CHAPTER 4

METHODOLOGY

4.1 Introduction

In this chapter methods of developing graphitic nanofibers and carbon nanotubes are detailed out. These include the catalyst preparation, the experimental setup for different types of process and the procedure to run each of the experiment. In addition the characterizations of the developed materials using different instrument are also described in this chapter. Apart from that, the operations of hydrogen adsorption measurement at the given conditions using the specific instrument of measurement are also highlighted. At the end of this chapter, the simulation of hydrogen adsorption isotherm data is explained.

4.2 Synthesis of graphitic nanofiber

Unlike CNT, graphitic nanofiber (GNF) was synthesized using the developed catalyst which was prepared using precipitation method (Haber, 1991). The synthesis of GNF was done using thermal CVD that was based on a heterogeneous process. The synthesis of GNF was divided into two parts. The first part was an initial approach in which the experiment was carried out using the existing equipment of CVD. The next part is where the modification and improvement of the CVD were accomplished to obtain better yield of GNF.

4.2.1 Catalyst preparation

Iron (III) oxide (Fe_2O_3) and nickel (II) oxide (NiO) catalysts development were optimized using Taguchi method. Three parameters such as the calcination temperature, calcination time and weight of salt at three levels of variations were arranged in matrix form according to L_9 as shown in Table 4.1.

Table 4.1 Parameters and levels used to synthesize Fe_2O_3 and NiO catalyst

Parameters	Levels		
	Low	Medium	High
Temperature (°C)	300	400	500
Calcinations time (hours)	2	4	6
Salt weight (g)	3	5	7

The calcinations temperature was chosen within the range of 300 and 500°C. The temperature was selected at 300°C because it was reported that the crystal structure starts to form at 250°C (Bumajdad et al., 2007). Typically, the higher the calcination temperature the better the crystallinity but this means that the crystal size would grow bigger due to sintering process (Barbosa et al., 2001). For example, at calcination temperature more than 700°C, the particles aggregate into very large nanoparticles (Echegoyen et al., 2007; Ermakova et al., 2000; Lee et al., 2007). Therefore, the given temperature range was sufficient to produce the catalysts.

Based from literature studies, most calcination processes were conducted between 4 to 6 hours (Barbosa et al., 2001; Cai et al., 2006; Jennings, 1987; Tanaka et al., 2004). If calcination time lower than 4 hours, the catalyst might not be fully developed whereas if the calcination time is more than 6 hours, the crystal size might grew bigger due to sintering process. In spite of this typical range, the study of calcination less than 4 hours was put on a test. Hence, a calcination time at 2 hours was selected to be one of the levels in the Taguchi orthogonal array to check the possibility to produce catalyst at lower calcination time. Apart from calcination temperature and time, the amount of salt precursors used could also affect the size of the catalyst produced. It is reported that the higher the concentration of the salt precursor the greater the crystal size of the catalyst (Xu et al., 2008). Therefore, for this purpose, the amounts of salt precursors between 3 to 7 g were chosen. The systematic parameter design of experiment for both Fe_2O_3 and NiO catalyst synthesis is given in Table 4.2.

Table 4.2 L_9 orthogonal array for synthesis of Fe_2O_3 and NiO catalyst

L_9	Temperature (°C)	Time (hour)	Weight of Salt (g)
1	300	2	3
2	300	4	5
3	300	6	7
4	400	2	5
5	400	4	7
6	400	6	3
7	500	2	7
8	500	4	3
9	500	6	5

There are several techniques in synthesizing the metal catalyst such as precipitation, deposition, encapsulation, selective removal, treatment of intermediate solids or precursors and activation of the precursor (Haber, 1991). Many researchers have discussed on the techniques employed, using different analytical grade reagents, at different conditions (Janzen et al., 1999; Ni et al., 2006; Raming et al., 2002; Sookman et al., 2006; Souza et al., 2007; Zheng et al., 2007; Zhong et al., 2007). Nevertheless, precipitation method was preferred in the catalyst synthesis (Hayakawa et al., 2006; Khedr et al., 2006; McCaldin et al., 2006) since it resulted in smaller crystallite size. Small crystallite size is required as it gives large surface area which is essential in CNT reaction as it allows more contact with reactant gas. Thus, precipitation method was applied for the synthesis of both catalysts.

Fe_2O_3 catalyst was prepared by dissolving a specific amount of iron (III) nitrate nonahydrate, $Fe(NO_3)_3.9H_2O$ (purity 99.99+%, CAS number 7782-61-8, manufactured by Fisher Scientific) into 100 cm^3 of distilled water. The solution was stirred at room temperature until all the transition metal salts had completely dissolved. Then the iron metals in the solution were precipitated in 2 M ammonia solution. The dark brown precipitate was filtered through a filter paper with 0.45 μm GHP (hydrophilic polypropylene) membrane and washed for several times with distilled water at room temperature until it became nitrate-free. Later, the precipitate of hydroxides was dried over night at a temperature of 80°C. Due to drying; the precursor was broken into small lumps which were then calcined at a specific temperature in the furnace oven at atmospheric pressure for a specific hour. After calcination, the developed Fe_2O_3 was ground into fine powder using mortar and pestle.

