# A Study on Hydrogen Adsorption Using Different Nanostructured Materials

by

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Dissertation submitted in partial fulfilment of
the requirements for the Bachelor of Engineering (Hons)
(Chemical Engineering)

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# CERTIFICATION OF APPROVAL

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Chemical Engineering Programme
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BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

___________________________

(Dr Suriati binti Sufian)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2014

# 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.

(NOOR AMANINA BINTI GHAZALI)

# ABSTRACT

In the search for green energy alternative to replace gasoline in the future, hydrogen as a fuel has been proposed as an ideal energy source. Hydrogen has a higher chemical energy than hydrocarbon fuels. However, the storage of hydrogen is the main barrier to the further improvement of hydrogen technology. Nanostructures materials have received special attention as a great potential for hydrogen storage for their structures such as large surface area and theoretically high binding energy.

The project is focusing on the study of hydrogen adsorption using nanostructured materials that are nanodiscs and nanocrystalline (hexagonal shape) hydrotalcite. The selected nanomaterials for this research are Boron Nitride nanodiscs and nanocrystalline hydrotalcite derived mixed oxides containing magnesium, cobalt, and aluminum. In addition, the structures of both nanomaterials are also monitored to investigate on how the differential structure could be related to the hydrogen uptakes. In this project, it is founded that hydrotalcite adsorbs more hydrogen (1.3wt%) than Boron Nitride nanodiscs (0.27wt%) because the hydrotalcite have more surface area, with less dense structure which allows more hydrogen uptake than BN nanodiscs.

# ACKNOWLEDGEMENT

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# CHAPTER 1

## INTRODUCTION

### 1.1 BACKGROUND OF STUDY

Energy and environmental problems are two of most significant problems which we will have to face over the next 50 years. Since the beginning of 21st century, the limited supply of fossil fuels problem other than the growing impact of $CO_2$ emissions on the environment became very apparent. These problems are connected as $CO_2$ is produced during the combustion of fossil fuels. Over the last decades, there is an exponential increase to global carbon emissions as well as for the global temperature. In referring to decreasing fossil fuels supply and global warming, the best solution to both problems is to replace the energy economy from fossil fuels to renewable energy. Hydrogen fuel cells are being considered to replace gasoline as a primary energy source.

Hydrogen has the simplest structure of any element and is the most common gas in the universe. Car manufacturers are beginning to use it as a fuel to replace gasoline such as Honda (Honda FCX), Toyota (Toyota FCV) and Peugeot (H2Origin-Fuel cell). In addition to producing less pollution, hydrogen has more power than gas when measured by weight. Not only that, the combustion of hydrogen produces water and therefore it is environmentally friendly. According to the US Energy Information Administration, hydrogen has three times the power of gasoline by weight and has the highest energy content of any known fuel (Froudakis, 2011). However, after so many years on hydrogen research, hydrogen fuel cells are still unable to be produced, stored and transported in a cost-effective manner. The storage of hydrogen had become the main problem itself before the hydrogen technology could be improved.

## 1.2 PROBLEM STATEMENT

Hydrogen has been recognized as an ideal energy carrier as it is environmental friendly. The downside of hydrogen is the fact that it is gaseous under ambient conditions with a very low density which is 0.08988 g/L while liquid hydrogen has the density of 70.99 g/L. Therefore, to produce the same amount of energy, hydrogen needs four times the volume of gasoline. This results in severe storage difficulties. High pressure storage is also impractical and unsafe mainly for mobile application.

To overcome the storage problem, nanostructured materials were introduced. Despite the high surface area of nanostructured materials as the likely candidates for hydrogen uptake, the hydrogen uptake density deemed too low for practical applications. Several experimental and modelling researches using different nanostructured materials had been done in the literature.

This project will be focusing on the study of hydrogen uptake using Boron Nitride nanodiscs and nanocrystalline hydrotalcite. So far the research on hydrogen adsorption using these nanodiscs and hydrotalcite is limited. BN nanodiscs and hydrotalcite are selected because these nanomaterials are stable, non-reactive to hydrogen and have excellent strength.

## 1.3 OBJECTIVES

The objective of this study is to:

1. To characterize BN nanodiscs and nanocrystalline hydrotalcite.
2. To study the hydrogen uptake capacity of BN nanodiscs and nanocrystalline hydrotalcite using fixed bed column.

## 1.4 SCOPE OF STUDY

The scope of study is to recognize the field of research in the project as below:

1. Characterization of BN nanodiscs and nanocrystalline hydrotalcite will be done using Brunauer–Emmett–Teller (BET) and Scanning Electron Microscopy (SEM) to identify the structural properties of these nanomaterials.
2. Measurement of hydrogen uptake of BN nanodiscs and nanocrystalline hydrotalcite by setting the pressure ranging 1 to 5 bar at temperature of 25˚C using volumetric analysis method with a specially fabricated fixed bed reactor with a hydrogen gas analyzer.

# CHAPTER 2

## LITERATURE REVIEW

### 2.1 HYDROGEN STORAGE

The hydrogen can be used as a fuel (Schlapbach & Zuttel, 2001) directly in internal combustion engines or fuel cells could be employed to produce electricity and then power for drive train in automotive applications. In both cases, it is a cleaner and environmentally friendlier energy source. The hydrogen ($H_2$) reacts with oxygen ($O_2$) to form water ($H_2O$) and releases heat.

Liquid cylinders and high pressure tanks are the best examples on the traditional storage approach. However, at ambient condition 1 kg of hydrogen gas occupies a volume of $11m^3$. This simply means that the hydrogen storage denotes the reduction of vast volume of hydrogen gas. Work must be applied to compress the gas or the temperature must be decreased to below the critical temperature in order to increase hydrogen density. Up to 40% of its energy content lost due to liquefaction as liquid which imposes severe energy costs (Crabtree, Dresselhaus, & Buchanan, 2004). Apart from that, it is highly impractical and unsafe to use high pressure tanks for mobile applications. It is also rather challenging for transportation use as to ensure that it is sufficient to drive distance comparable to gasoline-powered cars (Crabtree et al., 2004).

An alternative approach is to bind hydrogen to other materials to avoid unsafe high pressure conditions. Hydrogen storage can be achieved by chemisorption or physisorption. Physisorption-based methods are commercially the better fit as it offers on board hydrogen refueling, provided that new materials with high reversibility of uptake and release of hydrogen are realized. A way to increase the hydrogen storage capacity of a material without affecting the recharging ability of the system is to increase the surface area per volume (Özdoğan & Berber, 2009). The 2015 goal of the U.S. Department of Energy (DOE) is a capacity of >5.5 wt.% at ambient temperature and pressure ("Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles," 2009). Apart from large surface area, the use of nanomaterial adsorption is recommended because it can be uses in higher than critical temperature with low pressure condition hence it is much safer.

## 2.2 BORON NITRIDE AND HYDROTALCITE FOR HYDROGEN STORAGE

Boron nitride is a chemical compound with chemical formula BN. It is produced synthetically from boric acid or boron trioxide and nitrogen. Because of excellent thermal and chemical stability, boron nitride ceramics are traditionally used as parts of high-temperature equipment. Boron nitride has potential use in nanotechnology.

As an important potential application for nanomaterials, the hydrogen storage of BN was intensively studied by theoretical calculations. Several reaches conducted using BN with different structures such as nanopowder, nanosheets and nanotubes had also been done. However, the results obtained were varied greatly due to different models and calculation methods adopted. Some reports claimed that both physisorption and chemsorption are not energetically favoured and conclude that BNNTs are not good candidates for hydrogen storage (Zhou et al., 2006).

The other reports stated that hydrogen storage capacity of BNNT ranges is obviously much better than for CNT and can reach or even exceed the commercial standard presented by the US Department of Energy (Mpourmpakis & Froudakis, 2007). This is because the dipolar nature of B-N bonds in BNNT leads to stronger adsorption of hydrogen.

Nanocrystalline hydrotalcite have gained considerable attention in being designed as to store hydrogen due to their wide variety of chemical compositions. Not only that, their textural and surface morphology that can be tuned. Hydrotalcite is basically is layered double hydroxide.

Hydrotalcite can be designed in such a way that it has high surface area and favourable pore volume that can adsorb hydrogen efficiently in so many ways. However, the study using hydrotalcite in current literature is limited.

Most works are on the theoretical, modelling and synthetic studies, while experiments on chemistry and applications are rather few due to difficulties in acquiring high-quality massive samples suitable for these kinds of researches (Özdoğan & Berber, 2009).

