STUDY ON CARBOXYL FUNCTIONALIZATION OF CARBON NANOTUBES USING ACID TREATMENT METHOD

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by

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LIST OF SYMBOLS

Symbol	**Description**	**Unit**
T	Temperature of the solution	^{o} C
[HCl]	Concentration of the hydrochloric acid	mol/L
[NaOH]	Concentration of sodium hydroxide mixed with CNTs	mol/L
[std NaOH]	Concentration of the titrant in the back-titration	mol/L
$V_{std\ NaOH}$	Volume of the titrant in the back-titration	mL
n_{SAG}	Number of moles on CNTs surface acid groups	mol
V_A	Volume of the solution taken from the V_B	mL
V_B	Volume of the sodium hydroxide mixed with CNTs	mL
V_{HCl}	Volume of the hydrochloric acid	mL

LIST OF ABBREVIATIONS

ACs	Activated Carbon
CNTs	Carbon Nanotubes
CNPs	Carbon Nanoparticles
CVD	Chemical Vapor Deposition
-COOH	Carboxyl Group
D-band	Defective carbon network exist in the sample
FTIR	Fourier Transform Infrared Spectroscopy
G-band	Graphitized carbon network exist in the sample
HCl	Hydrochloric Acid
H_2SO_4	Sulphuric Acid
HNO_3	Nitric Acid
KBr	Potassium Bromide
MTDC	Malaysian Technology Development Corporation
MWCNTs	Multi Walled Carbon Nanotubes
NaOH	Sodium Hydroxide
-OH	Hydroxyl Group
RBM	Radial Breathing Modes
SERC	Science and Engineering Research Centre
SWCNTs	Single Walled Carbon Nanotubes

KAJIAN PADA PEMFUNGSIONALISASIAN KARBON NANOTUBE DENGAN MENGGUNAKAN KAEDAH RAWATAN ACID

ABSTRAK

Pengenalan kumpulan karboksil pada permukaan karbon nanotube (CNTs) dengan menggunakan kaedah rawatan asid adalah berguna bagi pengubahsuaian CNTs. Dalam projek ini, kesan masa rawatan asid, kepekatan campuran asid (H_2SO_4/ HNO_3) dan nisbah asid pada fungsionalisasi CNTs dikaji. Rawatan asid telah dilakukan dengan merendamkan CNTs dalam campuran asid H_2SO_4/HNO_3 dengan masa yang berbeza, kepekatan asid berbeza, dan nisbah asid yang berbeza. Selepas CNTs difungsionalisasi dengan menggunakan rawatan asid, FTIR dan titrasi asid-bes masing masing telah dijalankan untuk menentukan permukaan kumpulan berfungsi pada CNTs secara kualitatif dan kuantitatif. Zeta Potential digunakan untuk mengkaji caj dan kestabilan CNTs fungsionalisasi. Selain itu, pengraphitan daripada CNTs fungsionalisasi telah diperiksa dengan menggunakan Raman Spektroskopi. Secara ringkas, CNTs yang dirawat dengan kepekatan campuran asid 10 M dalam masa 16 jam dengan nisbah 3:1 daripada H_2SO_4/HNO_3 mempunyai nilai tertinggi kepekatan kumpulan asid iaitu 4.15 mmol/g CNT. Selain itu, CNTs yang dirawat oleh 10 M kepekatan campuran asid dalam masa 16 jam dengan nisbah 3:1 daripada H_2SO_4/HNO_3 menunjukkan hasil yang terbaik dalam zeta potential iaitu -38,6 mV. Untuk Raman Spektroskopi, jika puncak G-band lebih tinggi daripada puncak D-band, ia bermakna CNTs mempunyai kecacatan rendah dan permukaan CNTs masih rata. Jika puncak G-band lebih rendah daripada puncak D-band, ia menunjukkan bahawa CNTs mempunyai kecacatan tetapi masih dalam keadaan yang rata.

