{in}=50% (mg/g) for CNTs 20°C: 75.9 40°C: 66.4 60°C: 51.8 80°C: 41.8 100°C: 31.2 q_e at C_{in}=50% (mg/g) for CNTs(APTS) 20°C: 114 40°C: 98 60°C: 81.3 80°C: 67.7 100°C: 52.9	CNTs (APTS) give the highest value of physisorption and chemisorption which is q_e: 114 at 20°C which this value will be decreased due to increment in temperature.

The adsorption isotherms of CO_2 via CNTs and CNTs (APTS) can also be referred as in the figure 9;

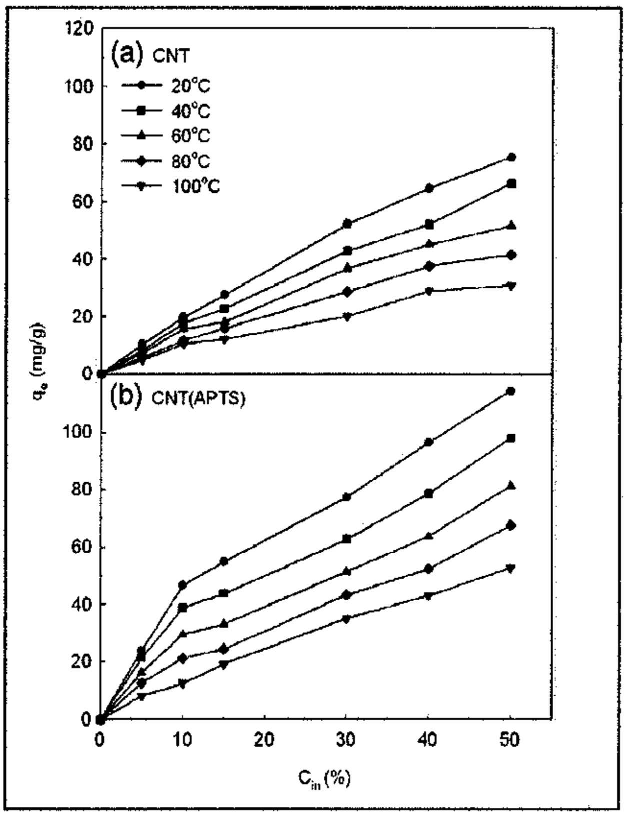


Figure 10: Adsorption isotherms of CNTs and CNTs (APTS) at multiple temperatures (Su *et al*, 2009)

The surface nature of CNTs were improved after the modification including the increase on affinity between CO_2 and CNTs surface and the increase in surface of amine group which in result more CO_2 can be adsorbed.

2.3.3 Study 3: CO$_2$ adsorption in singlewall carbon nanotubes

In this study, the author studied the CO$_2$ adsorption behavior of raw CNTs, purified CNTs and activated carbons [1]. In this study, type of CNTs being used is singlewall carbon nanotubes. In before, this type of CNTs had been study for a adsorption of benzene and methanol with an uptake up to 100-300mg/g (M. Eswaramoorthy, 1999).

Table 3: CO$_2$ adsorption in single-walled carbon nanotubes

<table>
<tr><td colspan="5">Title: CO$_2$ adsorption in single-walled carbon nanotubes</td></tr>
<tr><td colspan="5">Author: Martin Cinke, Jing Li, Charles W. Bauschlicher Jr., Alessandra Ricca, M. Meyyappan</td></tr>
<tr><td>Type of CNT or adsorbent</td><td>Properties of CNT or adsorbent</td><td>Adsorption Condition</td><td>Adsorption uptake</td><td>Remark</td></tr>
<tr><td>1. Raw CNTs (SWCNTs)
2. Purified CNTs (SWCNTs)</td><td>Physical properties raw CNTs(BET analysis)
1. BET area: 1587 m^2/g
2. Total pore volume: 1.55c cm^3/g
3. Micropore volume: 0.28 cm^3/g
4. Fe: 22 wt%

Physical properties purified CNTs(BET analysis)
1. BET area: 1587 m^2/g
2. Total pore volume: 1.55c cm^3/g
3. Micropore volume: 0.28 cm^3/g
4. Fe: 0.4 wt%</td><td>1. Temperature: 0, 35, 125, 200 °C
2. Pressure : 1 atm</td><td>Volume of CO$_2$ adsorbed at 35°C, 1 atm.
1. Raw CNTs: 48cm^3/g
2. Purified CNTs: 90cm^3/g</td><td>Purified CNTs gives higher value of CO$_2$ adsorption because of the less influenced form Fe. However, the adsorption capacity reduced due to the increment in temperatures.</td></tr>
</table>

The adsorption isotherms of CO_2 via raw CNTs and purified CNTs can also be referred as in the figure 10 and figure 11;

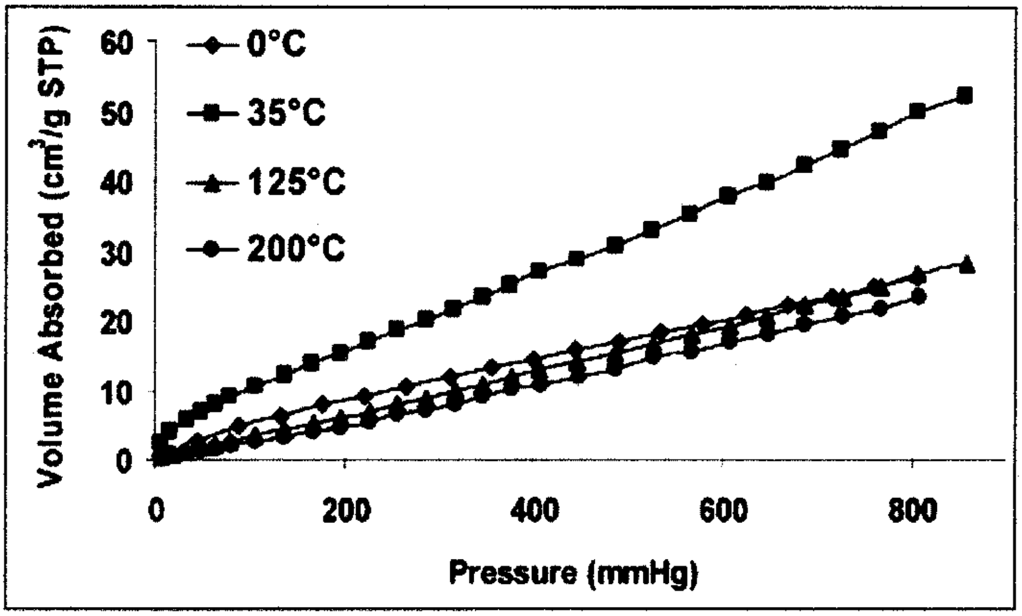


Figure 11: Isotherm for CO_2 adsorption of raw CNTs (M. Eswaramoorthy, 1999)

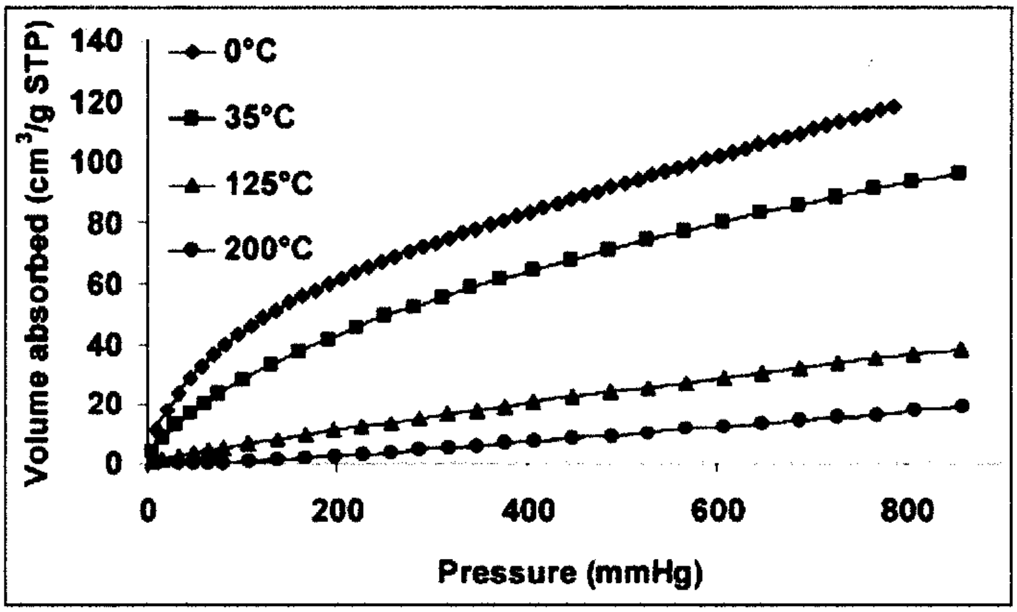


Figure 12: Isotherm for CO_2 adsorption of purrified CNTs (M. Eswaramoorthy, 1999)

Referring to the Figure 10 and figure 11, Purified CNTs gives higher value of CO_2 adsorption because of the less influenced form Fe. However, the adsorption capacity reduced due to the increment in temperatures.