## 2.3 EXPERIMENTS ON HYDROGEN ADSORPTION

Hydrogen is an ideal material as an alternative source. However, hydrogen can be hardly be utilized as it is lack of appropriate storage materials. High pressure tanks, liquid hydrogen and metal hydrides had been tested as possible storage materials (Jhi, 2006), however they also have a number of hindrances such as low capacity, safety problem and impractical release temperature. Recently, the hydrogen storage development shifted its focus to nanostructured materials with physisorption as they have large surface area and potentially high binding energy. A summary on past experiments on hydrogen adsorption is listed at appendices.

Recent experimental studies addressed the metal doping of nanostructured materials such as graphene, fullerene, nanofibers and CNT. Graphene doped with Ni (0.14 wt.%) and B (0.63 wt.%) has a hydrogen uptake of 2.81 wt.% at 77 K and 106 kPa, which is more than twice of that of pristine graphene (Y. Wang et al., 2011). Saha and Deng also found that hydrogen adsorbed are 0.85 wt.% on Pd/C60 and 0. 69 wt.% on Ru/C60, respectively, as compared with 0.3 wt.% on the pure C60 fullerene measured at 300 bar and 298 K (Saha & Deng, 2011).

Hydrogen can also be stored in nanostructures. Tibbetts et al. (Tibbetts, Meisner, & Olk, 2001) reported a 1 wt.% capacity of carbon nanostructures and high temperature and pressure were reported as ineffective efforts. As an alternative, boron nitride nanostructures can be considered for such application. Wang et al. published a comparison of carbon and boron nitride structures in terms of hydrogen storage capacities and reported that 2.6 wt.% $H_2$ could be adsorbed in an h-BN structure while nanostructured graphite could store up to 7.4 wt.% $H_2$, both after 80 h milling process (P. Wang, Orimo, Matsushima, Fujii, & Majer, 2002).

Similar to carbon nanotubes, BN nanotubes are also observed as possible hydrogen storage media. In the pioneering experiment by Ma et al. (Ma et al., 2002) a 1.8 wt.% hydrogen uptake was recorded for BNNTs at 10 MPa while the bamboo-structured BN fibers had a 2.6 wt.% hydrogen uptake. This is a remarkable increase compared to a value of 0.2 wt.% for a commercial powder. Chemical absorption was proposed to be the main absorption mechanism.

Oku et al. (Oku, Kuno, Kitahara, & Narita, 2001) focused on BN fullerene materials and proposed that BN fullerene would be a good candidate for hydrogen storage applications as it has better heat resitance. Then they also calculated the hydrogen storage capacities of BN fullerenes and concluded that BN stored $H_2$ easier than carbon fullerenes (Oku & Kuno, 2003; Oku & Narita, 2002).

Tang et al. (C. C. Tang, Y. Bando, X. X. Ding, S. R. Qi, & D. Golberg, 2002) synthesized BNNTs with collapsed structures. The collapsed structured BNNTs had a specific area up to 789 $m^2/g$ compared with conventional values for BNNTs of 254 $m^2/g$. These collapsed BNNTs were reported to possess 4.2 wt.% hydrogen absorption ability at 10 MPa. The collapsed structures of BNNT effectively increase the hydrogen adsorption capacity due to the high specific surface area.

Instead of a gravimetric method adopted in the mentioned experiments, Chen et al. (Chen et al., 2005) used an electrochemical measurement to test hydrogen accumulation in BNNTs and resulted only 0.25 wt.% of hydrogen absorption. However, BNNTs are still supposed to possess a higher chemical activity than a conventional BN powder. The rather uncertain data is thought to be due to a normal atmosphere of 0.1 MPa used in the latter experiments.

From the thermogravimetric analysis shown at Figure 2, Saner Okan et al observed that 80% residual mass BNNTs were still available at 1000°C. On the other hand, commercial CNT showed thermal stability up to 550°C and then started to lose weight and completely decomposed at 875°C. Therefore, BNNTs showed greater thermal stability at higher temperatures (Saner Okan et al., 2012).

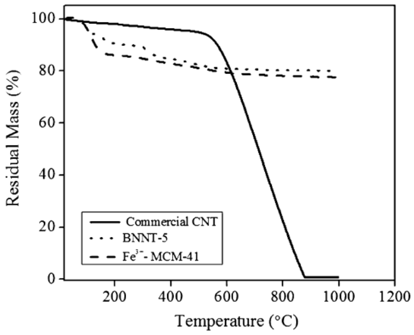


*Figure 1: TGA curves of CNTs, Fe3+-MCM-41 and BNNT-5 (Saner Okan et al, 2012)*

Figure 3 shows the hydrogen uptake capacity of 0.85 wt.% of the synthesized BNNTs was compared with commercial CNTs having hydrogen uptake capacity as 0.42 wt.%. These differences in hydrogen uptake values stemmed from the dipolar nature of B−N bonds in BNNT which lead to stronger adsorption of hydrogen (Reddy, Arava, E., & Walker, 2010). Moreover, the variety of CNTs in diameter and helicity results in the change of their electronic properties which affect hydrogen storage capacity. In contrast, the electronic properties of BNNTs are independent of helicity, diameter, and number of walls (Blase, Rubio, Louie, & Cohen, 1994). Therefore, BNNTs can be a good candidate for hydrogen storage applications at room temperature.

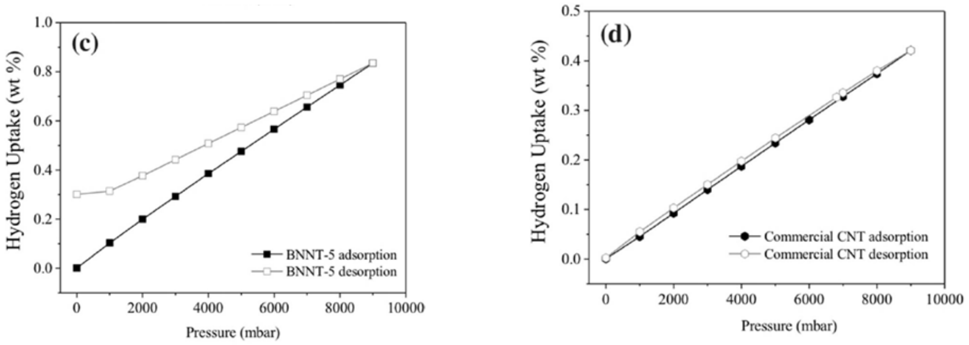


*Figure 2: Hydrogen adsorption and desorption isotherms of (c) BNNT-5 and (d) commercial CNTs (Saner Okan et al, 2012)*

(Baierle, Piquini, Schmidt, & Fazzio, 2006) stated that different from the adsorption of atomic hydrogen, the adsorption of the $H_2$ molecule is a physisorption process. A physisorbed molecule can spontaneously leave the surface after a certain time. Physisorption is therefore observed mostly at low temperatures. Another experiment (Ma et al., 2002) shows that higher storage pressure enable higher capacity of hydrogen uptake as shown in Figure 4.

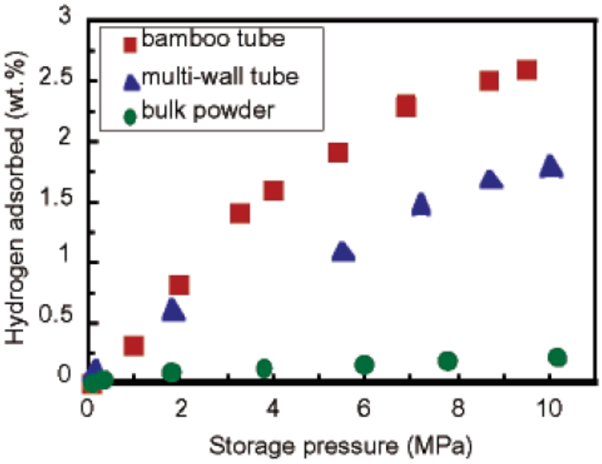
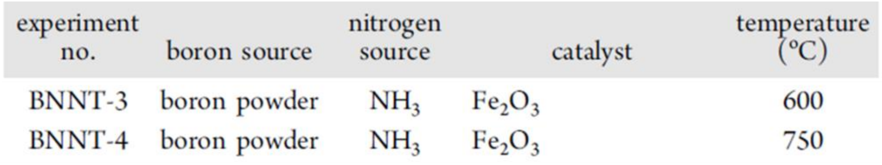


*Figure 3: Hydrogen adsorbed (wt%) vs Storage pressure (Mpa) (Ma et al, 2002)*

It is states that after the samples were returned to ambient pressure, about 70 wt% of the adsorbed hydrogen was found to be retained, suggesting the majority of the hydrogen is chemisorbed. The significantly slow equilibration time at each pressure (4 hours) also indicates that the adsorption may be mainly a chemical interaction. The retained amount of hydrogen was released completely by subsequently heating the sample to 573 K. After the complete desorption, the hydrogen uptake capacity remained almost unchanged in the following cycle, indicating the high reversibility of the adsorption desorption processes.