STUDY ON THE FUNCTIONALIZATION OF CARBON NANOTUBES USING ACID TREATMENT METHOD

ABSTRACT

The introduction of carboxyl groups on carbon nanotubes (CNTs) surfaces by using acid treatment method are useful for further modification of CNTs. In this project, the effect of acid treatment time, concentration of acid (H_2SO_4/ HNO_3) mixture and the acid ratio on functionalized CNTs is studied. Acid treatment was performed by impregnating CNTs in acid mixture of H_2SO_4 and HNO_3 with different treatment time, different concentration of acid, and different ratio of acid. After functionalization of CNTs using acid treatment, Fourier Transform Infrared Absorption Spectroscopy (FTIR) and acid base titration using back titration characterization were carried out to determine the surface acid functional groups on CNTs qualitatively and quantitatively. Zeta Potential is using to study the charge and stability of functionalized CNTs. Other than that, the graphitization of the treated CNTs was examined using Raman Spectroscopy. In short, FTIR spectroscopy of CNTs treated by 10 M concentration of acid mixture of 16 hours with ratio 3:1 of H_2SO_4/HNO_3 has the highest value of acid group concentration which is 4.15 mmol/g CNT. On the other hand, CNTs treated by 10 M concentration of acid mixture of 16 hours with ratio 3:1 of H_2SO_4/HNO_3 shows the best result in zeta potential which is -38.6 mV. For Raman Spectroscopy, if G-band higher than the intensity of the D-band, it means that the CNTs have low defect and the surface of CNTs is still graphitized. If G-band lower than the intensity of the D-band, it indicates that the synthesized CNTs contained defects as well as low-graphitized forms of carbon.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

1.1.1 Carbon Nanotubes

Carbon nanotubes (CNTs), first discovered in the 1990s, have become one of the most eye-catching materials and have attracted great attention in the nanoscience community, because of their unique structure and truly remarkable electronic and mechanical properties. Since the disclosure of CNTs by Iijima (1991), the CNTs have attracted very much attention from scientists around the world (Iijima and Ichihashi, 1991).

CNTs display fabulous chemical and mechanical stabilities, high thermal and electrical conductivities that have attracted very much attention from researchers around the globe (Liu et al., 2014). Hence, CNTs have enormous commercial potential in applications including adsorbent, polymer composites, heterogeneous catalyst supports, biomedical applications and sensors (Gong et al., 2013). A CNTs can be thought as a sheet of graphene rolled into a cylinder.

There are two types of CNTs which is multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). MWCNTs consist of multiple rolled layers (concentric tubes) of graphene. Figure 1.1 shows the diagram of SWCNTs and MWCNTs.