2.3.4 Surface Modification of CNT via Acid Treatment

CNTs fabricated by the method of catalytic chemical vapor deposition method and being oxidized by HCl, H2SO4, HNO3 and NaOCl solutions for enhancing benzene, toluene, ethylbenzene and pxylene (BTEX) adsorption in an aqueous solution. During the oxidation, the surface nature of CNTs was changed, which makes CNTs that adsorb more BTEX. The NaOCl-oxidized CNTs show the greatest enhancement in BTEX adsorption, followed by the HNO3-oxidized CNTs, and then the H2SO4-oxidized CNTs (Lu C. S., 2008).

Table 4: Surface modification of carbon nanotubes for enhancing BTEX adsorption from aqueous solutions

<table>
<tr><td colspan="5">Title: Surface modification of carbon nanotubes for enhancing BTEX adsorption from aqueous solutions</td></tr>
<tr><td colspan="5">Author: Chungsying Lu, Fengsheng Su, Suhkai Hu</td></tr>
<tr><td>Type of CNT or adsorbent</td><td>Properties of CNT or adsorbent</td><td>Adsorption Condition</td><td>Adsorption uptake</td><td>Remark</td></tr>
<tr><td>1. CNTs (SWCNTs)
2. CNTs (MWCNTs)
3. CNTs modification:
a. NaOCl
b. HNO_3
c. H_2SO_4
d. HCl</td><td>1. Surface area: 1458 m^2g^{-1}
2. Pore volume: 0.332 cm^3g^{-1}
Pore diameter:0.23 nm</td><td>1. Temperature: 0, 35, 125, 200 °C
2. Pressure : 1 atm
3. Rotary velocity: 180rpm
4. Time: 4 hrs
5. BTEX C_{in}: 120 mg/l</td><td>q_e of CNTs(NaOCl), mg/g
B: 212.3
T: 172
E: 180
X:170

q_e of CNTs(NaOCl), mg/g
B: 105.7
T: 160.8
E: 153.1
X:108.9</td><td>CNTs (NaOCl) have the greatest adsorption capacity of BTEX, followed by the CNT (HNO_3).</td></tr>
</table>

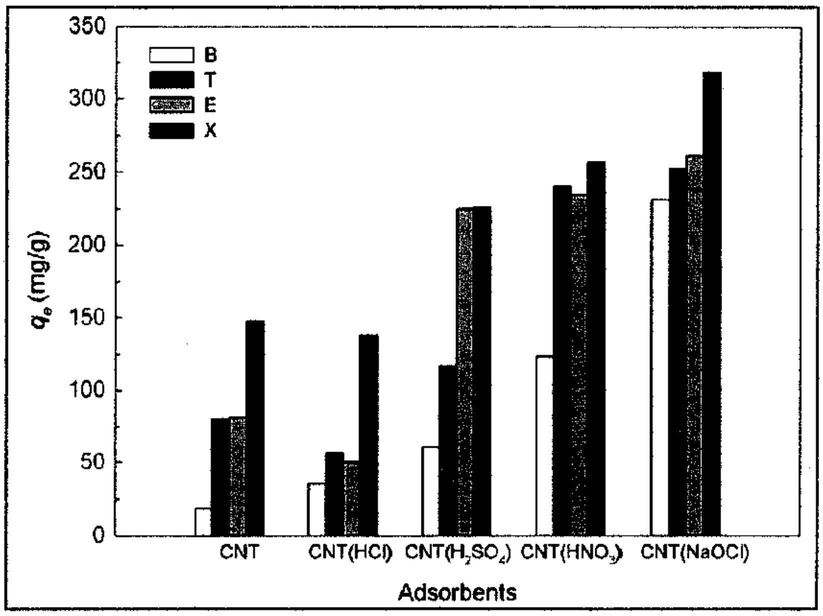
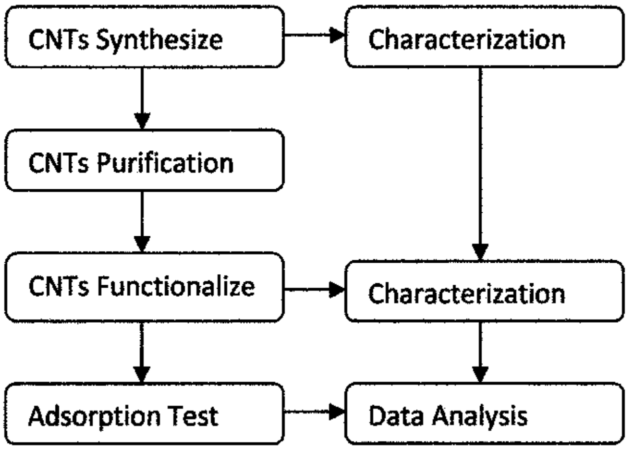


Figure 13: Equilibrium amount of BTEX adsorbed on as-grown and oxidized CNTs with a C0 of 200 mg/l (Lu C. S., 2008)

Referring to figure 12, the surface nature of CNTs was changed after the H2SO4, NHO_3 and NaOCl oxidation, which makes CNTs that adsorb more BTEX. The CNT (NaOCl) have the greatest adsorption capacity of BTEX, followed by the CNT (HNO_3), CNT (H_2SO_4), CNT, and then the CNT (HCl).

CHAPTER 3: PROPOSED METHODOLOGY

3.1 Flow of Proposed Methodology



3.2 Details on Proposed Methodology

3.2.1 CNTs Synthesis

MWCNTs being synthesized using Floating Catalyst CVD Method (FCCVD) which is the essential method to produce MWCNTs. This method is chosen because of its several advantages which are potential for continuous preparation, low cost, high purity and simple post treatment. This method basically consist of two important step which is MWCNTs grow and equipment cleaning which both have to done in order to make sure the equipment is always ready for the next batch of MWCNTs synthesize. There are a few pictures to visualize the MWCNTs synthesis and after the synthesis, MWCNTs which embedded on the surface of coarse boat have to be scrubbed and collected in the vials as a record.