For the synthesis of nickel (II) oxide (NiO), 5 g of nickel nitrate hexahydrate, $Ni(NO_3)_2.6H_2O$ (purity 99.999%, CAS number 13478-00-7, and manufactured by Sigma Aldrich) was dissolved into 100 cm^3 of distilled water before it is mixed with 2 M of ammonia solution. However, unlike iron solution, the nickel salt solution was stirred at temperature of 250°C using magnetic stirrer until paste was formed. Later, the precursor which was in the form of thick green paste was dried overnight at temperature of 80°C. It was then calcined at a specific temperature for a specific time before it was ground into fine powder until no lumps were observed.

4.2.2 Chemical vapor deposition: Preliminary experiment

4.2.2.1 Optimization of CVD experimental procedure

For optimum results and systematic approach, Taguchi orthogonal array table was performed by choosing three control factors or parameters that could affect the formation of GNF. The parameters are reaction time, C_2H_4/H_2 flow rate and reaction temperature. Table 4.3 shows the parameters and three levels of each parameter used in the synthesis of GNF using Taguchi method. The reaction time parameter is at minimum of 2 hours which has been taken from the previous study at University of Nottingham (Bououdina et al., 2005; McCaldin et al., 2006) and at maximum of 4 hours. The temperature range is chosen because GNF starts to grow at temperature

500°C (McCaldin et al., 2006) since there is GNF deposition at 400°C (Koizumi et al., 2006). But the temperature range is at the maximum of 700°C because the higher the temperature, the greater the impurities (Lim et al., 2004) and the production cost would be higher.

Table 4.3 Parameters and levels used in synthesis of graphitic nanofibres

Parameters	Levels		
	Low	Medium	High
Reaction Time (hours)	2	3	4
C_2H_4/H_2 flow rate ratio (ml/min)[a]	10/90	20/80	30/70
C_2H_4/H_2 flow rate ratio (ml/min)[b]	90/10	80/20	70/30
Reaction Temperature (°C)	500	600	700

Note: [a] for Fe_2O_3 catalyst only,
[b] for NiO catalyst only

The *SNR* larger-is-better analysis was computed in which GNF reaction yield was selected as the output response. Similar with CNT analysis, the orthogonal array of L_9 type was used and is represented in Table 4.4.

Table 4.4 Parameter design for preliminary GNF synthesis using L_9 OA.

L_9	Reaction time (hours)	C_2H_4/H_2 flow rate (ml/min)[a]	C_2H_4/H_2 flow rate (ml/min)[b]	Reaction Temperature (°C)	Sample Name	
					Fe_2O_3	NiO
1	2	10/90	90/10	500	1FG	1NG
2	2	20/80	80/20	600	2FG	2NG
3	2	30/70	70/30	700	3FG	3NG
4	3	10/90	90/10	600	4FG	4NG
5	3	20/80	80/20	700	5FG	5NG
6	3	30/70	70/30	500	6FG	6NG
7	4	10/90	90/10	700	7FG	7NG
8	4	20/80	80/20	500	8FG	8NG
9	4	30/70	70/30	600	9FG	9NG

Note: [a] using Fe_2O_3 catalyst only
[b] using NiO catalyst only

4.2.2.2 Experimental set up

An experimental set-up was designed by using thermal CVD where the schematic diagram is shown in Figure 4.1. The experiment was run at University of Nottingham, UK as part of the collaboration work between the university and Universiti Teknologi PETRONAS. A 50-mm inner diameter and 1525-mm length of tube reactor was placed inside the electric furnace. The quartz boat was filled with 0.05 g of Fe_2O_3. There were three gas lines (H_2, Ar and C_2H_4) controlled by the mass flow controller. Initially, the air in the system was evacuated using vacuum pump. Later, the system was filled with Ar at 1000 ml/min and the temperature was set at a rate of 10°C/min. At equilibrium temperature, the reaction began by flowing C_2H_4/H_2 mixture into the reactor.