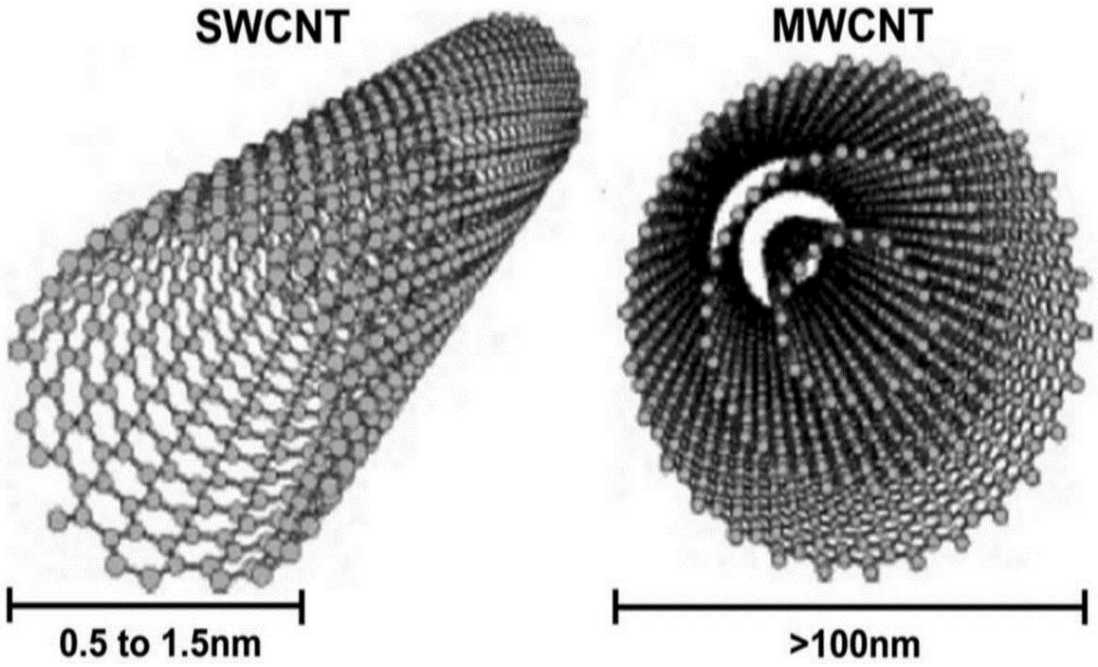

Figure 2.1 : Diagram of SWCNTs and MWCNTs

1.1.2 Modification of Carbon Nanotubes

CNTs have poor solubility and processibility in spite of their huge potential applications, brought about by the natural appealing van der Waals interactions. In this manner, CNTs are accumulated and exist as packs in their native state (Hirsch and Vostrowsky 2005). Other than that, synthesized carbon nanotubes (CNTs) prepared by chemical vapor deposition (CVD), laser ablation and arc discharge methods unavoidably contain carbonaceous impurities and metal catalyst particles. The carbonaceous impurities typically include amorphous carbon and carbon nanoparticles (CNPs) while the metal impurities are usually residues from the transition metal catalyst (Hou et al., 2013). Hence, it is necessary to modify the CNTs by purify and functionalize it to overcome the problem above.

By functionalizing CNTs, their chemical and physical affinity towards solvents and other materials can be improved. Other than that, functionalization of CNTs also can improve their adsorption capacity and the dispersion of CNTs in aqueous solution consequences decrease aggregate formation. The adsorption characteristics of CNTs can be altered by the introduction of desired functional groups on its surface (Kumar et al., 2014). Besides, the presence of functional groups on CNTs allow them to react readily with other chemical reagents with the aim to obtain, for instance, to attach biomolecules for the fabrication of CNTs based biosensors and CNTs nanocomposites. Surface oxidation treatment using concentrated acids like sulphuric acid (H_2SO_4) and nitric acid (HNO_3) is the most widely used to perform a functionalization of CNTs due to the high efficiency. The functionalization technique will result the formation of functional group that attach at the CNTs (Santangelo et al., 2012) .

1.2 Problem Statement

Carbon nanotubes (CNTs) have attracted a great attention because they display a wide range of unique properties, especially for adsorption. However, because of the strong intrinsic van der waals forces, CNTs tend to aggregate and entangle together spontaneously. This will greatly limit their application. There are many potential applications that CNTs can offer, the covalent functionalization of CNTs is of fundamental importance. Introduction of functional groups, such as carboxyl groups is not only can improve CNTs solubility in various solvents, but also are useful for the further chemical link with other compounds, such as biomolecules , inorganic compounds and polymers, and the CNTs self-assembly into devices structures (Zhao et al., 2013).

The oxidation of CNTs by concentrated HNO_3/H_2SO_4 acid mixture creates the maximum number of carboxylic groups with respect to other oxidants. It is important for CNTs to be functionalized to have maximum number of oxygenated groups. This is because the possibility of CNTs to further react with other chemical reagent is higher (Rasheed et al., 2007). So, in this project, the effect of treatment time, the concentration of acid mixture, and ratio of an acid on the amount of functional groups and the acidity of CNTs are investigated.

1.3 Objective of this project

i. To study the effect of acid treatment time on the amount of oxygenated groups on the functionalized CNTs.

ii. To study the effect of concentration of acid mixture (H_2SO_4/HNO_3) on the amount of oxygenated groups on the functionalized CNTs.

iii. To study the effect of the acid ratio between H_2SO_4 and HNO_3 on the amount of oxygenated groups on the functionalized CNTs.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In this part, properties and utilizations of CNTs are first described in detail. Next, the chemical modification techniques for CNTs are investigated in view of the adsorption application of CNTs. At last, the oxidation using acid treatment of CNTs will be reviewed.