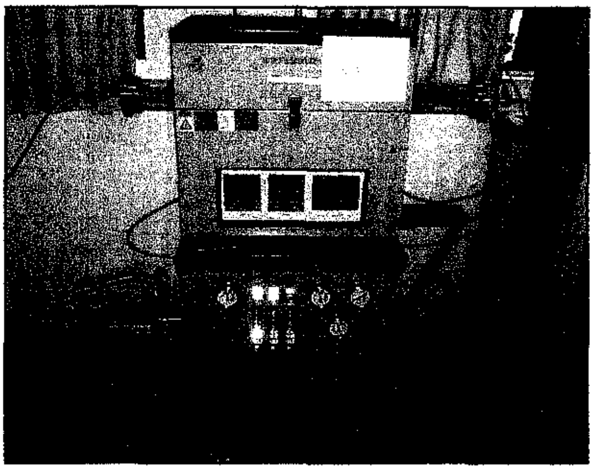


Figure 14: Floating Catalyst CVD (FCCVD) Equipment

Figure 15: FCCVD During Equipment Setup

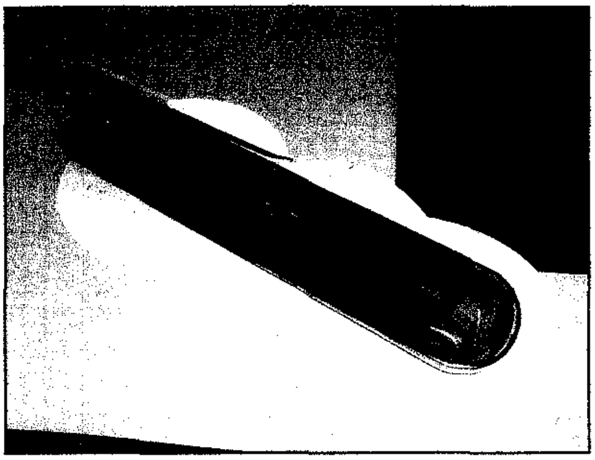


Figure 16: MWCNT Collected on the Coarse Boat

3.2.2 CNTs purification

a) 0.3g of CNTs was poured into the solution hydrogen peroxide with is 30% concentrated.

b) Magnetic stirrer was used for 12 hours to enhance the dispersion of CNTs with hydrogen peroxide.

c) The filtration was carried out using membrane filtration (0.27micro m).

d) Purified CNTs collected in the 16ml vials.

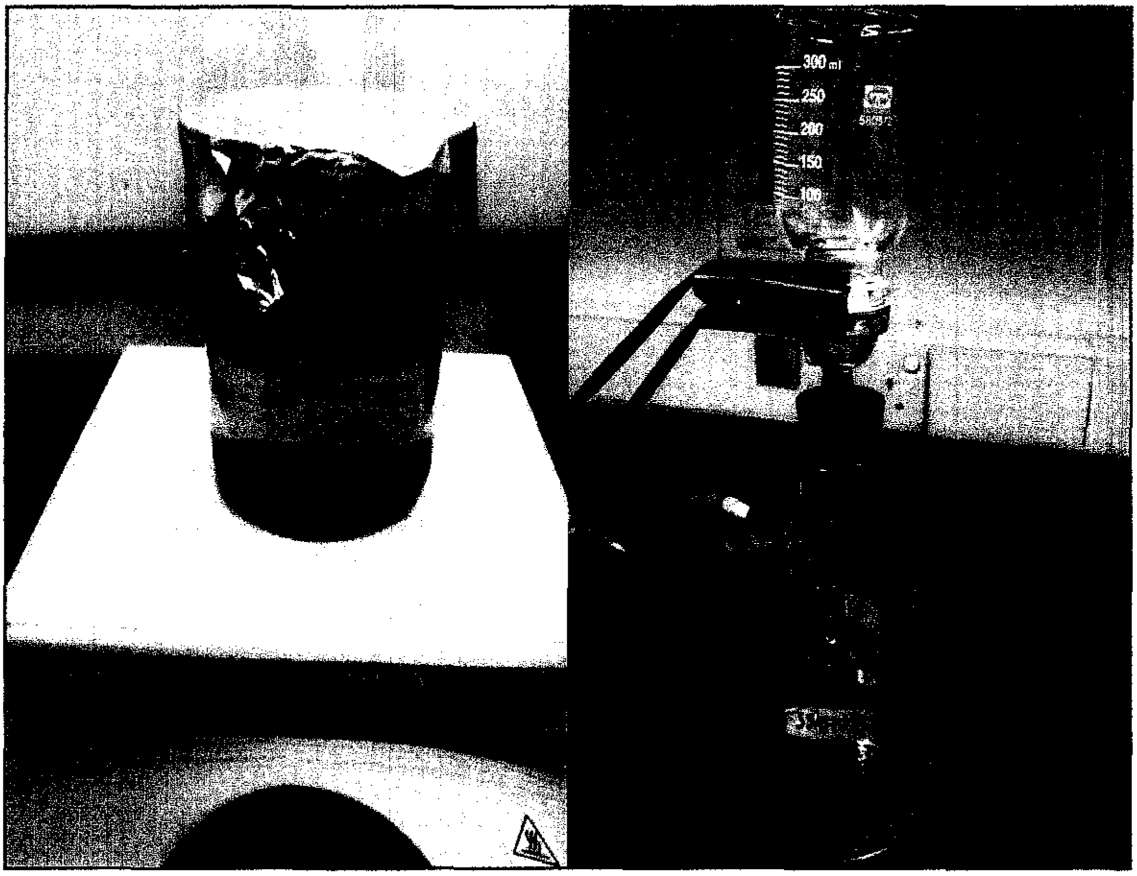


Figure 17: MWNTs Purification

3.2.3 CNTs Functionalization

a) 0.3g of purified CNTs were dispersed into flask containing:
    I. Hydrochloric Acid
    II. Nitric Acid

b) Magnetic Stirrer was used for 6 hours to enhance the dispersion of CNTs with the acids.

c) Purpose was to determine the optimum modification method via acid treatments of CNTs for enhancing CO_2 capture or adsorption application.

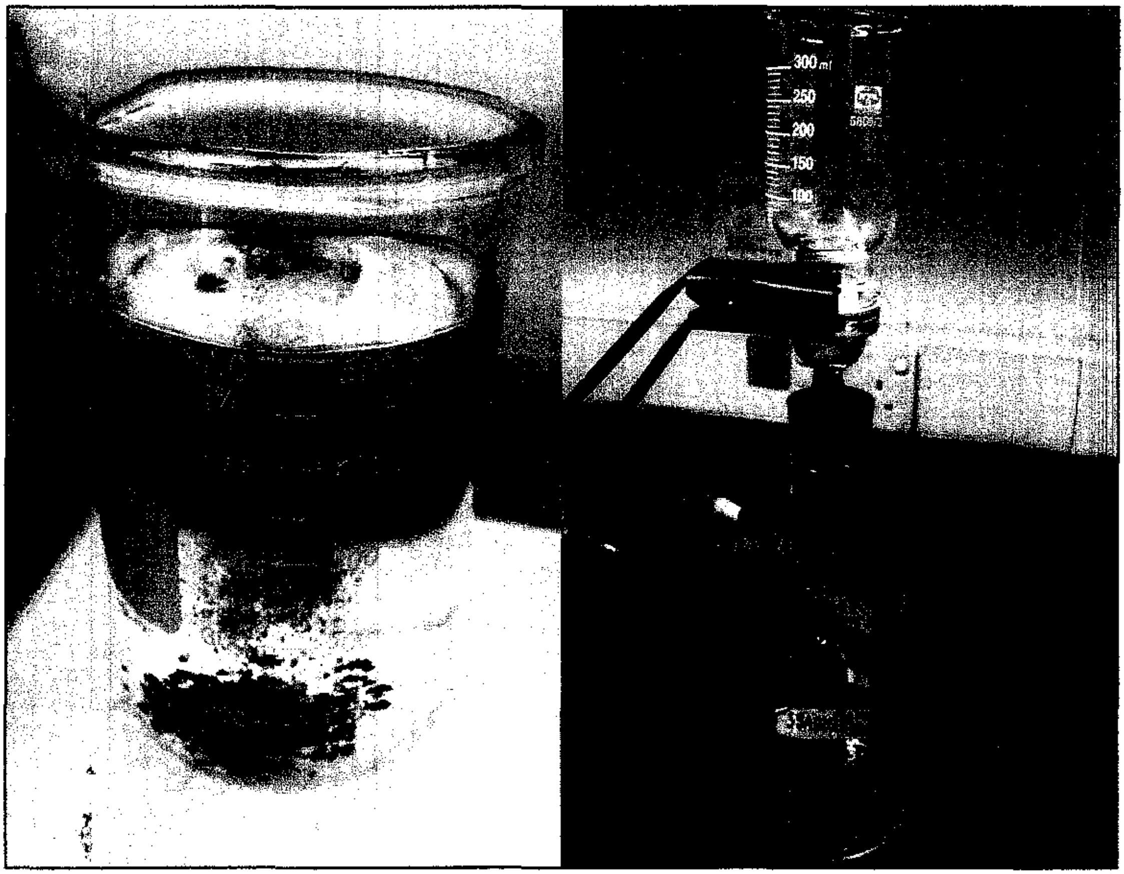


Figure 18: MWCNTs Functionalization

3.2.4 Adsorption test

Magnetic suspension balance provided by UTP which located at block 3:

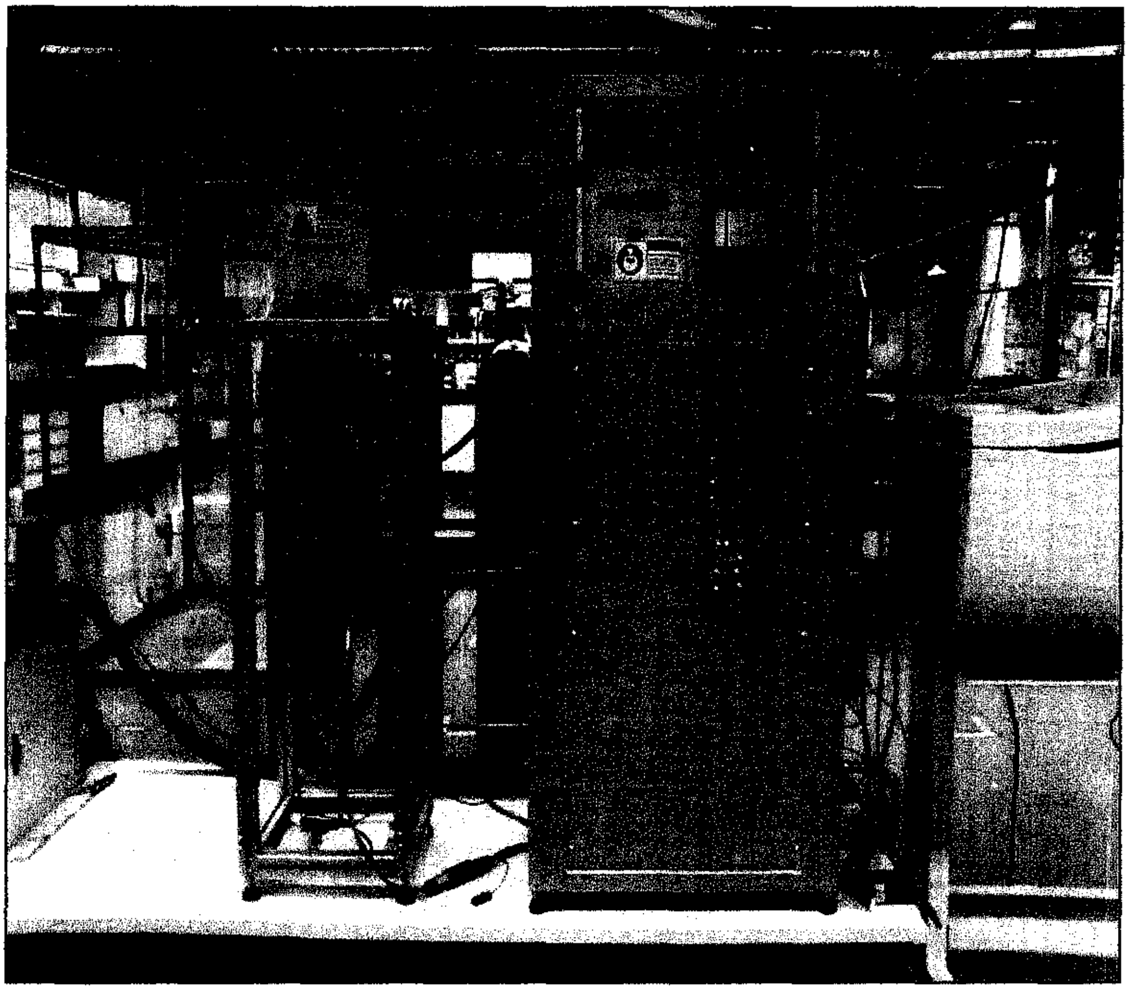


Figure 19: Magnetic Suspension Balance Equipment.

3.2.5 Analytical method

a) Field Emission Scanning Electron Microscopy (FESEM)
b) Raman spectrometer
c) Thermo gravimetric analyzer
d) Brunauer, Emmett and Teller (BET)
e) Infrared spectrometer (FTIR)

Table 5: Equipments for Characterization

No	Equipment	Reason
1	Field Emission Scanning Electron Microscopy (FESEM)	To analyze the surface morphology of the MWCNTs.
2	Raman spectrometer	To evaluate the quality of MWCNTs.
3	Thermo gravimetric analyzer (TGA)	To determine thermal stability of MWCNTs throughout temperature difference.
4	Brunauer, Emmett and Teller (BET)	To determine the MWCNTs surface area.
5	Infrared spectrometer (FTIR)	To determine the presence of functional groups via infrared spectrum.

3.3 Gantt Chart

No	**Description / Week**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Literature Review														
2	Methodology Improvement														
3	Chemical and Apparatus Preparation														
4	MWCNTs Synthesis														
5	First Characterization														
6	MWCNTs Purification														
7	SWCNTs Purification														
8	MWCNTs Functionalization														
9	SWCNTs Functionalization														
10	Second Characterization														
11	MWCNTs & SWCNTs Characterizations														
12	CO_2 Adsorption Test														
13	Data Analysis														
14	Progress Report Submission														
15	Final Report Submission														
16	Viva / Final Presentation														

CHAPTER 4: LIST OF EQUIPMENT/CHEMICAL

4.1 List of Equipment

No	Equipment	Description
1	Membrane Filter	To remove impurities and particulates contained in the air during CNTs purification.
2	Oven	To dry purified CNTs after being filtered before undergo modification process.
3	Field Emission Scanning Electron Microscopy (FESEM)	To analyze the morphology of adsorbent (CNTs).
4	Raman spectrometer	To evaluate the structure information of adsorbent (CNTs).
5	Thermo gravimetric analyzer (TGA)	To determine the thermal stability of adsorbent (CNTs).
6	Brunauer, Emmett and Teller (BET)	To determine the surface area of adsorbent (CNTs).
7	Infrared spectrometer (FTIR)	To determine chemical properties of adsorbent

4.2 List of Chemical

a) Hydrogen Peroxide
b) Hydrochloric Acid
c) Sulphuric Acid
d) Nitric Acid

CHAPTER 5: RESULT AND DISCUSSION

5.2 MWCNTs Characterization Using FESEM

For MWCNTs Characterization, the equipment of Field Emission Scanning Electron Microscopy (FESEM) has been used due to clearer images and 3 to 6 times better compared to conventional SEM. Basically, FESEM being used to identify the structure of the MWCNTs through images. In addition, the impurities also can be observed and compare between before purify and after purify. Below are a few pictures during MWCNTs Characterization using FESEM.