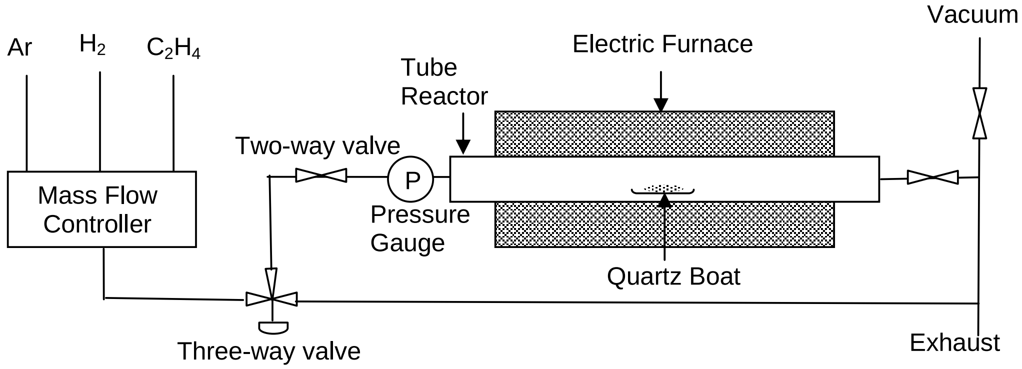

Figure 4.1 Schematic diagram of the initial experimental setup

Figure 4.2 Preliminary experimental setup of thermal CVD

4.2.3 Chemical vapor deposition: Modified experiment

The setup was done at Universiti Teknologi PETRONAS. Modifications to the rig at University of Nottingham, UK were carried out which includes the equipment design, the experimental procedure and the parameter conditions. The modification is essential to improve the yield, purity and surface area of GNF.

4.2.3.1 Optimization of CVD experimental procedure

Similarly, the orthogonal array of L_9 type was used and is represented in Table 4.5. The parameters were maintained to be reaction time, C_2H_4/H_2 flow rate and reaction temperature. However, for the development of GNF using Fe_2O_3 as the catalyst, though keeping the ratio of these gases consistent, the total flow rate of C_2H_4 and H_2 was increased from 100 ml/min to 500 ml/min. This is because the internal diameter of the reactor increased by 25 mm and the increase of hydrogen flow could accelerate the reduction of catalyst, which would then increase the development of GNF.

Table 4.5 Parameters design for modified GNF synthesis using Fe_2O_3 as the catalyst.

L_9	Reaction Time (hours)	C_2H_4/H_2 flow rate (ml/min)	Reaction Temperature (°C)	Sample Name
1	2	50/450	500	L_1Fe
2	2	100/400	600	L_2Fe
3	2	150/350	700	L_3Fe
4	3	50/450	600	L_4Fe
5	3	100/400	700	L_5Fe
6	3	150/350	500	L_6Fe
7	4	50/450	700	L_7Fe
8	4	100/400	500	L_8Fe
9	4	150/350	600	L_9Fe

For GNF synthesis using NiO as the catalyst, the total flow rate of C_2H_4 and H_2 was 300 ml/min. This value was lower than that when Fe_2O_3 catalyst is used because unlike Fe_2O_3, NiO required less amount of H_2 to reduce the catalyst.

Table 4.6 Parameters design for modified GNF synthesis using NiO catalyst

L_9	Reaction Time (hours)	C_2H_4/H_2 flow rate (ml/min)	Reaction Temperature (°C)	Sample Name
1	2	270/30	500	L_1Ni
2	2	240/60	600	L_2Ni
3	2	210/90	700	L_3Ni
4	3	270/30	600	L_4Ni
5	3	240/60	700	L_5Ni
6	3	210/90	500	L_6Ni
7	4	270/30	700	L_7Ni
8	4	240/60	500	L_8Ni
9	4	210/90	600	L_9Ni

4.2.3.2 Experimental set up

The schematic diagram is referred in Figure 4.3 with the key indicators while the actual setup can be seen in Figure 4.6. The purpose of experimental modification was was to obtain higher reaction yield. During the setup, the overall volume of the reactor was increased from the initial volume in the preliminary experiment because the total volume of the reactor could give a higher reaction yield (Shaijumon et al., 2005; Son et al., 2007; Zeng et al., 2002). Thus, the internal tube diameter was increased to 75 mm. This is because with higher cross sectional area of tube reactor, more gases could be in contact with the catalyst.

Five gas lines were set up where each of them was provided with an individual flow meter. Three out of five gas lines were meant for flammable gases such as hydrogen (H_2), ethylene (C_2H_4) and methane (CH_4) while the other two lines were meant for non-flammable gases like argon (Ar) and nitrogen (N_2). However, for this experiment only Ar, H_2 and C_2H_4 lines were utilized. The ceramic boat filled with catalyst was placed at the centre of the tube reactor. At the gas inlet, a pressure gauge was attached to indicate the pressure of the gas inlet. If the reactor was over pressure then three-way valves would shift the gas line direction straight to ventilation to release the gas. A pump was attached at the vacuum line for system evacuation purpose i.e. to create vacuum environment in the system.

Two dreschel bottles, labelled as *A* and *B* were included to detect any leakage in the system. Initially bottle *A* was filled up with water. For a normal operation, the reaction was run at 1 atm where the gas flowed continuously to the gas inlet of the reactor and left the system at the gas outlet. Therefore the bubbles of the gas in water of bottle *A* indicated that the gas outlet flowed freely before going to the ventilation. If there was no bubble whilst the system still maintain at 1 atm, then a leakage anywhere along the line could be easily detected. On the other hand, if there was a leakage in the evacuated system, the ambient pressure which was higher that the pressure in the system would force the water to be transferred from bottle *A* to bottle *B*. Hence the dreschel bottles could be considered as a good alarm for any leakage or over pressure in the system.