2.2 Properties of Carbon Nanotubes

First of all, CNTs have better acid and alkaline stability, provide chemically inert surfaces for physical adsorption and interact strongly with adsorbates (Ren et al., 2011). CNTs also is extraordinary flexibility and resilience, which is now being observed by Thomson et al. (1999). CNTs a new material, belong to the carbon family. Unique morphology, relatively high reactivity, thermal and chemical stability, and ability to interact with different classes of compounds are some of the characteristics of CNTs (Kumar et al., 2014).

Moreover, good load transfer between polymer matrices and the outer surface of CNTs suggest that these exceptional mechanical properties will be reflected in composites (Thomson et al., 1999). Other than that, CNTs possess unique physical properties such as their morphology, light mass density, hollow and layered structure, curvature of sidewalls, higher radiation and thermal resistance (Yu et al., 2014).

The structure of CNTs at the atomic scale is far more well-defined and uniform compared to activated carbon (ACs). When compared with ACs, CNTs have higher specific surface area which is from 50 to 1315 m^2/g (Peigney et al., 2001). From the perspective of their structure, it can be say that CNTs are single crystals while ACs are polycrystalline materials. Those physical properties make CNTs exhibit an outstanding and enhanced adsorptive properties (Liang et al., 2014).

2.3 Application of Carbon Nanotubes

Numerous potential applications have been proposed for CNTs. One of them is in catalyst fields where CNTs provide the possibility of tuning catalyst morphology, surface chemistry and composition to improve their catalytic activity and selectivity, and the possibility of building up macrostructure catalyst. This can fulfil the demands on mechanical strength and pressure drop, high surface area and mesoporous material, and good thermal stability in oxidizing atmospheres compared to that of ACs (Rodriguez-reinoso, 1998).

Adsorption is one of the most effective and economic methods for the removal of toxic components from wastewater and it is one of the application of Carbon Nanotubes. This is on the grounds that adsorption forms in view of this idea are straightforward, financially savvy, simple to work and profoundly productive (Gupta et al., 2016). Meanwhile, CNTs have been applied as one of the most anticipated potential adsorbents for the removal of environment pollutants because of their high adsorption capacity and good regeneration capability (Yu, 2013).

Fast urbanization and industrialization of human development has brought about serious ecological issue, for example, water contamination. A lot of wastewater from ventures that contain potentially toxic components like metal ions, harmful gems, and natural toxic substances are arranged into oceanic stream and cause undesirable changes in the environment. Thus, the expulsion of risky contaminants in wastewater preceding its transfer is urgent in view of safety concerns and environmental consequences (Fu and Wang, 2011).

Adsorption is one of the most effective and economic methods for the removal of toxic components from wastewater. The major factor affecting adsorption by CNTs is shape and size, surface area, site density, being opened or close-ended, surface functional group (acidic and basic site), surface charge, the method by which CNTs were synthesized, impurities (e.g., catalyst, amorphous carbon and O-containing groups), porosity, and treatment. This is on the grounds that adsorption forms in view of this idea are straightforward, financially savvy, simple to work and profoundly productive (Gupta et al., 2016). Meanwhile, CNTs have been applied as one of the most anticipated potential adsorbents for the removal of environment pollutants because of their high adsorption capacity and good regeneration capability (Yu, 2013).

To make it simple, due to the adsorptive and catalytic properties of CNTs, they are widely used in environment monitoring and wastewater treatment for the detection and removal of pathogens, heavy metals and pesticides, gas pollutant and dyes. It also can be used in energy conversion and storage such as in fuel cells, lithium ion batteries, solar cells and hydrogen cells (Abbas et al., 2016; Wei et al., 2012).

2.4 Functionalization of Carbon Nanotubes

The process is known as purification of CNTs using reflux. Fundamentally, this process is the most popular and simple modification of CNTs, which is oxidation of CNTs under strong acidic and oxidative conditions. Impurities from raw CNTs surface are removed in acid modifications. Besides, tube caps of CNTs would be opened and holes in the side walls would be formed in such extreme conditions, as a consequences, oxygen functional group (e.g., -OH,-C=O,-COOH) are created and bonded covalently to CNTs (Abbas et al., 2016).