Characterization is also important to show how the different structure, pore size and surface area of nanomaterials could results in different hydrogen uptake. In an experiment by (Saner Okan et al., 2012), two different kinds of BNNTs which were synthesized at different reaction temperatures have different kind of structure. The SEM images in Figure 5 shows that as the reaction temperature increases, the diameter of BN fibrils increases while the length of BN fibrils decrease; which results in a denser structure. The BNNTs with denser structure shows the less capability of hydrogen uptake.



| experiment no. | boron source | nitrogen source | catalyst | temperature (°C) |
|---|---|---|---|---|
| BNNT-3 | boron powder | $NH_3$ | $Fe_2O_3$ | 600 |
| BNNT-4 | boron powder | $NH_3$ | $Fe_2O_3$ | 750 |

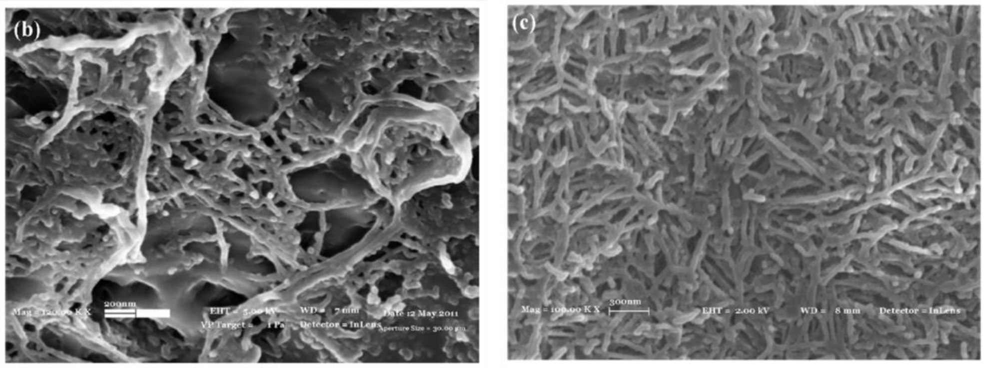


*Figure 4: Results of (b) BNNT-3 and(c) BNNT-4 (Saner Okan et al, 2012)*

The experimental studies on BNNTs’ hydrogen storage are limited and similar to theoretical works, the results are inconsistent. However, a confirming conclusion can be made, as from the studies it can be said that the defects, doping and deformation of

BNNTs may remarkably improve their ability to adsorb hydrogen (Han, Kang, Lee, van Duin, & Goddard, 2005).

A compilation of several literature studies can be found at Appendices. The literature table comprises of researches conducted on hydrogen adsorption study using other nanomaterials.

This study is focusing on how different nanostructured materials will give different hydrogen uptake. However, as the project focused on the study for hydrogen adsorption using BN nanodiscs and nancrystalline hydrotalcite as the research using these nanomaterials are limited. These nanomaterials also have potential for hydrogen adsorption as they are non-reactive to hydrogen and have thermal stability.

# CHAPTER 3

## METHODOLOGY/PROJECT WORK

## 3.1 PROJECT FLOW CHART

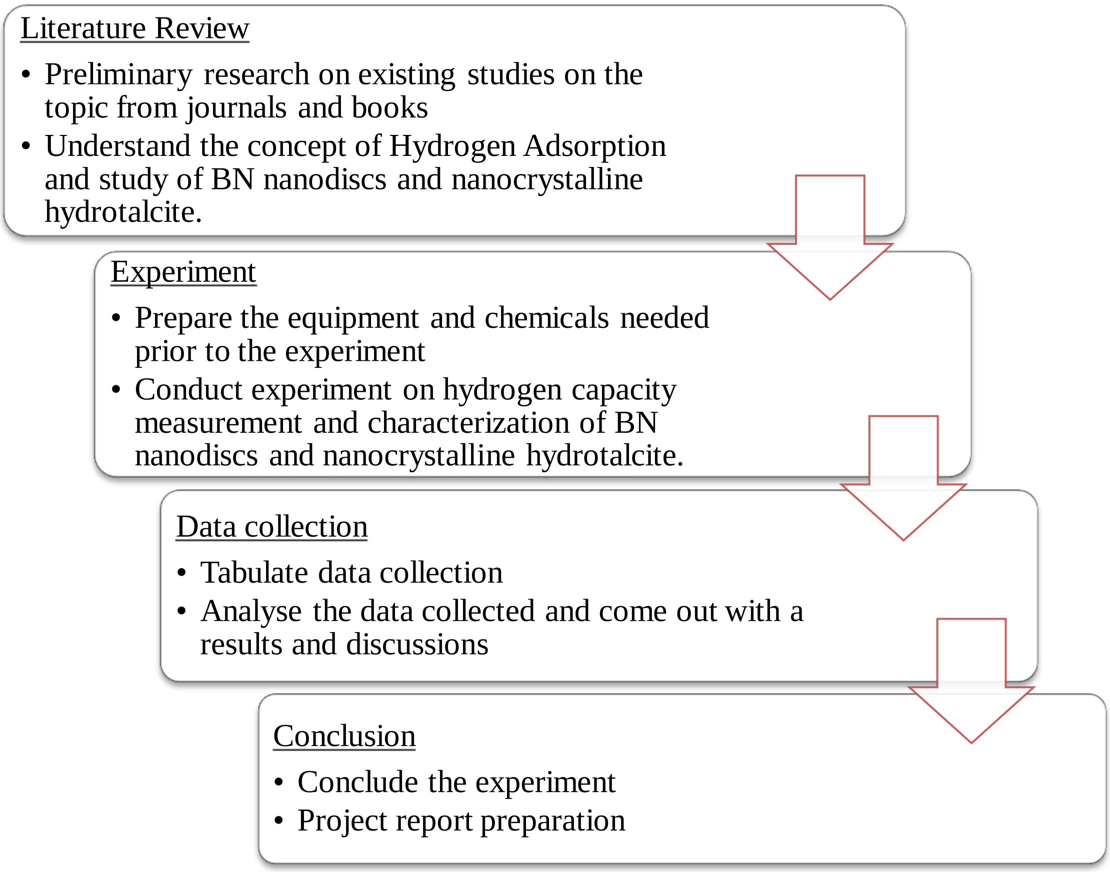


*Figure 5: Project flow chart*

## 3.2 PREPARATION FOR THE EXPERIMENT

### 3.2.1 Materials and Apparatus

*Table 1: Materials and apparatus list*

| | Materials/Apparatus | Unit |
|---|---|---|
| 1 | Boron nitride nanodiscs | 50 grams |
| 2 | Nanocrystalline hydrotalcite | 25 grams |
| 3 | H2 cylinder gas (H2 10%, N2 90%) | 1 |
| 4 | Pure N2 cylinder gas | 1 |
| 5 | Beakers | 5 |
| 6 | Vials | 20 |
| 7 | Temperature thermocouple | 1 |
| 8 | Weigh balance | 1 |

### 3.2.4 Proposed Experiment Procedure

The experiment set up was assembled as shown in Figure 7 (Salam, Sufian, Lwin, & Murugesan, 2013). The procedure for hydrogen adsorption using BN nanodiscs and nanocrystalline hydrotalcite are:

1. A sample of adsorbant is to be sent for characterization using BET and SEM.

2. For hydrogen capacity measurement, the full experimental setup is as shown in Figure 7.

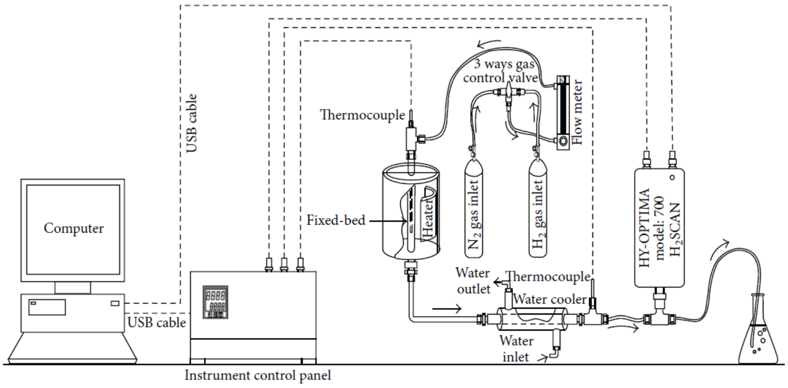


*Figure 6: Diagram of the full fixed bed setup (Salam et al, 2013)*

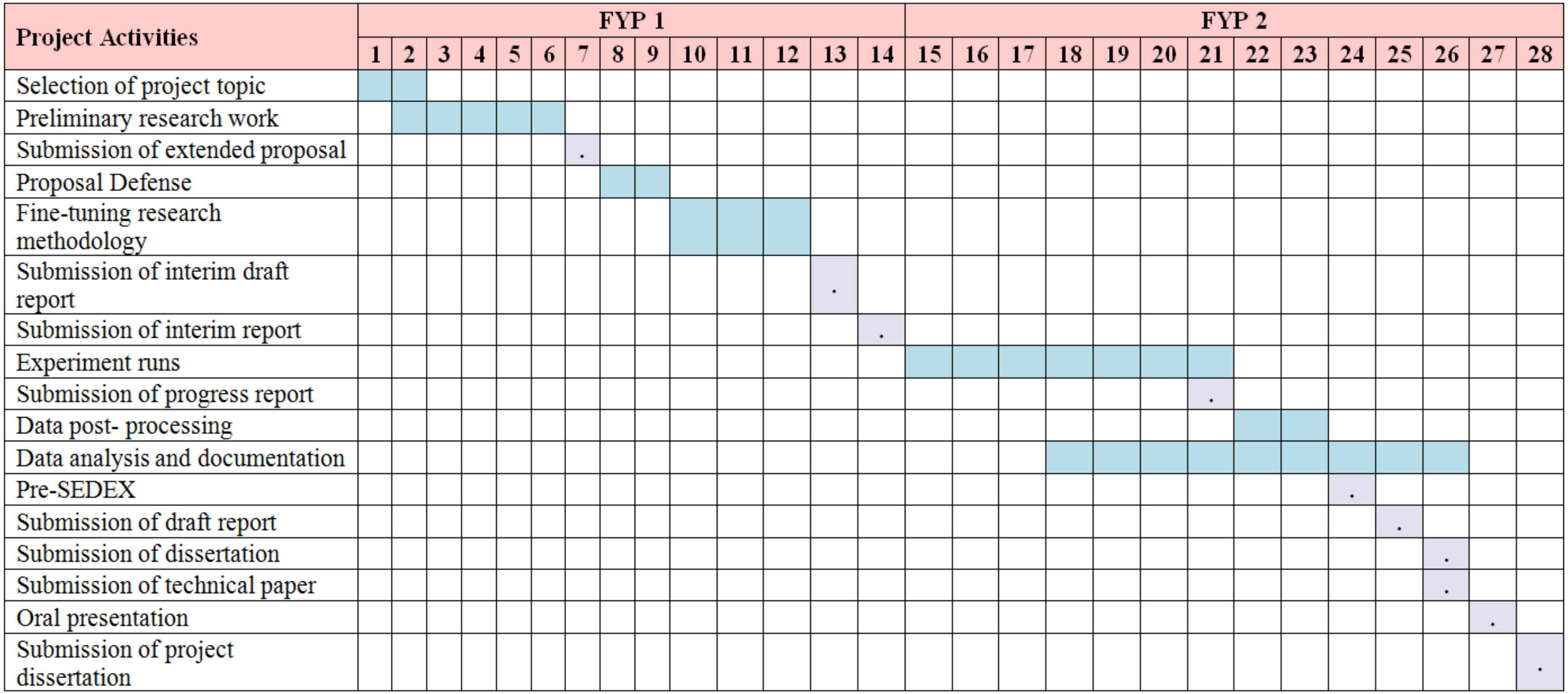
   The system first calibrated without including adsorbent into the bed. Next, purified nitrogen was used to evacuate any remaining gas in the bed. The bed was then kept until it reaches room temperature. The adsorbent was then placed on the bed. After that, the required amount of hydrogen gas and nitrogen gas was exposed to fixed bed to conduct hydrogen adsorption on the adsorbent. The data acquisition of the gas concentration was then measured via RS232 converter using a hyperterminal of the Windows XP programme.

3. The data collected was tabulated and analysed.

4. A comparison study of results with relevant literature reviews was done for discussion and conclusion.

## 3.4 GANTT CHART

*Table 2: Gantt Chart*



| Project Activities | FYP 1 | | | | | | | | | | | | | | FYP 2 | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 |
| Selection of project topic | 🟦 | 🟦 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Preliminary research work | | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | | | | | | | | | | | | | | | | | | | | | | |
| Submission of extended proposal | | | | | | | . | | | | | | | | | | | | | | | | | | | | | |
| Proposal Defense | | | | | | | | 🟦 | 🟦 | | | | | | | | | | | | | | | | | | | |
| Fine-tuning research methodology | | | | | | | | | | 🟦 | 🟦 | 🟦 | | | | | | | | | | | | | | | | |
| Submission of interim draft report | | | | | | | | | | | | | . | | | | | | | | | | | | | | | |
| Submission of interim report | | | | | | | | | | | | | | . | | | | | | | | | | | | | | |
| Experiment runs | | | | | | | | | | | | | | | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | | | | | | | |
| Submission of progress report | | | | | | | | | | | | | | | | | | | | | . | | | | | | | |
| Data post- processing | | | | | | | | | | | | | | | | | | | | | | 🟦 | 🟦 | | | | | |
| Data analysis and documentation | | | | | | | | | | | | | | | | | | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | | |
| Pre-SEDEX | | | | | | | | | | | | | | | | | | | | | | | | . | | | | |
| Submission of draft report | | | | | | | | | | | | | | | | | | | | | | | | | . | | | |
| Submission of dissertation | | | | | | | | | | | | | | | | | | | | | | | | | | . | | |
| Submission of technical paper | | | | | | | | | | | | | | | | | | | | | | | | | | . | | |
| Oral presentation | | | | | | | | | | | | | | | | | | | | | | | | | | | . | |
| Submission of project dissertation | | | | | | | | | | | | | | | | | | | | | | | | | | | | . |

# CHAPTER 4

## RESULTS AND DISCUSSION

## 4.1 CHARACTERIZATION OF BORON NITRIDE

### 4.1.1 Brunauer–Emmett–Teller (BET)

BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser.

***Table 3: BET result for Boron Nitride nanodiscs and hydrotalcite***

| Sample | BET Surface Area ($m^2/g$) | Pore Volume ($cm^3/g$) | Pore Size (Å) |
|---|---|---|---|
| Boron Nitride nanodiscs | 10.3343 | 0.052028 | 201.3796 |
| Hydrotalcite | 124 | 2.72 | 160 |
| BN powder (Wank, George, & Weimer, 2004) | 15-20 | N/A | N/A |
| BN powder (Wank, George, & Weimer, 2001) | 0.5-40 | N/A | N/A |
| Hydrotalcite, MCAM 031 (Salam et. al, 2013) | 321 | N/A | 140 |

Table 3 shows the BET surface area, pore volume and also pore size for both hydrotalcite and BN nanodiscs. The BET surface area of BN nanodiscs is 10.3 $m^2/g$ which is comparable to (Wank, George, & Weimer, 2004) with the surface area of 20 $m^2/g$. However, other research had found that their BN has higher surface area which is 0.5-40 $m^2/g$ (Wank, George, & Weimer, 2001).

As for hydrotalcite, the surface area is found to be 124 m²/g. This is comparable with (Salam et al., 2013) which the surface area of 165 m²/g and adsorbs 1.3wt% of hydrogen.

The significant of having larger surface area is that the hydrogen uptake will be higher. Hence, it will be more favourable to have larger surface area. It can be also expected that hydrogen can diffuse into the nanomaterials if the pore size is sufficiently larger than the size of hydrogen molecule.