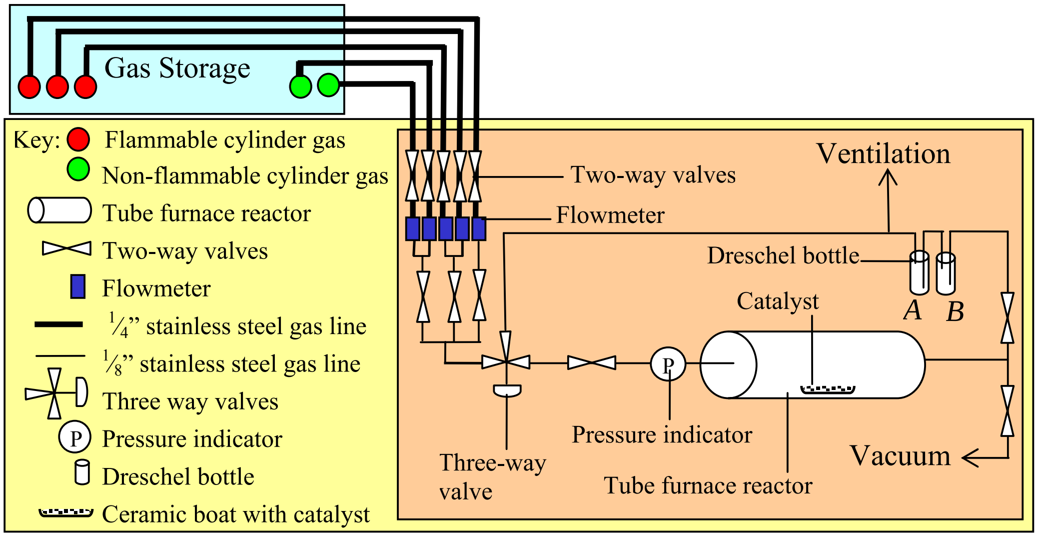

Figure 4.3 Schematic diagram of the modified experimental setup

Figure 4.4 Modified experimental setup of the modified thermal CVD

4.2.3.3 Hydrogen calibration

Before conducting an experiment, the H_2 flowmeter was calibrated. Although there was an equation to find the hydrogen flow rate based on the scale given, it was essential to calibrate the flowmeter to ensure the accuracy of the flowmeter reading. At the beginning, H_2 was flowed at a specific scale reading indicated in the flowmeter. The gas would then be directed to a graduated cylinder filled with water which was positioned in an upside down manner. As soon as H_2 reached the cylinder, it would displace the water. The volume of H_2 that filled the cylinder over the time would be the actual gas flow rate of H_2. Thus, the specific scale reading of the flowmeter corresponded to the measured flow rate. The calibration was done for several times at different reading for a consistency in data collection.

4.2.3.4 Procedure

The tube reactor system was evacuated using vacuum pump. Under vacuum pressure, the furnace was set at 200°C. As soon as the system reached 200°C, the vacuum pump was run for the second time. This was to ensure that all moisture in the reactor was removed. Later the system was purged with Argon (Ar) at 1000 ml/min. When the pressure in the system reached 1 atm, the Ar flowrate was reduced to 100 ml/min and the furnace was set to a desired reaction temperature with an increment of 10°C/min. When the temperature reached equilibrium, Ar flow was stopped and the flowrate of C_2H_4/H_2 mixture was increased to the right flow rate ratio. Once the reaction completed, the gas system was evacuated before the furnace temperature was cooled down by flowing Ar into the system continuously.

4.3 Synthesis of carbon nanotube

Carbon nanotube (CNT) would be synthesized using a commercial ferrocene ($Fe(C_5H_5)_2$) catalyst. This type of metallocene catalyst has been extensively applied in previous study (Atieh Hussien, 2005; Barreiro et al., 2006; He et al., 2005; Shaijumon et al., 2005). However, the application of Taguchi method as part of the design of experiment was not implemented. In addition, only Shaijumon & Ramaprabhu have specifically developed MWNT using ferrocene for hydrogen adsorption application but they have used acetylene as the carbon source. In this research, benzene would be used instead since this vapor provides similar carbon:hydrogen ratio as the acetylene.

The synthesis would be done in a homogeneous process using floating catalyst chemical vapor deposition (FC-CVD) method. The advantage of using FC-CVD method is that no catalyst support or substrate is needed. Furthermore, higher reaction yield could be produced since CNT would be formed along the tube reactor. This is because the higher the volume, the more yield can be produced (Shaijumon et al., 2005; Son et al., 2007; Zeng et al., 2002).

4.3.1 Optimization of CNT experimental conditions

To synthesize CNT in a systematic approach, a design of experiment based on Taguchi method was applied. Taguchi method allows determination of optimum results within selected experimental conditions. Taguchi orthogonal array table was used by choosing three parameters that could affect the formation of CNTs. Although reaction temperature is the key parameter affecting the synthesis of CNT

(Journet et al., 1998; Teo et al., 2003), in this work the reaction temperature parameter was kept constant at 850°C. This is because the maximum yield of CNT was produced at the selected temperature based on the previous research done by (Atieh Hussien, 2005). The experiment done by (Atieh Hussien, 2005) was repeated to confirm his findings. It was found that when the temperature is less than 850°C, the result would give CNT with less purity while at temperature more than 850°C, the formation of GNF would be produced.