Through functionalization of carbon nanotubes, i.e., the attachment of appropriate chemical functionalities onto their conjugated *sp*2 carbon scaffold, the prerequisites for facilitating the production of possible applications of such nanostructures are established. The derivatives tubes exhibit improved properties with respect to solubility and ease of dispersion, manipulation and processibility and can be considered a true subdivision of organic molecules (Hirsch and Vostrowsky, 2005).

CNTs in all their forms are difficult to disperse and dissolve in water and in organic media, and they are extremely resistant to wetting. For a long time, they defied chemical characterization, synthetic chemical treatment and any solution chemistry. Functionalization can improve solubility and processibility, and will allow combination of the unique properties of nanotubes with those of other types of materials (Kuzmany et al., 2004).

Functional groups present on the CNTs surface are determined quantitatively by using Boehm’s titration measurements (Kumar et al., 2014). The presence of oxygen-containing groups facilitates the exfoliation of CNT bundles and increases the solubility in polar media, thus CNTs become more hydrophilic (Khani and Moradi, 2013). The carboxyl groups on CNTs surface are useful sites for further modification and increase the sorption as well as ion exchange capacity on CNTs (Sitko et al., 2012). Furthermore, the carboxylic and hydroxyl groups functionalized CNTs are valuable for the removal of various organic and inorganic pollutants like metal ions from aqueous solution (Kumar et al., 2014). Zeta potential is a measure of the magnitude of the electrostatic or charge repulsion/attraction between particles, and is one of the fundamental parameters known to affect stability. Azadi et al. (2010) found that treatment in boiling nitric acid can decrease the zeta potential of the carbon nanotubes to more negative values. Stability of the functionalized CNTs by using zeta potential are studied by Riddick (1968) and it is tabulated in Table 2.1.

Table 2.1 Lists of stability characteristics in relation to zeta potential

Stability Characteristic	Average zeta potential in mV
Maximum agglomeration and precipitation	0 to +3
Range of strong agglomeration and precipitation	+5 to - 5
Threshold of agglomeration	-10 to -15
Threshold of dispersion	-16 to -30
Moderate stability	-31 to -40
Good stability	-41 to -60
Very good stability	-61 to -80
Extremely good stability	-81 to -100

2.4.1 Covalent Functionalization

The covalent modification of CNTs occurs by the attachment of functional groups to their sidewalls or ends. Covalent functionalization of CNTs in general is the carboxylation of terminal carbons and defect sites of CNTs, sidewall halogenation, cyclo additions, radical additions, electrophilic and nucleophilic additions, ozonolysis, and grafting of polymers (Kumar et al., 2014)

During the purification of CNTs with acidic treatment, oxidative damage of CNTs takes place and CNTs with closed tips are transformed into shorter nanotubes with opened ends, which are typically in the form of carboxylic acids and oxygenous functional group. This can be shown in Figure 2.1 (Chiang et al., 2011). The oxidation of carbon surface not only increases hydrophilic structures over the surface but also more oxygen containing functional groups, which enhances the ion exchange capacity.