Figure 20: Raw MWCNT FESEM Image

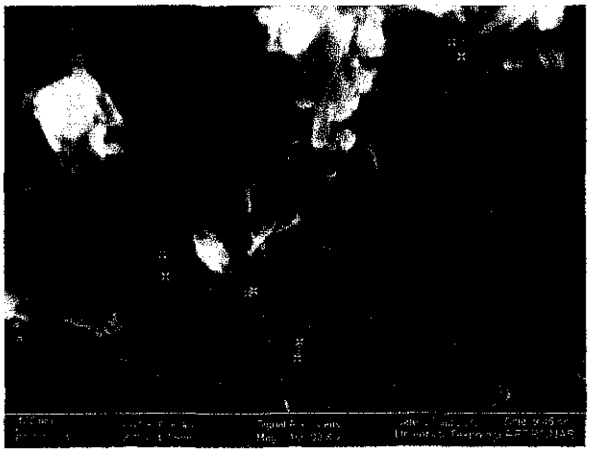


Figure 21: SWCNT FESEM Image

Referring to the Figure 19 and 20, carbonaceous can be observed on the surface of the raw MWCNTs and the changes can be observed due to the reduced in size of the carbonaceous. Carbonaceous can be labeled as one of the impurities contains inside the MWCNTs. Besides carbonaceous, there are others impurities such as debris, catalyst particle and fullerenes regardless on the method used to synthesis the MWCNTs and these impurities normally influences the desired properties of MWCNTs. The FCCVD synthesis method consists of decomposing a carbon containing gas over a supported catalyst. In order to enhance and improve yield and quality, further studies have to be done in order to find the best method of MWCNTs purification as the purification of the MWCNTs proven to be difficult and need to have a few steps of purification in order to remove this carbonaceous. However, no complication occurred during metal removal from MWCNTs and single purification was sufficient enough to eliminate metal containing inside MWCNTs after synthesis. From the FESEM images also observed that after Functionalization via acid treatment, great amount of carbon-containing defects along the surface of MWCNTs detected which can be easily introduced functional group and thus provide numerous chemical adsorption sites for CO_2 capture. For the pore sizes of the MWCNTs, there are similar distribution in the pore size range of 20-30nm for Raw MWCNTs and 15-35nm for functionalize MWCNTs.

5.3 MWCNTs and SWCNTs Characterization Using FTIR

IR Spectroscopy on FTIR is one of the important steps for functional group determination especially after Functionalization of MWCNTs. However, there are a common experimental difficulties involves while obtaining IR spectra as FTIR can only be used for highly oxidized carbon surfaces, otherwise the intensity of the absorption band is very poor. Referring to Figure 21, there are three different "absorption versus wave number of IR". When comparing the FTIR spectra, peaks appear at 1737cm^{-1}, 1364cm^{-1} and 1217cm^{-1} for the acid-treated CNTs relative to the as-grown CNTs. This clearly shows that acid treatment has introduced some functional groups onto the surface of the CNTs. The amount of these functional groups present on the surface depends on the reflux time and/or the acid strength. The peak appearing at 1737cm^{-1}

can be ascribed to the CO stretching vibration of carboxyl or carbonyl groups while that at 1364cm^{-1} is associated with NO_2 stretching vibrations and the peak at 1217cm^{-1} corresponds to C–O stretching and O–H bending vibrations. It can be concluded that FTIR analysis also provides evidence for the existence of defects in the walls of the CNTs. Compared to a few studies which had been made by researchers, the presence of this functional groups is a good sign of the success of this prepared modified CNTs (Lu, 2008). The functional groups which are attached to MWCNTs increase the polarity and further alter the surface changes.

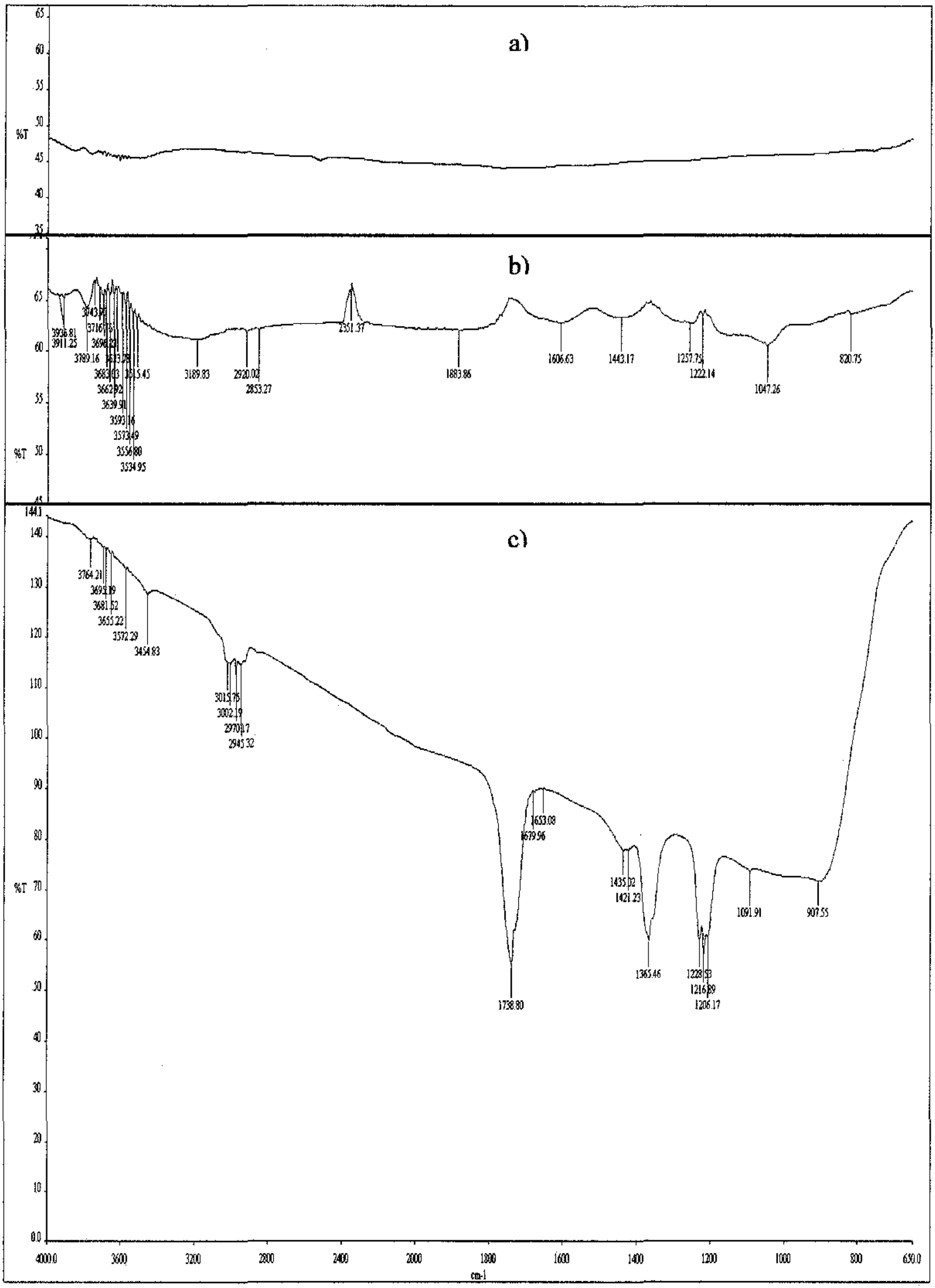


Figure 22: FTIR Result for Raw MWCNTs (a), MWCNTs + HCL (b), and MWCNTs + HNO_3 (c)

5.4 CO2 Adsorption via Surface Polarity

Modification MWCNTs via acid treatment also called as oxidation will increase the total acidity of MWCNTs which originated from the presence of more carboxyl, lactones and phenol groups on the MWCNTs wall. Carboxylic groups are the major acidity distributor followed by lactonic and phenolic groups. In addition, the total basicity also keeps increasing due to the addition of the oxygen functional groups. Modified MWCNTs (HNO3) is having a greater amount of carboxylic and oxygen group compared to MWCNTs (HCL) which make it higher in basicity in which this properties is really needed for CO_2 capture. Theoretically, CO_2 is acidic and that is why too much of CO_2 in the atmosphere is not good at all as neutral environment is safer. Because of the acidity of CO_2, the adsorption can be happen. In other words, base Functionalization (basicity of MWCNTs) can enhance the CO_2 adsorption compared to raw MWCNTs due to acid-base interaction between CO_2 (acid) and the basic active site in the surface of MWCNTs. Besides, hydroxyl groups evidence that CO_2 interact with the O atoms of framework –OH groups is an electron-accepter via its carbon atom. Thus, with this acid-base interaction modified MWCNTs with Nitric Acid id the most suitable method of MWCNTs via acid treatment for the purpose of CO_2 adsorption application (Jian-Rong, 2011).