The main parameters were selected as the as the control variables which are reaction time, hydrogen flow rate and catalyst weight. These three variables are the common factors that influence the formation of CNTs (Teo et al., 2003). As discussed in Chapter 2, reaction time is one of the main parameters affecting the quality of produced CNTs. As reaction time increases, more CNT could be produced in addition to increase in formation of amorphous carbon. Thus, sufficient reaction time should set up to avoid the increase in the quantity of the amorphous carbon. Reaction time range from 30 to 50 minutes is selected based on the previous finding (Atieh Hussien, 2005). The amount of catalyst was significant in determining the final structure of CNT. Although other studies had used Argon as a carrier gas (Barreiro et al., 2006; Hawkins et al., 2009; He et al., 2005), but the proposed work would used hydrogen gas instead. Apart from the hydrogen gas price of gas cheaper than that of Argon, it was found that hydrogen can accelerate the carbon formation (Atieh Hussien, 2005). This has been proved by a recent studies carried by (Ajayan et al., 2009) who used hydrogen as carrier gas in developing CNT using ferrocene catalyst. Table 4.7 shows the parameters and levels used in the synthesis of CNTs using Taguchi method.

Table 4.7 Parameters and levels used in the synthesis of CNTs.

Parameters	Levels		
	Low	Medium	High
Reaction Time (min)	30	40	50
H_2 flow rate (ml/min)	100	200	300
Mass of catalyst weight (g)	0.2	0.3	0.4

The range parameters are small since all unnecessary parameters that lead to formation other than CNTs have been screened out. The orthogonal array of L_9 type was used as a result of choosing three parameters with three levels and it is represented in Table 4.8. L and subscript 9 mean Latin square and the repetition number of the experiment, respectively.

Table 4.8 L_9 orthogonal array for CNT synthesis

L_9	Sample Name	Reaction Time (min)	H_2 flow rate (ml/min)	Mass of catalyst (g)
1	1R	30	100	0.2
2	2R	30	200	0.3
3	3R	30	300	0.4
4	4R	40	100	0.3
5	5R	40	200	0.4
6	6R	40	300	0.2
7	7R	50	100	0.4
8	8R	50	200	0.2
9	9R	50	300	0.3

4.3.2 Experimental setup

An experimental setup was assembled using floating catalytic chemical vapour deposition (FC-CVD) method at Universiti Putra Malaysia (UPM) as part of collaboration work under E-science fund. A 60-mm inside diameter and 1000-mm length of ceramic tube reactor was located in an electric furnace with four ceramic boats were placed inside the tube reactor. Figure 4.1 shows the schematic diagram of the experimental setup. The first ceramic boat which is on the right hand side (as in Figure 4.5) was filled with a specific amount of ferrocene ($Fe(C_5H_5)_2$). The position of the ceramic boat that filled with the catalyst was positioned outside of the electric furnace. The heat source which would heat up the catalyst did not come from the electric furnace but from the heating belt that was wrapped around the end of the tube reactor. There were two inlet gas lines (argon and hydrogen) and one outlet gas line. Argon gas was used as the purging gas while hydrogen gas was used as the carrier gas that bubbled through benzene before entering the reactor. The actual experimental setup can be referred in Figure 4.6.

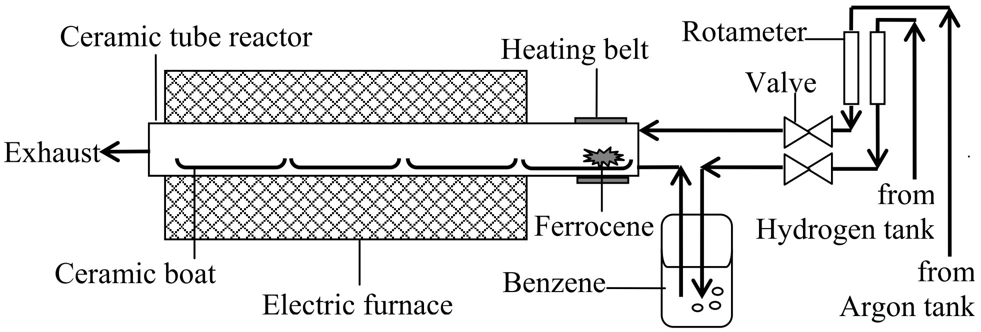

Figure 4.5 Schematic diagram of FC-CVD system

Figure 4.6 Experimental set up of FC-CVD system in the lab

4.3.3 FC-CVD Procedure

The reactor was heated at 850°C and argon gas was introduced to the system to purge the air out of the reactor. After the temperature had reached equilibrium temperature at 850°C, the catalyst was vaporized by heating it at 180°C. As soon as the catalyst began to vaporize, the supply of argon gas was closed. The reaction occurred at atmospheric pressure during introduction of benzene to the system. This was done by bubbling the hydrogen gas at a specific volumetric flow rate into 200 ml of benzene. After a specific reaction time, the reaction was stopped by closing the supply of hydrogen gas. Then the reactor was cooled down by purging the argon gas back to the system before the sample was collected from the ceramic boat placed inside the reactor. The experiment was repeated using different parameters as described in Table 4.2.