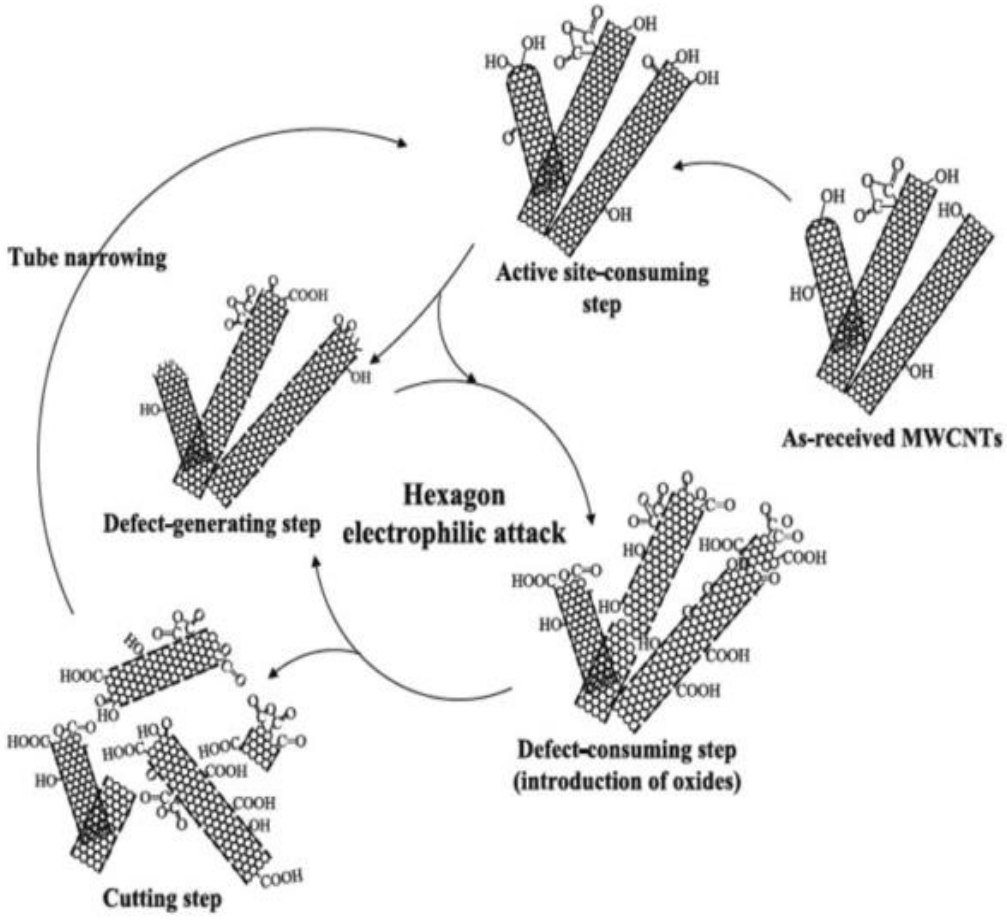

Figure 3.1 : Schematic illustration of the oxidation and defect creation mechanism in mild H_2SO_4/HNO_3 mixture

Table 2.1 list out the different oxidation methods of CNTs in the literature and the acid group quantity measured by Boehm titration after oxidation. Oxidation of CNTs is being done in different conditions with oxidants including HNO_3, H_2SO_4, H_2O_2, NH_4OH and NaClO. The highest acid groups quantity reported is 4.0mmol/g CNTs by Gong et al. (2013).

Table 2.2 lists out the metal ions in water removed by the CNTs, oxidation method of the CNTs and the adsorption capacity after oxidation. The best performance of functionalized CNTs is reported by Tofighy and Mohammadi (2011).

Table 2.1 : List of oxidation methods of CNTs and the acid groups quantity after oxidation

Reference	Amount of CNTs (g)	Type of oxidants	Volume of acids (ml)	Acid Concentration	Temperature (T ^{o}C)	Treatment Time (Hours)	Ratio $H_2SO4{:}HNO_3$ (v/v)	Acid Groups Quantity (mmol/g CNTs)	Remarks
(Gong et al., 2013)	0.1	HNO_3	25	66 wt%	80	24	-	2.0	-
	0.1	$H_2SO4{:}HNO_3$	25	98 wt%, 66 wt%	80	24	1:1	1.4	-
							2:1	2.3	
							3:1	4.0	
							4:1	3.4	
							5:1	3.1	
(Saleh, 2011)	1.0	HNO_3	100	70 wt%	60	6	-	0.08	Dispersed for 1h by sonication initially. Refluxed while stirring vigorously. Allowed to cool at room temperature after refluxing.
					80			0.012	
					100			0.02	
					120			0.026	
					140			0.027	
	1.0	$H_2SO4{:}HNO_3$	100	70 wt%	60	6	3:1	0.01	Dispersed for 1h by sonication initially. Refluxed while stirring vigorously. Allowed to cool at room temperature after refluxing.
					80			0.02	
					100			0.04	
					120			0.08	
					140			0.15	