### 4.1.2 Field – Emission Scanning Electron Microscope (FESEM)

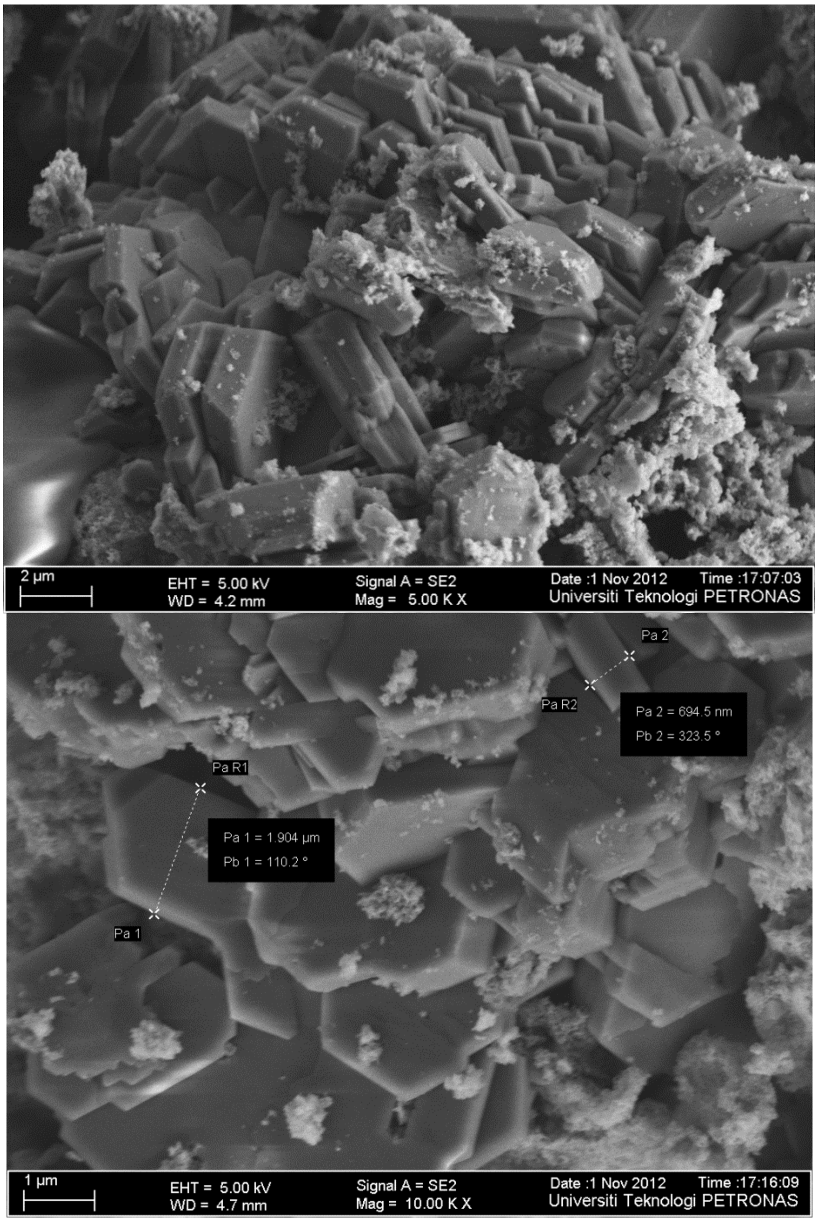


*Figure 7: FESEM of hydrotalcite*

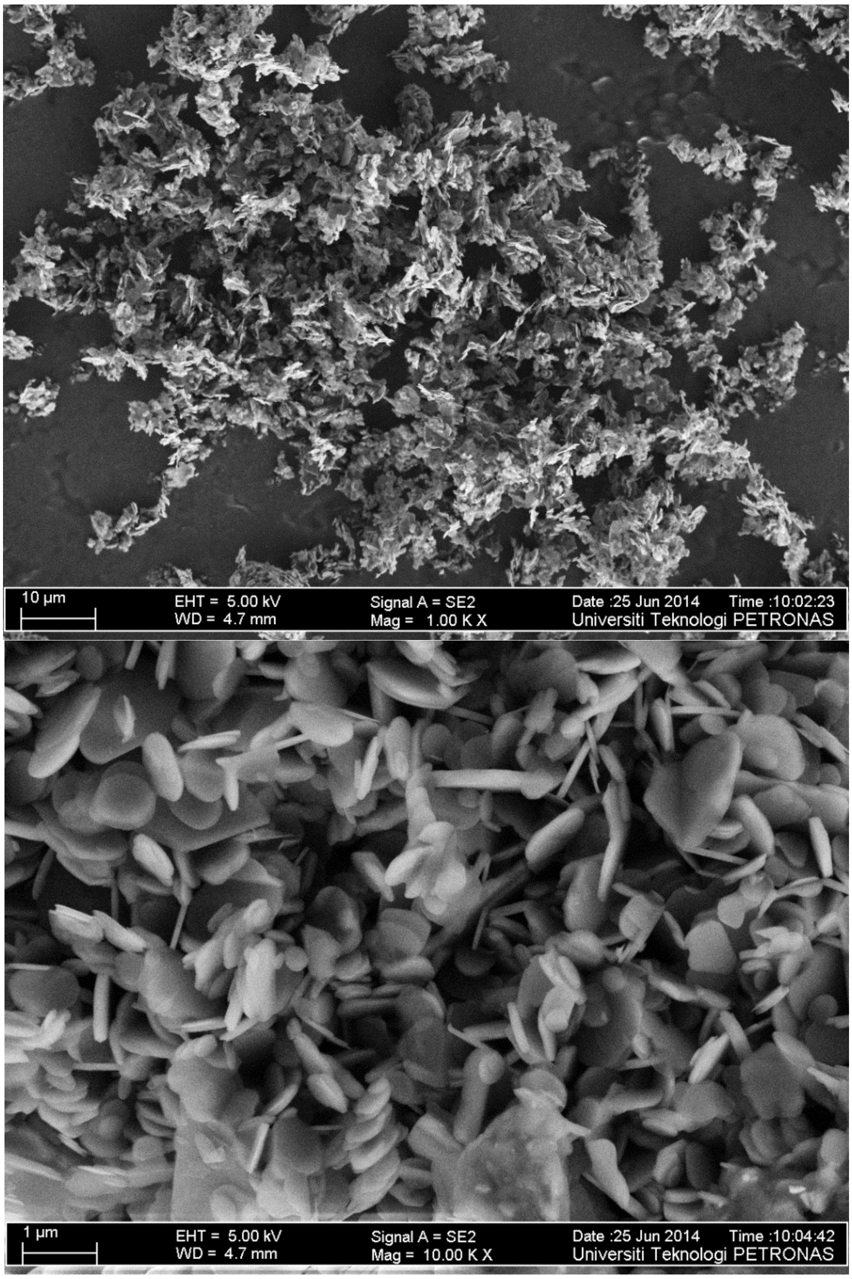


***Figure 8: FESEM of Boron Nitride nanodiscs***

The SEM image in Figure 8 shows that the hydrotalcite have hexagonal shapes while Figure 9 portrays the surface morphology of Boron Nitride nanodiscs shows a disc-like structure of BN nanodiscs.

The hexagonal shape of hydrotalcite enable the adsorption of $H_2$ molecule suggests that the structure allow nearest neighbour interactions hence gave better adsorption. The disc structure of BN nanodiscs with negligible pores results in a denser structure hence the less capability of hydrogen uptake.

## 4.2 HYDROGEN ADSORPTION STUDY

The hydrogen adsorption studies are currently done using hydrotalcite and Boron Nitride nanodiscs with the flow of 5% Hydrogen gas (balance: Nitrogen gas). After the hydrogen adsorption study is conducted, all the data are formed to breakthrough curve graphs. The pink region area on upper side of the breakthrough curve graph as shown in Figure 9 is the adsorbed amount of hydrogen.