4.4 Characterization and analysis of developed CNT and GNF

All developed materials were characterized. In material characterization, several techniques were used to determine the internal structure by magnifying and visualizing the sample using microscope such as scanning electron microscopy and transmission electron microscopy. In addition, from characterization, the elements and the components in a sample was determined such as analytical equipment like x-ray diffractometer and Raman spectroscopy. Moreover, other properties like density and surface area could be measured using analytical equipment.

4.4.1 Raman spectroscopy

For spectroscopy study, the Raman spectroscopy analysis was carried out using a Labram HR800 Horiba Jobin Yvon at room temperature with Argon-ion laser operated at 514.532 nm. The Raman spectra were obtained with a fixed grating over a range of 100 to 1800 cm^{-1}. From the analysis, the purity of a sample could be estimated from the degree of graphitization and the relative value of amorphous to the carbon that could be calculated from the *G* and *D* band intensities (I_G and I_D). Apart from that, it is said that as the *G* band gets nearer to the *G* band of a pure graphite (1575 cm^{-1}), the better hydrogen adsorption would be (Sharon et al., 2007). In other words, carbon materials that possess more sp^2 carbon and less sp^3 carbon should be better a carbon material for hydrogen adsorption.

4.4.2 X-ray diffraction

The XRD studies were carried out using Bruker AXS D8-Advance diffractometer with Cu Kα radiation of wavelength, λ=0.15406 nm, with operating voltage and current at 40 kV and 40 mA, respectively. Each sample was scanned with 2θ of 20° to 80° and the data was collected in step mode with an interval of 0.02°. In order to determine the composition of the samples, direct comparison method was done by using powder diffraction databases, ICDD (International Centre for Diffraction Data) or formerly known as JCPDS (Joint Committee on Powder Diffraction Standards).

4.4.3 Surface area analyzer

Quantachrome Autosorb 1 was used as the surface area analyzer in determining the BET specific surface area of each sample using nitrogen (N_2) as the sorption gas. Prior to the analysis, the samples were degassed for 4 hours at 250°C.

4.4.4 Scanning electron microscope

The morphology of each GNF and CNT samples were studied with Phillips XL30 SEM at accelerating voltage of 20 kV and ESEM Phillips XL30 at accelerating voltage at 30 kV, respectively. For further observation, a field emission scanning electron microscopy (FESEM) known as SUPRA 55VP is used at accelerating voltage of 0.02 to 30 kV.

4.4.5 Transmission electron microscope

The structural of CNT and GNF samples were analyzed using transmission electron microscopy (TEM) observation that was performed by Jeol JEM 2000FX II at accelerating voltage of 200 kV and Phillips TEM 400 at accelerating voltage of 100 kV. Samples for TEM were prepared by ultrasonic dispersion of the GNF samples with ethanol (Zhang et al., 2000). Later, the suspension was dropped onto carbon grid and dried in the air before the TEM analysis was done. Additional characterization for CNT samples was carried out using high resolution transmission electron microscopy (HRTEM) observation that was performed by Tecnai 20.

4.4.6 Gas pycnometer

A density of the sample was determined by using gas pycnometer of Quantachrome Ultrpycnometer. Initially, the sample was dried in the oven furnace at 100°C for at least 30 minutes in order to remove any moisture trapped in the sample. Then the mass of the sample was measured before it was placed inside the chamber of the gas pycnometer. The measurement was run for at least six times using Helium (He) as the purging gas.

4.5 Gravimetric measurement of hydrogen adsorption

The hydrogen adsorption measurement was carried out using two types of gravimetric measurement instruments; intelligent gravimetric analyzer and magnetic suspension balance. The former one was used for hydrogen adsorption at 77 K and up to 20 bar while the latter one was conducted to measure hydrogen adsorption at a high pressure of 100 bar or more at room temperature (298 K).

4.5.1 Hydrogen adsorption at low temperature

The gravimetric measurement of hydrogen adsorption at low temperature was carried out using Intelligent Gravimetric Analyzer (IGA-001). The instrument was supplied by Hiden Isochema Ltd. (refer to Figure 4.7). It provided a precise measurement of the magnitude and kinetics of gas and vapour sorption from a high vacuum to 20 bar. It was an ideal equipment for the hydrogen adsorption measurement using microporous materials which required high vacuum degassing conditions. This analyzer had a UHV vessel which could withstand high pressure and temperature. Apart from hydrogen storage capacity, it could automatically determine the isotherm at one or more temperatures, real-time kinetic analysis and surface area analysis.