Reference	Amount of CNTs (g)	Type of oxidants	Volume of acids (ml)	Acid Concentration	Temperature (T ^{o}C)	Treatment Time (Hours)	Ratio $H_2SO4:HNO_3$ (v/v)	Acid Groups Quantity (mmol/g CNTs)	Remarks
(Azadi et al., 2010)	0.2	HNO_3	50	10 M	60	0 5 24	-	0.2 0.27 0.98	Boiled using a hot plate and reflux system.
(Datsyuk et al., 2008)	1.0	HCL	200	Not Stated	Not Stated	2	-	1.0	-
	0.3	HNO_3	25	65 wt%	Not Stated	48	-	3.7	Refluxed under magnetic stirring
	0.3	H_2SO_4:H_2O_2	25	96 wt%. 30 wt%	Not Stated	5	-	2.0	Ratio H_2SO_4:H_2O_2 is 70:30
	0.3	NH_4OH:H_2O_2	25	25 wt%. 30 wt%	80	5	-	1.6	Ratio NH_4OH:H_2O_2 is 50:50

Table 2.3 List of metal ions removed by the CNTs, oxidation method of the CNTs and the adsorption capacity after modification

Adsorbate (Metal)	CNTs Oxidation Method	Maximum Adsorption Capacity, qm (mg/g)	Reference
Ni^{2+}	Dispersed 400ml 3M HNO3, ultrasonically stirred for 24 hours	Oxidized CNTs = 42.9036	(Yang et al., 2009)
Ni^{2+}	Dispersed in 4M HNO_3 for 2 hours, washed and dried, then oxidized by concentrated HNO_3, refluxed at 150 °C for 2 hours.	As – produced CNTs = 18.08 Oxidized CNTs = 49.26	(Issa and Meunier, 2007)
Cu^{2+}	Refluxed in concentrate HNO_3 at about 120 °C for 4 hours	Cu^{2+} 0.0404	(Gao et al., 2009)
Ni^{2+}		Ni^{2+} 0.0311	
Cd^{2+}		Cd^{2+} 0.0260	
Zn^{2+}		Zn^{2+} 0.0152	
Cd^{2+}	Treated with a (v/v 3:1) mixture of concentrated H_2SO_4 and HNO_3, then sonicated for 3 hours at 40 °C in an ultrasonic bath.	raw-MWCNT = 3.19 Oxidized MWCNT =24.15	(Marinkovi et al., 2010)
Cr^{4+}	Dispersed in 3M HNO_3 and ultrasonically stirred for 24 hours.	Oxidized CNTs = 4.2615	(Hu et al., 2009)

Adsorbate (Metal)	CNTs Oxidation Method	Maximum Adsorption Capacity, qm (mg/g)	Reference
Cu $^{2+}$	Immersed in HNO_3 (65 %) and shaken in an ultrasonic bath for 30 min, then stirred continuously for 36 hours at 298 K. Immersed in NaClO (60 %) and shaken in an ultrasonic bath for 30 min, then stirred continuously for 3 hours at 358 K.	As-produced CNTs = 8.25 HNO_3 – modified CNTs = 13.87 NaOCL-modified CNTs = 47.39	(Wu, 2007)
Pb $^{2+}$	Immersed in concentrated HNO_3 (65 %) for 20 hours.	Pb $^{2+}$ 101.046	(Tofighy and Mohammadi, 2011)
Cu $^{2+}$		Cu $^{2+}$ 50.3755	
Cd $^{2+}$		Cd $^{2+}$ 75.8350	
Zn $^{2+}$		Zn $^{2+}$ 58	
Co $^{2+}$		Co $^{2+}$ 69.633	
Pb $^{2+}$	Added into the solution of 3 M HNO_3, ultrasonically stirred for 24 hours.	Oxidized CNTs = 4.09	(Xu et al., 2008)
Pb $^{2+}$	Dispersed into concentrated HNO_3 solution and refluxed for 2 hours at 140 °C	MWCNTs = less than 4 Oxidized MWCNTs = 59	(Wang et al., 2007)

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

All chemical and reagents utilized as a part of the study are recorded in Table 3.1.