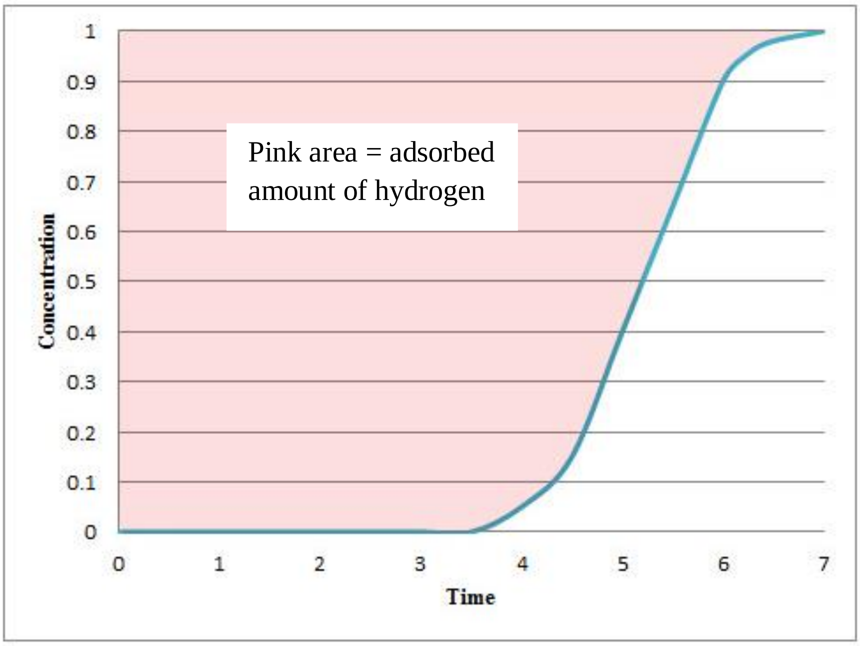


*Figure 9: Typical breakthrough curve of gas adsorption*

With the breakthrough curve, the capacity of the reactor for hydrogen adsorption can be calculated by using the following equation (Rodrigues, de Moraes Jr, da Nóbrega, & Barboza, 2007):

$$M_{ads} = \frac{Q_T(MW)}{(\frac{RT}{P_A})}\left[\Delta t - \int_0^t \left(\frac{y}{y_0}\right) dt\right], \tag{1}$$

$$W = \frac{M_{ads}}{M_{bed}}, \tag{2}$$

where *t* is the total adsorption time, y and $y_0$ are the initial concentrations respectively, $M_{ads}$ is the adsorbed mass, $Q_T$ is the gas flow, $P_A$ is the partial pressure of inlet $H_2$ gas, W is the adsorbed amount while $M_{bed}$ is the mass of bed.

Figure 10 shows the $H_2$ breakthrough curve using MCAM 211e and BN nanodiscs.

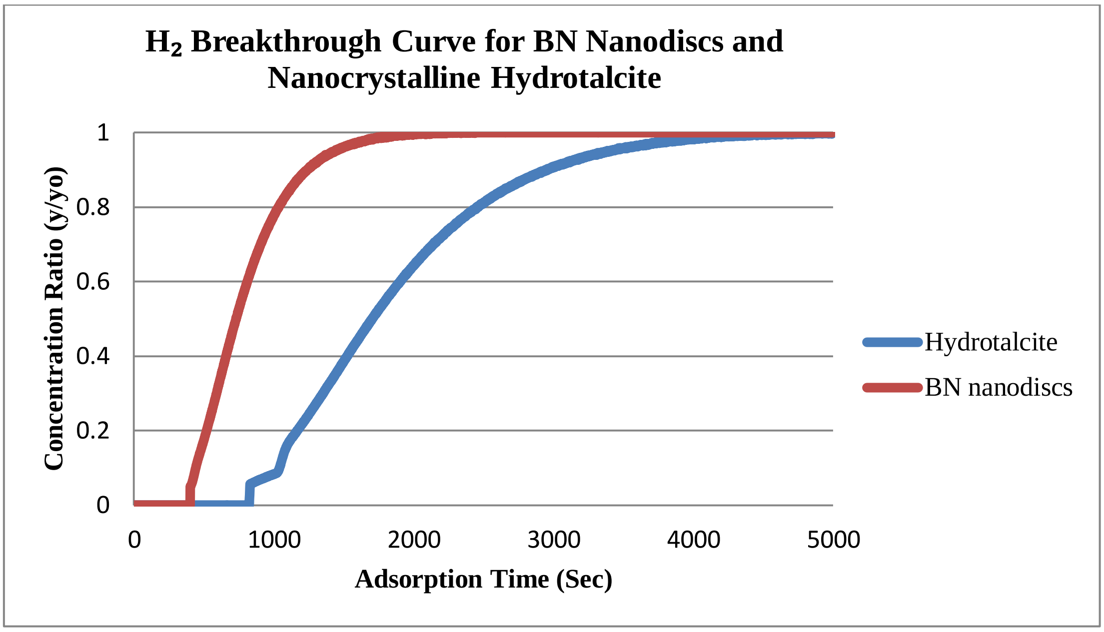


*Figure 10: $H_2$ Breakthrough using Boron Nitride nanodiscs and MCAM 211.*

Using the equations earlier, the amounts of hydrogen adsorbed are as follows:

*Table 4: Adsorption result*

| **Sample** | **Adsorbed mass, $M_{ads}$ (mg)** | **Hydrogen adsorption (wt%)** |
|---|---|---|
| MCAM 211 | 13.00 | 1.30 |
| Boron Nitride nanodiscs | 2.72 | 0.27 |

From this table, it can be observed that hydrotalcite is able to uptake more hydrogen than the BN nanodiscs. One of the explanation is that hydrotalcite has larger surface area, which is 124 $m^2/g$ (Salam et al., 2013) while the Boron Nitride nanodiscs is only 10.33 $m^2/g$. Larger surface area thus favour more hydrogen uptake.

In the research done by (Saner Okan et al, 2012), the FESEM image of BNNT is as shown in Figure 11. As to compare with the FESEM image of BN nanodiscs, the BN nanotubes have a lot of pores, smaller diameter and longer fibrils which means it is more porous, with larger surface area of 122 $m^3/g$. Therefore, it enables the nanotubes to adsorb more hydrogen than BN nanodiscs which is 0.84wt%.

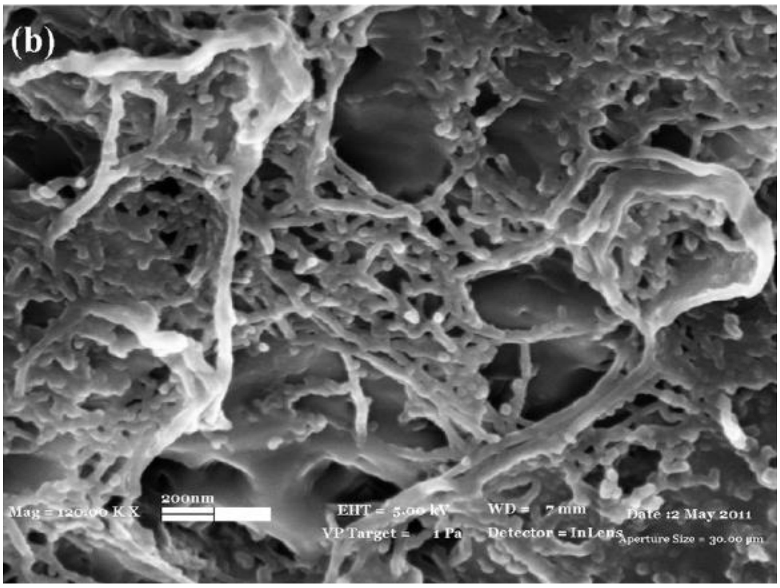


*Figure 11: BN nanotubes (Saner Okan et al, 2012)*

As for hydrotalcite, the disc-shape is then compared with the hydrotalcite from (Salam et al, 2013). Both of these hydrotalcite are composed of magnesium, cobalt and aluminium. However, the synthesized hydrotalcites produced have different structure. While hydrotalcite from this project is hexagonal-shaped, Salam et. al. (2013) hydrotalcite is comprised of coral-like structure with slit-shape pores. It also has higher surface area which is 321 $m^2/g$ and thus enables the hydrogen uptake up to 3wt%. The neighbour interactions between the slit-shape pores allow the nanomaterials to have better hydrogen uptake.