Figure 4.7 Intelligent gravimetric analyzer

Initially, the sample was loaded into the IGA system by placing into a sample basket made from 42 μm micromesh stainless steel. The mesh is designed to permit gas flow through the bucket in order to have a maximum gas-surface contact. The sample was then outgassed at approximately 10^{-6} Torr or 12 hours using external heating system.

After degassing, the sample was isolated and brought into temperature of 77 K by immersing the outer sample containers into liquid nitrogen. The static measurement for adsorption analysis was started when the sample temperature was equilibrium at 77 K. For the first 150 mbar, the pressure rate was set to 50 mbar/min. A higher pressure rate could cause the sample to be blown out of the sample container since initially the sample was in vacuum condition. When the system pressure was at 150 mbar, the pressure rate was changed to 200 mbar/min. The desorption process was done as soon as the adsorption reached final equilibrium at the pressure of 20 bar.

4.5.2 Hydrogen adsorption at high pressure

Magnetic suspension balance (MSB) was supplied by Rubotherm GmBH. The features of MSB have been discussed in the previous chapter and the actual instrument can be referred in Figure 4.8. The blank and buoyancy measurements were done prior to the adsorption measurement. The blank measurement was run once a while to check the consistency of the balance reading while the buoyancy measurement was done each time when loading a new adsorbent sample. All measurements were recorded by Mess-Pro software provided by Rubotherm.

Figure 4.8 Magnetic suspension balance

4.5.2.1 Blank measurement

The blank measurement was carried out to determine the volume of the container. It was conducted by using nitrogen (N_2) gas at room temperature at 25°C. Here, the measurement was done on the empty sample container i.e. without the present of an adsorbent. Initially, the system was evacuated for 30 minutes until the pressure was at –0.002 bar. Later N_2 was flowed into the system up to 5 bar. The balance reading that measured the weight of the container was taken when the system was at equilibrium. The experiment was repeated for the pressure of 10, 15 and 20 bar.

At the end of the measurement a set of data consisted of weight of the empty container with respect to the pressure range from 0 to 20 bar at room temperature was obtained.

4.5.2.2 Buoyancy measurement

The buoyancy measurement was done to determine the volume of the adsorbent sample. As soon as the sample was loaded into the container, a high pressure test was carried out to ensure that there would be no leakage in the system. Then the sample was pretreated under vacuum pressure of 10^{-6} Torr at 250°C for 8 hours. This was done to ensure that all impurities and moisture were removed from the sample. Next the buoyancy measurement was done by flowing helium (He) gas into the system at room temperature (25°C). The pressure was increased from 0 to 5 bar. At equilibrium, the balance reading that measured the weight of the sample and the container was taken. The experiment was repeated for the pressure of 10, 15, 20 and 40 bar. At the end of the measurement, a set of data consisted of weight of the sample and the container with respect to the pressure range from 0 to 40 bar at room temperature was obtained.

4.5.2.3 Adsorption measurement

The adsorption measurement was accomplished in order to determine the amount of H_2 uptake in the developed sample. Initially, the system was evacuated for an hour at 25°C right after the buoyancy measurement was completed. Then H_2 was flowed into the system at a flow rate of 50 ml/min until the pressure was at 1 bar. At equilibrium, the balance reading that measured the mass of the adsorbed sample and the container was recorded. The experiment was repeated for the pressure of 5, 10 bar and up to 100 bar, where the pressure was increased by 10 bar in every stage. The flow rate of H_2 was increased gradually from 50 to 150 ml/min depending on the existing pressure in the system. At the end of the measurement, a set of data consists of the weight of the adsorbed sample and the container with respect to the pressure range from 0 to 100 bar at room temperature was obtained. When the adsorption process was completed up to 100 bar, the desorption process was carried out from 100 to 0 bar. Similar procedure was followed where the balance reading was recorded each time the system had reached equilibrium. The hydrogen adsorption was also done at 150 bar using limited number of samples.

4.6 Hydrogen adsorption simulation

Based from Figure 4.7, in *Step 1*, hydrogen adsorption simulation was done after the isotherm data (i.e. training data) of the obtained adsorption measurement was obtained. Then, the neuro-fuzzy system training process began with the initial fuzzy logic system. *Step 2* was to create a fuzzy logic system by using a Fuzzy Design Wizard (FDW), by specifying two inputs and one output. The advantage of coming up with such initial rules were that it enhanced the performance of the learning process. For example, IF surface area=high AND pressure=low THEN mass uptake=low. However, in this case the FDW analysed the data sets and proposed a system structure. Once the structure was accepted, FDW created a system with default membership function definitions and default rules.

Step 3 was to optimize the performance by parameterized the neuro-fuzzy learning method. There were two important parameters. One was the learn rate for rules and the other one was the learn rate for membership functions. These parameters defined how much the Neuro-fuzzy algorithm modified a rule or a membership function in each learning step. Training phase or simulation took place in *Step 4* in which the Neuro-fuzzy system modified rules and membership functions in order to obtain a predicted result as close to the experimental data as possible. In *Step 5*, after the simulation had been performed, the predicted training data ($Q_{\text{i,predicted}}$) obtained was compared with the experimental data ($Q_{\text{i,experimental}}$) by calculating the mean absolute relative errors (*MAREs*). This was done in order to ensure reliability and accuracy of forecast data that produced by the system. If the *MAREs* were less than 8%, the forecasted data was displayed as the result.