CHAPTER 6: CONCLUSION

The chemisorption and physisorption of CNTs are enhanced by modifying it with different acid treatments which leads to the increment in volume of the CO_2 that can be captured. Single step purification significantly not enough for CNTs purification and it only gives up to 40% purification and multi purification needed in order to achieve higher than 90% purification. Yields of the purified and functionalized material varied from 30 to 50% depending on the oxidation and purification time. In short, by modifying CNTs with different acid treatment, the difference of CO_2 adsorption capacity throughout the different of functionalization and adsorption behavior can be compared. Thus, the best acid treatment can be identified for the best functionalization for CO2 adsorption application.

CHAPTER 7: REFERENCES

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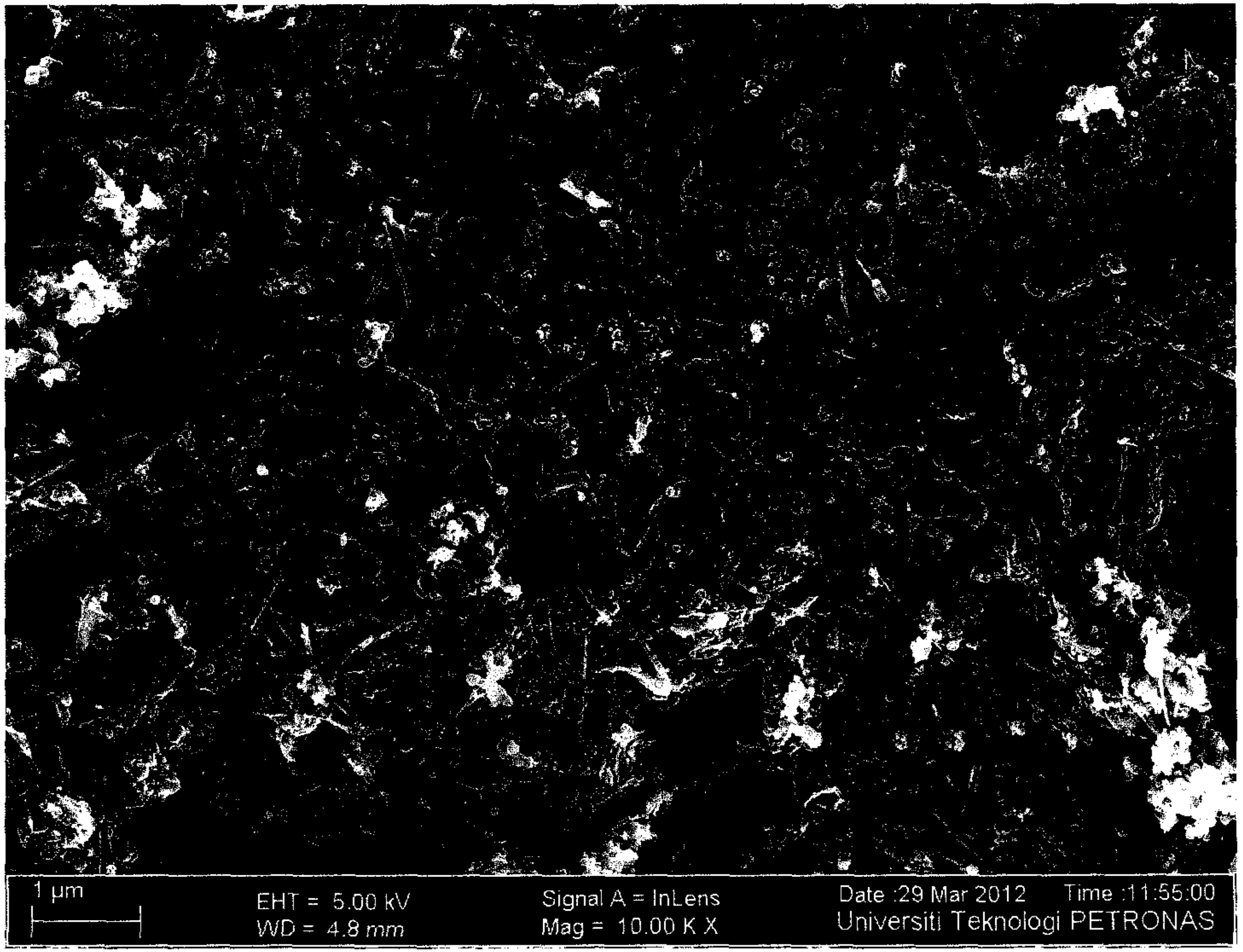
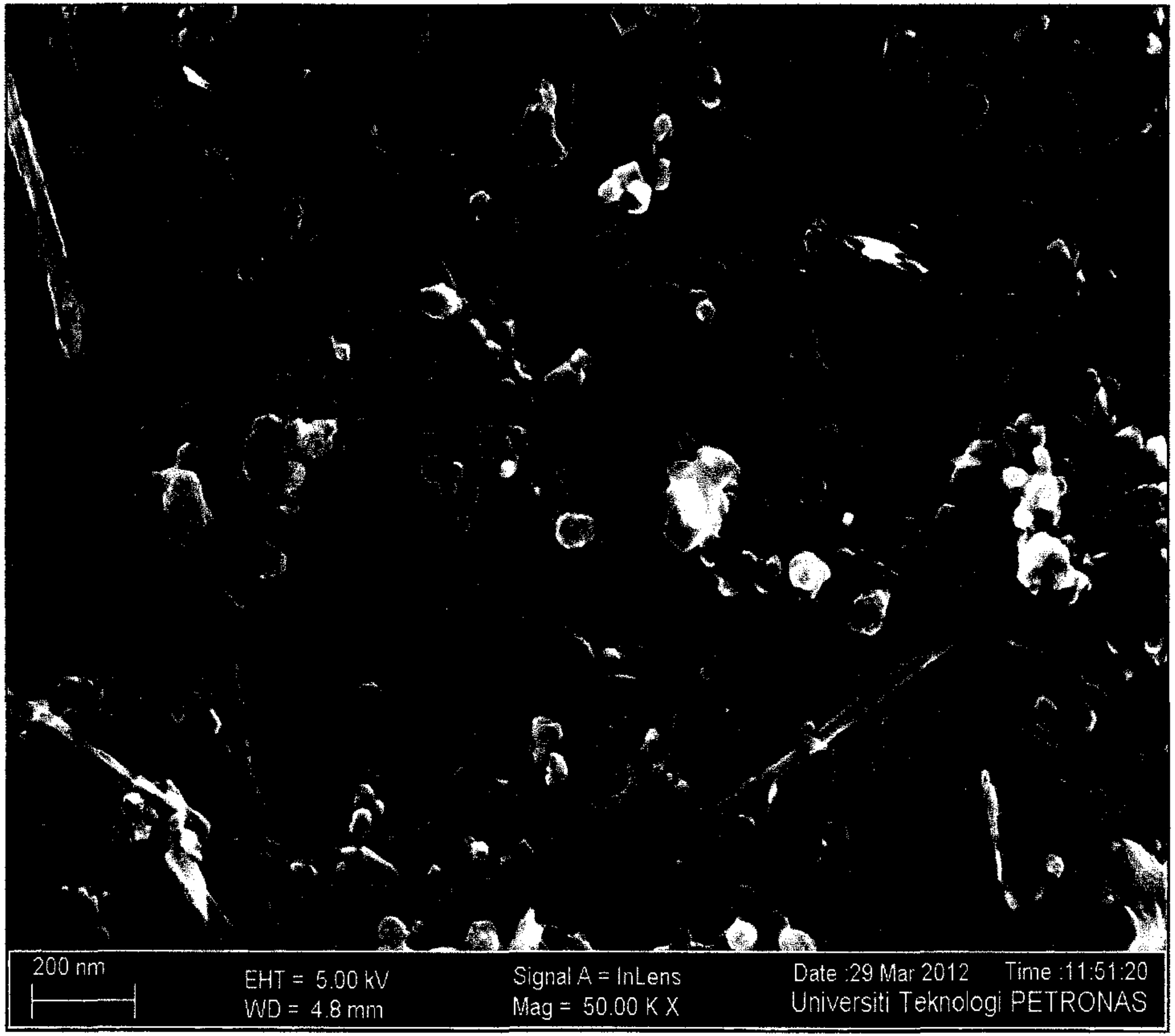
CHAPTER 8: APPENDIXES