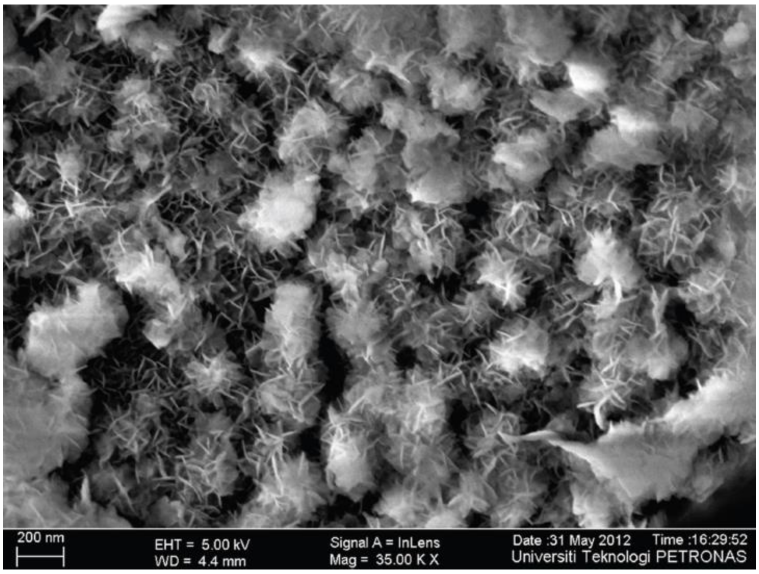


*Figure 12: Hydrotalcite (Salam et al, 2013)*

It is likely that the binding energy is sensitive to the contact area of hydrogen with the nanomaterials. When the contact area is larger, it simply put that the overlap of electron charge distribution between hydrogen and the atoms at the pores is improved which causes in bigger exchange-correlation energies and consequently in larger binding energies (Y. Zhao, Kim, Dillon, Heben, & Zhang, 2005).

Apart from that pore volume also effect on how much hydrogen can adsorb. The higher pore volume would allow the nanomaterial to support more hydrogen. This is also proven as the hydrotalcite has higher pore volume (2.72 $cm^3/g$) than BN nanodiscs (0.052028 $cm^3/g$).

The van der Waals forces which set the distance of the atoms contact number with the hydrogen are different at different pores size. When the pore sizes increases, the binding energy also decreases as resulted from decreased binding distance (Ye et al., 1999). This explains on why the hydrotalcite with smaller pores size can uptake more hydrogen than BN nanodiscs. As the specific surface area increases, the hydrogen uptake capacity increases. The higher hydrogen storage of hydrotalcite can be attributed to its nanomorphology.

# CHAPTER 5

## CONCLUSION AND RECOMMENDATION

From the experiment, it is found that different nanostructured materials will result different BET surface area. Due to that, the hydrogen uptake of hydrotalcite which has higher BET surface area is higher (1.3 wt%) as compared with BN nanodiscs (0.27 wt%). However, both results has yet to meet the DOE target which is 5 wt%.

The search for the right material that can adsorb such amount of hydrogen need to be carried out before we can utilize the use of hydrogen as the future fuel. Nevertheless, from the literature, changing the chemistry or structure of chosen materials has been tested to develop storage systems to meet the target. Hence, researchers have to work on the following important points:

1. To study more efficient type of nanostructured materials.
2. To vary the adsorption conditions such as using lower temperature and higher pressure on the experiment to improve hydrogen uptake.
3. To run the adsorption experiment using different measurement such as gravimetric measurement.

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# APPENDICES

i) Literature review table

<table>
<tr><th>No.</th><th>Year</th><th>Author</th><th>Title</th><th>Materials for $H_2$ adsorption</th><th>Conditions</th><th>$H_2$ capacity (wt.%)</th><th>Method used</th><th>Conclusion/ Remark</th></tr>
<tr><td>1</td><td>2011</td><td>(Giraudet & Zhu, 2011)</td><td>Hydrogen adsorption in nitrogen enriched ordered mesoporous carbon doped with nickel nanoparticles</td><td>1. CMK3<br>2. Ni-CMK3<br>3. CMK3-$NH_3$<br>4. Ni-CMK3-$NH_3$<br>5. CN<br>6. Ni-CN</td><td>P= 3MPa<br>$T_1$= -196.15˚C<br>$T_2$= 24.5˚C<br>$T_3$= 99.85˚C</td><td><table>
<tr><th>Mat</th><th>$T_1$</th><th>$T_2$</th><th>$T_3$</th></tr>
<tr><td>1</td><td>2.3</td><td>0.12</td><td>0.04</td></tr>
<tr><td>2</td><td>2.1</td><td>0.20</td><td>0.13</td></tr>
<tr><td>3</td><td>2.8</td><td>0.22</td><td>0.12</td></tr>
<tr><td>4</td><td>2.3</td><td>0.26</td><td>0.14</td></tr>
<tr><td>5</td><td>0.9</td><td>0.04</td><td>0.07</td></tr>
<tr><td>6</td><td>0.9</td><td>0.04</td><td>0.50</td></tr>
</table></td><td>Instrument: PCT-Win45D-Win<br>Volumetric method</td><td>@-196.15 ˚C<br>$H_2$ adsorbed decreases when there are incorporation of Ni<br>@24.85˚C and above,<br>$H_2$ adsorbed in doped carbon than pristine</td></tr>
<tr><td>2</td><td>2012</td><td>(Saner Okan et al., 2012)</td><td>Effect of reaction temperature and catalyst type on the formation of BNNTs by chemical vapour deposition and measurement of their hydrogen storage capacity</td><td>BNNTs at different reaction conditions:<br>1. BNNT-3<br>Catalyst: $Fe_2O_3$<br>Rxn T: 600˚C<br>2. BNNT-4<br>Catalyst: $Fe_2O_3$<br>Rxn T: 750˚C<br>3. BNNT-5<br>Catalyst: $Fe^{3+}$-MCM-</td><td>T= 25˚C<br>P= 100-900 kPa</td><td>1. BNNT-3<br>0.87<br>2. BNNT-4<br>0.75<br>3. BNNT-5<br>0.85<br>4. CNT<br>0.42</td><td>Intelligent Gravimetric Analyzer (IGA)<br>-Vacuum-pressure reactor</td><td>The dipolar nature of B-N bonds in BNNT lead to stronger adsorption of hydrogren</td></tr>
</table>

<table>
<tr><td></td><td></td><td></td><td></td><td>41/$Fe_2O_3$<br>Rxn T: 750˚C<br>4. CNT</td><td></td><td></td><td></td><td></td></tr>
<tr><td>3</td><td>2011</td><td>(Kim & Park, 2011)</td><td>Optimization of the pore structure of nickel/graphite hybrid materials for hydrogen storage</td><td>Ni/Porous Graphite<br>1. 8:2/Ni-0.02<br>2. 8:2/Ni-0.05<br>3. 8:2/Ni-0.10</td><td>T= 25˚C<br>P= 10 MPa</td><td>1. 8:2/Ni-0.02 3.5<br>2. 8:2/Ni-0.05 4.48<br>3. 8:2/Ni-0.10 3.7</td><td>BEL-HP device. Volumetric method.</td><td>Too many metal particles doped onto the Ni sample surfaces; causing severe blocking, resulting in a decrease of the $H_2$ contact probability</td></tr>
<tr><td>4</td><td>2011</td><td>(W. Zhao et al., 2011)</td><td>Optimization of activated carbons for hydrogen storage</td><td>Activated carbon</td><td>T= 25˚C<br>P= 5 MPa</td><td>6.6</td><td>Gravimetric Analyzer</td><td></td></tr>
<tr><td>5</td><td>2011</td><td>(Chien & Chuang, 2011)</td><td>Static and dynamic hydrogen adsorption on Pt/AC and MOF-5</td><td>1. Activated carbon (AC)<br>2. Platinum/AC<br>3. Metal organic frameworks (MOF-5)<br>4. Pt/AC_MOF-5</td><td>Static and Dynamic<br>$T_1$= -196.15˚C<br>$T_2$= 24.85˚C<br>P= 5 MPa</td><td><table>
<tr><th colspan="3">Static</th></tr>
<tr><td>Mat</td><td>$T_1$</td><td>$T_2$</td></tr>
<tr><td>1</td><td>1.415</td><td>0.0127</td></tr>
<tr><td>2</td><td>1.369</td><td>0.0258</td></tr>
<tr><td>3</td><td>1.399</td><td>0.0055</td></tr>
<tr><td>4</td><td>1.395</td><td>0.0092</td></tr>
<tr><th colspan="3">Dynamic</th></tr>
<tr><td>1</td><td>0.781</td><td>0.117</td></tr>
<tr><td>2</td><td>1.134</td><td>0.187</td></tr>
<tr><td>3</td><td>0.771</td><td>0.071</td></tr>
<tr><td>4</td><td>0.796</td><td>0.071</td></tr>
</table></td><td>Static<br>Volumetric ASAP2020 Sorption Meter<br><br>Dynamic<br>Step switch, pulse injection, T-variable adsorption/desorption</td><td>Pt/AC exhibited a significantly higher $H_2$ for dynamic than static, suggesting:<br>1. The $H_2$ dissociative step at high temperature<br>2. The subsequent spillover step</td></tr>
</table>