MAREs (%) =

$$\left(\frac{100}{N}\right)\sum_{i=1}^{N}\left|\frac{Q_{\mathrm{i,experimental}}-Q_{\mathrm{i,predicted}}}{Q_{\mathrm{i,experimental}}}\right| \tag{4.3}$$

For *MAREs* more than 8%, *Step 6* which was optimization and verification proceed. The results of neuro-fuzzy system could be manually optimized by tuning the membership functions. After modification, the training was repeated with the same sample data sets.

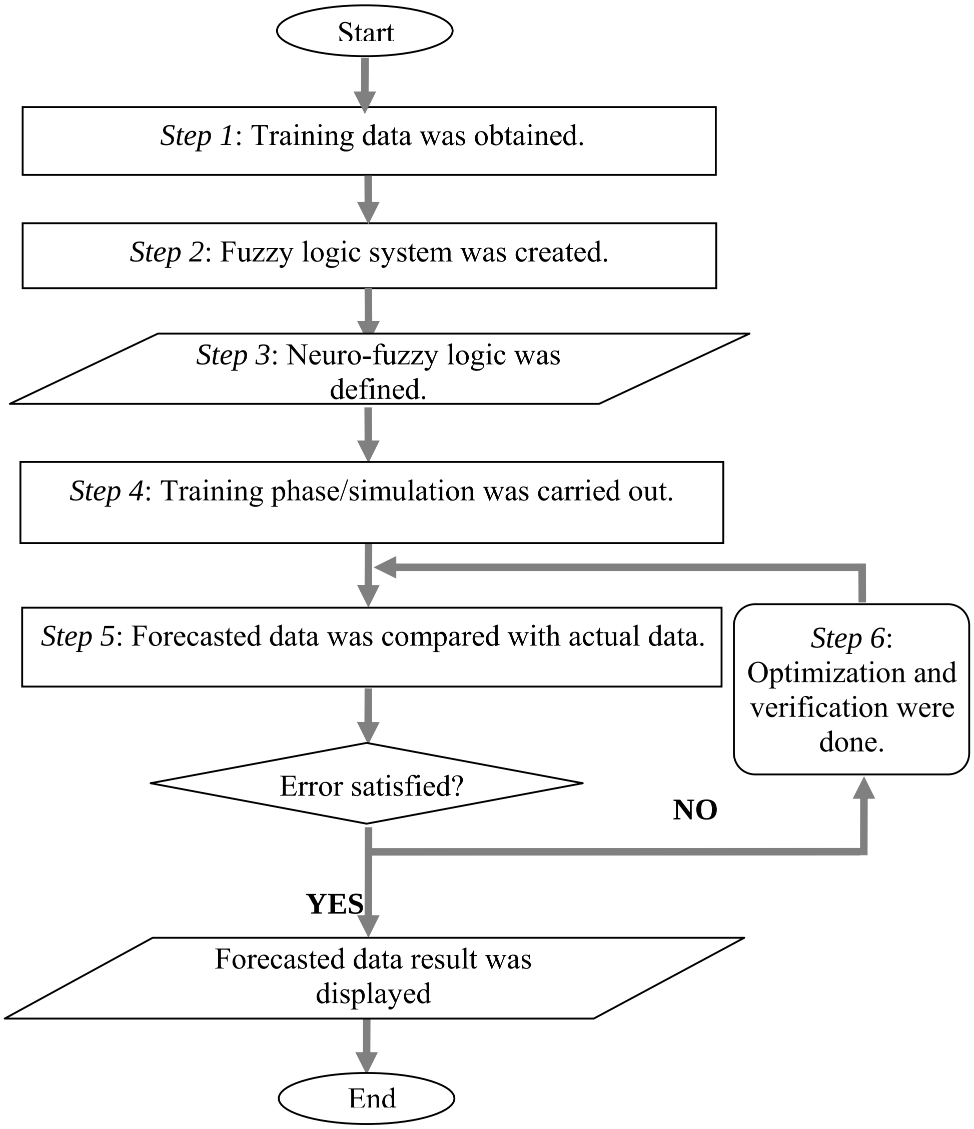

Figure 4.9 Flowchart of Neuro-fuzzy system design approach

4.7 Summary

The methodology of this research work can be classified into four parts. The first part is the synthesis of materials that are catalysts, carbon nanotubes and graphitic nanofibers. The second part is the characterization of the synthesized materials using TEM, SEM, x-ray diffractormeter, Raman spectroscopy, and surface area analyzer. The third one is hydrogen adsorption measurement using IGA and MSB. The last part consists of hydrogen isotherm prediction using assumption-free model that is Neuro-fuzzy.