a) FESEM images of Raw MWCNTs

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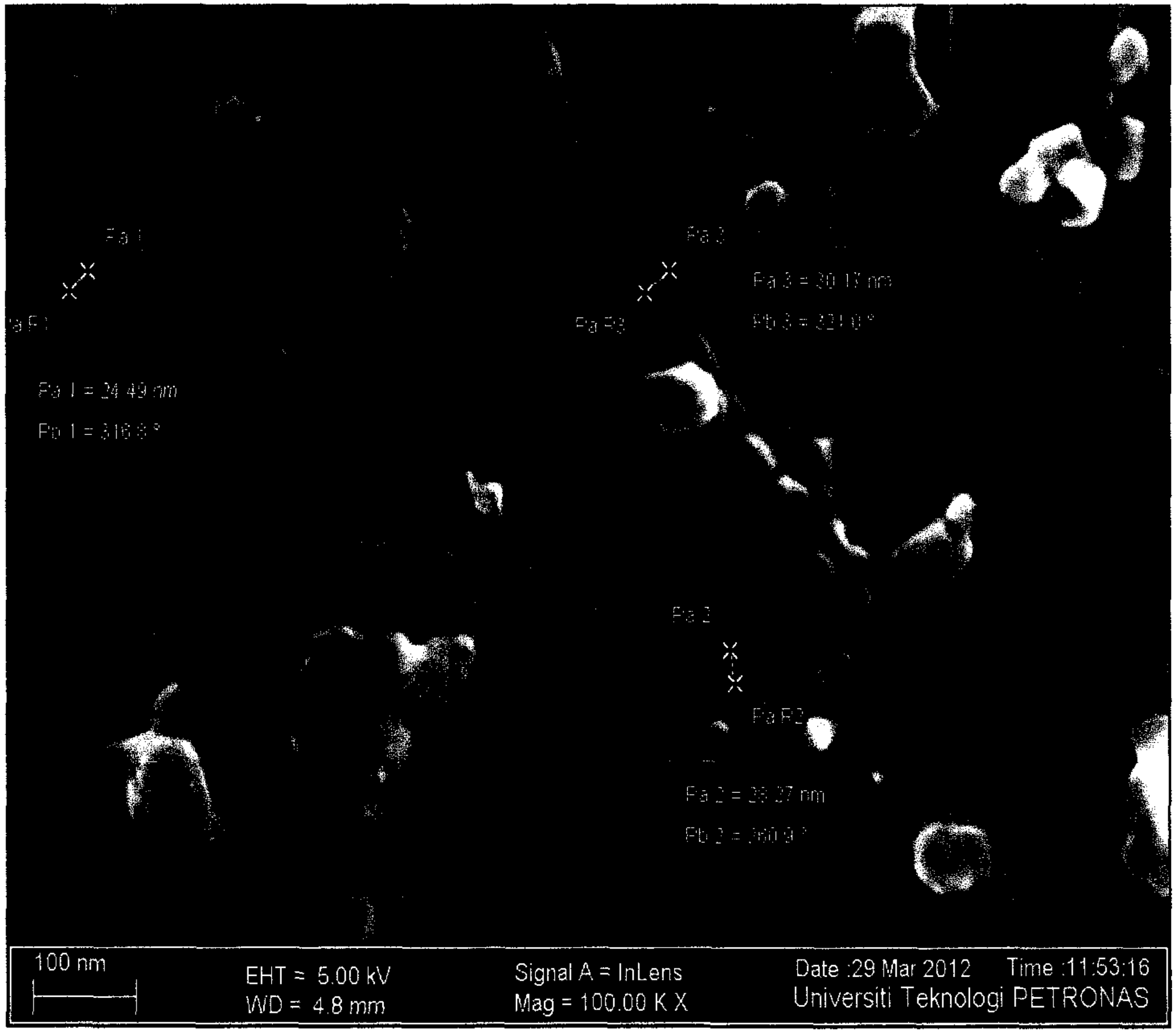
Universiti Teknologi PETRONAS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Pa R1
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Pb 1 = 316.8 °
Pa 3
Pa R3
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Pb 3 = 221.0 °
Pa 2
Pa R2
Pa 2 = 28.27 nm
Pb 2 = 260.9 °
100 nm
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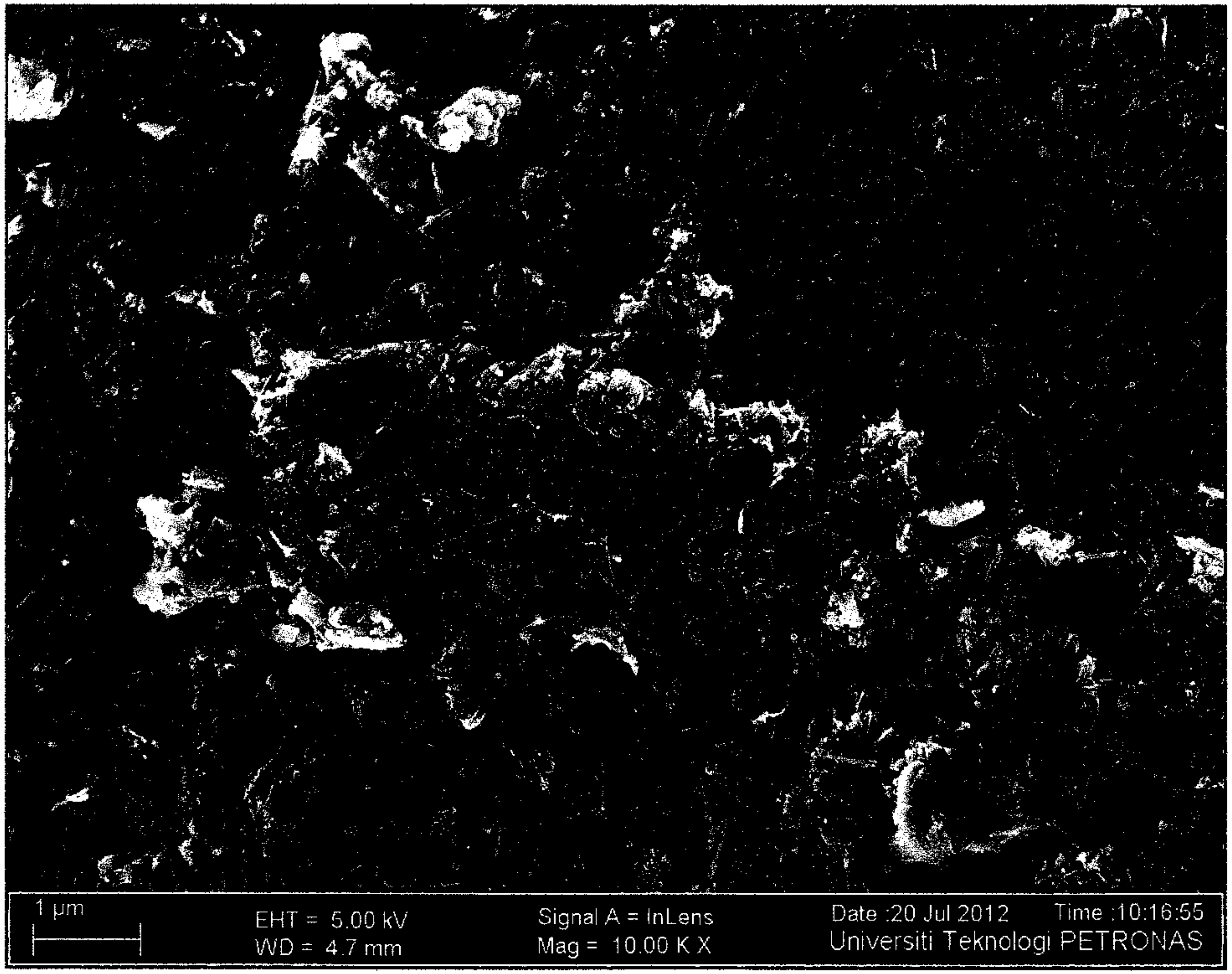
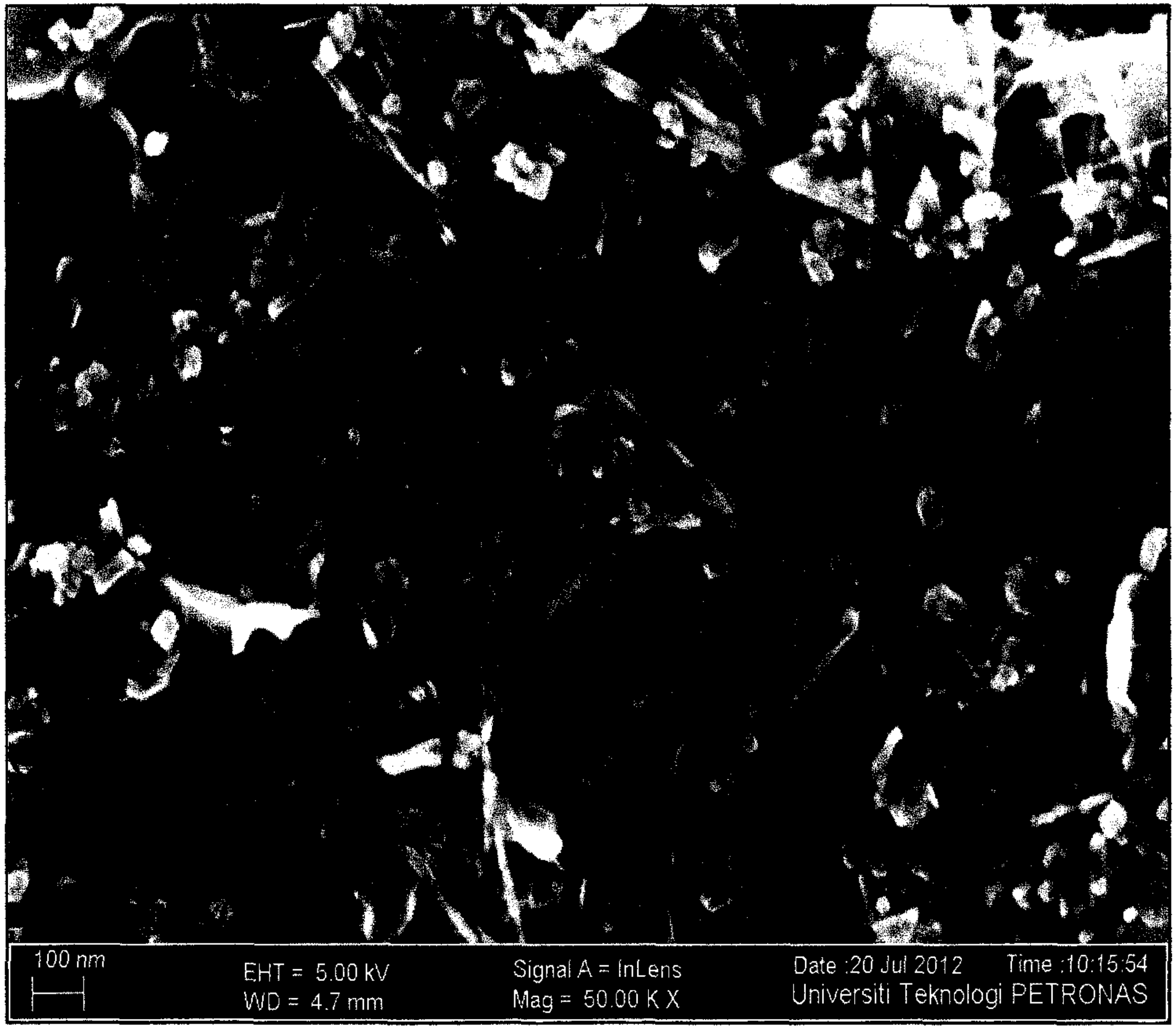
b) FESEM images of Modified MWCNTs