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 6 | 2012 | (Aboutalebi, Aminorroaya-Yamini, Nevirkovets, Konstantinov, & Liu, 2012) | Enhanced hydrogen storage in graphene oxide-MWCNTs composite at room temperature | 1. MWCNTs<br>2. GO<br>3. rGO-MWCNTs<br>4. GO-MWCNTs | T= 25˚C<br>P= 5 MPa | 1. MWCNTs<br>0.9<br>2. GO<br>1.4<br>3. rGO-MWCNTs<br>2.1<br>4. GO-MWCNTs<br>2.6 | | |
| 7 | 2012 | (Reyhani, Mortazavi, Mirershadi, Golikand, & Moshfegh, 2012) | $H_2$ adsorption mechanism in Mg modified multi-walled carbon nanotubes for hydrogen storage | 1. MWCNTs<br>2. Mg-doped MWCNTs | T= 30˚C<br>P= 0.13 Pa<br>*vacuum | 1. MWCNTs<br>1.4<br>2. Mg-doped MWCNTs<br>1.8 | Volumetric technique<br>100mg MWCNTs in quartz, de-gas 300˚C, introduce $H_2$ gas | |
| 8 | 2011 | (Y. Wang et al., 2011) | Hydrogen storage in Ni-B nanoalloy-doped 2D graphene | 1. Graphene<br>2. Ni-B graphene | T= -196.15˚C<br>P= 106 kPa<br>*high vacuum | 1. Graphene<br>1.35<br>2. Ni-B graphene<br>2.81 | Volumetric method<br>Using a pore and surface analyser (Quantachrome Adsoeb-1) | If too much doping;<br>-increases bulk density<br>-reduces porosity<br>-less surface area |
| 9 | 2011 | (Saha & Deng, 2011) | Hydrogen adsorption on Pd- and Ru-doped $C_{60}$ fullrene at an ambient | 1. Pd- $C_{60}$<br>2. Ru- $C_{60}$<br>3. Pristine $C_{60}$ | T= 25˚C<br>P= 30 MPa | 1. Pd- $C_{60}$ Pd<br>2.81<br>2. Ru- $C_{60}$<br>2.81<br>3. Pristine $C_{60}$<br>1.35 | Gravimetric method<br>Rubotherm magnetic suspension balance | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | temperature | | | | | |
| 10 | 2011 | (Huang et al., 2011) | Hydrogen storage in graphene decorated with Pd and Pt nano-particles using an electroless deposition technique | 1. Pristine graphene<br>2. Gr-Pt (2.2wt.%)<br>3. Gr-Pd (48.6wt.%) | T= 29.85˚C<br>P= 5.7 MPa | 1. Pristine graphene<br>0.067<br>2. Gr-Pt<br>0.15<br>3. Gr-Pd<br>0.156 | Volumetric method | |
| 11 | 2001 | (Tibbetts et al., 2001) | Hydrogen storage capacity of carbon nanotubes, filaments, and vapor-grown fibers | $La_{0.93}Ni_5$, $LaNi_5$ | T= 25˚C<br>P= 3.5MPa | $La_{0.93}Ni_5$, $LaNi_5$<br>1 | Using automatic gas reaction controller | |
| 12 | 2002 | (P. Wang et al., 2002) | Hydrogen in mechanically prepared nanostructured h-BN: a critical comparison with that in nanostructured graphite. | 1. h-BN<br>2. Graphite | | h-BN<br>2.6<br>Graphite<br>7.4 | Mechanical milling under hydrogen atmosphere | |
| 13 | 2002 | (Ma et al., 2002) | Hydrogen Uptake in | 1. BNNTs<br>2. Bamboo | T= 25˚C<br>P= 10Mpa | 1. BNNTs<br>1.8 | Gravimetric method | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Boron Nitride Nanotubes at Room Temperature | structured BN fibers | | 2. Bamboo structured BN fibers<br>2.6 | | |
| 14 | 2003 | (Oku & Kuno, 2003) | Synthesis, argon/hydrogen storage and magnetic properties of boron nitride nanotubes and nanocapsules. | BN nanomaterials produced from LaB6 and Pd/boron powder | T= 20–300 °C<br>P= NA | BN nanomaterials ~3 wt.%. | Hydrogen storage was measured by TG/DTA | |
| 15 | 2002 | (C. Tang, Y. Bando, X. Ding, S. Qi, & D. Golberg, 2002) | Catalyzed Collapse and Enhanced Hydrogen Storage of BN Nanotubes | Collapsed BNNTs | T= 25˚C<br>P= 10 Mpa | Collapsed BNNTs<br>4.2 | Gravimetric method | The collapsed surfaces of BN nanotubes effectively increase the hydrogen adsorption capacity due to the high specific surface area. |
| 16 | 2005 | (Chen et al., 2005) | Preparation and Electrochemical Hydrogen Storage of Boron Nitride Nanotubes | BNNTs | T= 25˚C<br>P= 101 kpa | BNNTs<br>0.25 | Using electrochemical method | The hydrogen desorption of nonelectrochemical recombination in cyclic voltammograms, which is |

<table>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>considered as the slow reaction at BN nanotubes, suggests the possible existence of strong chemisorption of hydrogen, and it may lead to the lower discharge capacity of BN nanotubes.</td></tr>
<tr><td>17</td><td>2010</td><td>(Reddy et al., 2010)</td><td>Synthesis and hydrogen storage properties of different types of boron nitride nanostructures</td><td>1. Flower-type BN<br>2. Straight-walled BNNTs<br>3. Bamboo-type BNNTs</td><td>T= 25˚C<br>P= 10 Mpa</td><td>Flower-type BN<br>1.5 wt%<br>Straight-walled BNNTs<br>2.7 wt%<br>Bamboo-type BNNTs 3.0 wt%</td><td>Using a high-pressure Seiverts' apparatus</td><td>The higher storage capacity of bamboo-type BNNTs is accredited to its higher surface area.</td></tr>
<tr><td>18</td><td>2012</td><td>(Salam et al., 2013)</td><td>Hydrogen Storage of a Fixed Bed of Nanocrystalline Mixed Oxides</td><td>Nanocrystalline hydrotalcite derived mixed oxides containing magnesium, cobalt, and aluminum (MCAM) $(\mathrm{M}_{(1-x)}\mathrm{Al}_x\mathrm{O}_{(1+x/2)}$</td><td>T= 25˚C<br>P= 200 kPa</td><td><table>
<tr><td></td><td colspan="2">Capacity (mg/g)</td></tr>
<tr><td>MCAM</td><td>Ads.</td><td>Des.</td></tr>
<tr><td>031</td><td>19.10</td><td>8.31</td></tr>
<tr><td>121</td><td>28.72</td><td>14.31</td></tr>
<tr><td>211</td><td>21.69</td><td>10.09</td></tr>
</table></td><td>Fabricated fixed bed reactor</td><td></td></tr>
</table>

<table>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td>301</td><td>9.25</td><td>5.34</td><td></td><td></td></tr>
<tr><td>19</td><td>2001</td><td>(Oku et al., 2001)</td><td>Formation, atomic structures and properties of boron nitride and carbon nanocage fullerene materials.</td><td colspan="5">The $H_2$ gas storage ability is only 1 wt.% because of the large atomic numbers of La and Ni. On the other hand, fullerene materials, which consist of light elements such as boron, carbon and nitrogen, would store more $H_2$ gas compared to the metal hydrides.</td><td colspan="2"></td></tr>
<tr><td>20</td><td>2002</td><td>(Oku & Narita, 2002)</td><td>Calculation of H2 gas storage for boron nitride and carbon nanotubes studied from the cluster calculation.</td><td colspan="5">As a result of comparison of DE; H2 molecules would enter into C60 from hexagonal rings easier than from pentagonal rings. Similarly, H2 molecules enter into B36N36 from hexagonal rings easier than from tetragonal rings. H2 molecule would pass from hexagonal rings of B36N36 easier than from hexagonal rings of C60. Since single-point energy is equal when H2 molecule is set at the center and outside the cage, energy for H2 discharge from fullerene-like materials is similar to that of H2 storage.</td><td colspan="2">Carbon fullerenes and boron nitride fullerenes are sublimed at 600˚C and 1000˚C, respectively.<br>Boron nitiride fullerenes would store $H_2$ molecules with smaller energy than carbon fullerenes, and would give good stability at high temperature.</td></tr>
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