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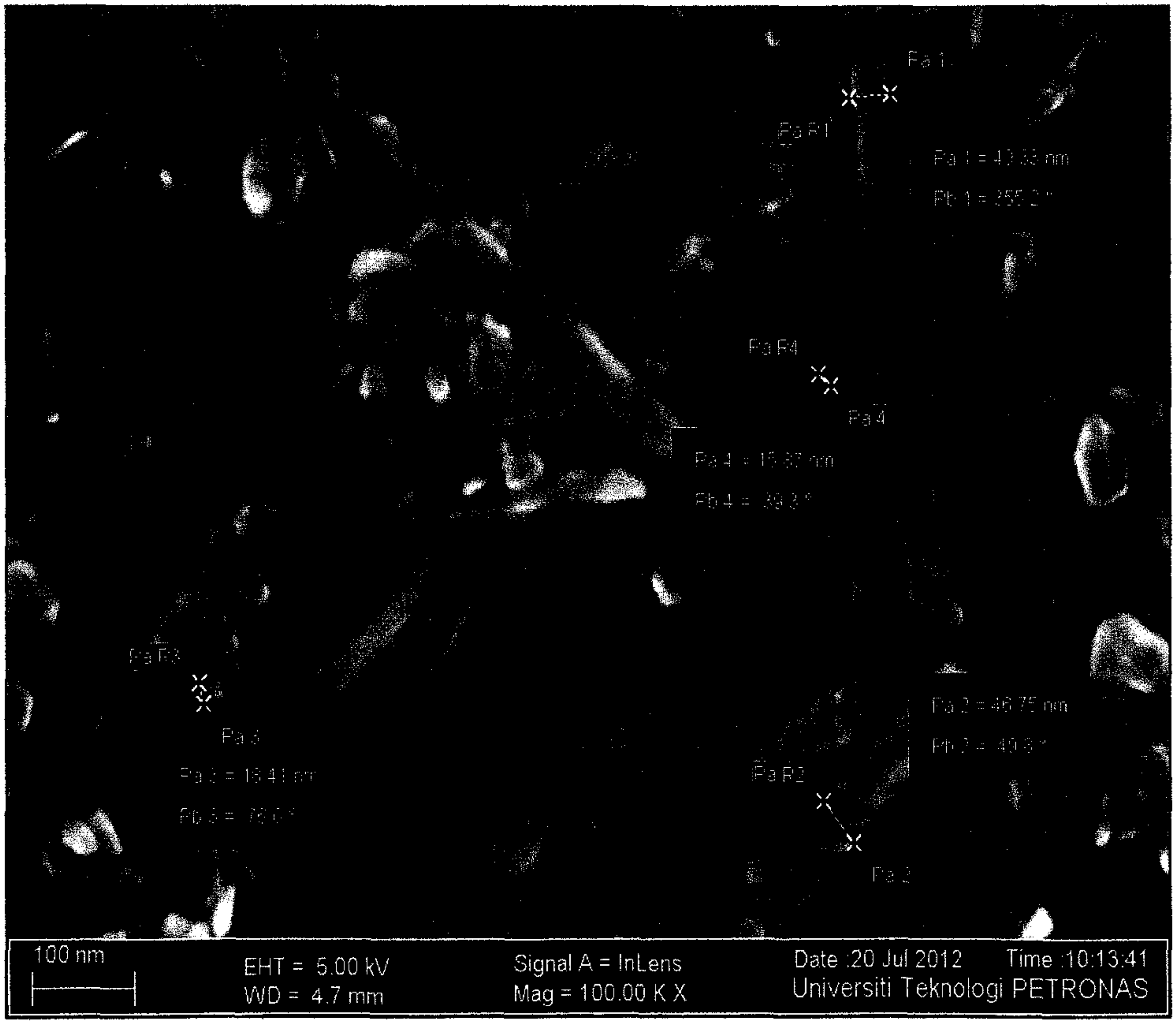
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