Table 3.1 Details of material used in this project

Chemical / Reagent	Assay	Supplier	Purpose of use
Carbon Nanotubes (CNTs)	Multi-walled Nanotubes	Malaysian Technology Development Corporation (MTDC) laboratory	Pristine CNTs for functionalization
Sulphuric Acid (H_2SO_4)	96 %	Fisher	For acid treatment of CNTs
Nitric Acid (HNO_3)	65 %	Fisher	For acid treatment of CNTs
Deionized Water	-	-	For dilution of concentrated acids.
Distilled Water	-	-	For washing process
Ethanol	95 %	Fine Chemicals	For the phenolphthalein
Phenolphthalein	~99 %	Fluka Chemika	pH indicator in titration process
Sodium Hydroxide (NaOH)	≥99 %	Merck	For titration purpose
Hydrochloric Acid (HCL)	37 %	Merck	For titration purpose
Potassium Bromide (KBr)	≥99 %	Acros	For FTIR purpose

3.2 Research Flow Chart

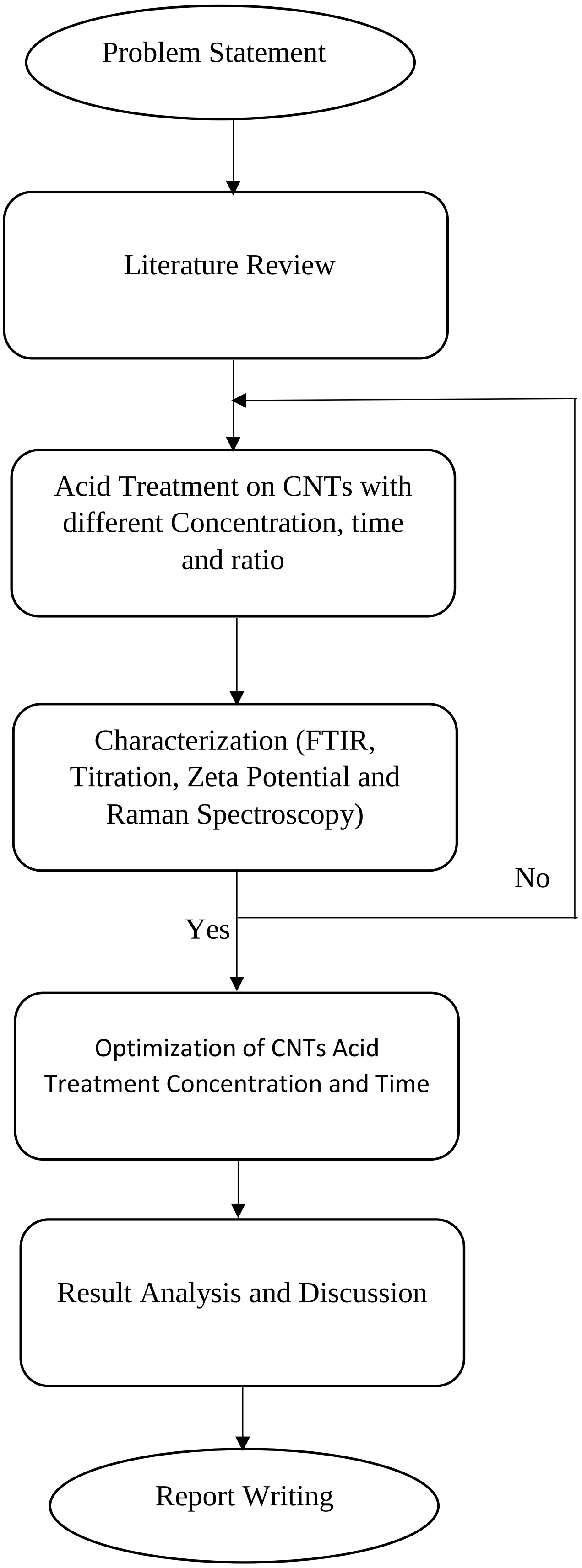

Figure 4.1 : Research Flow Chart

3.3 Functionalization of Carbon Nanotubes (CNTs)

Functionalization of CNTs have been done by oxidation with different treatment time, different concentrations of acid mixture and different ratio of acid (H_2SO_4/HNO_3) in 100^oC under moderate stirring (400ppm). The condition of time should be test first with different time and fix the concentration acid H_2SO_4 and HNO_3 at 8M. Table 3.2 shows experiment conditions of the functionalization.

Table 3.2 : Experiment conditions of the functionalization

Run	H_2SO_4 (ml)	HNO_3 (ml)	Ratio H_2SO_4:HNO_3	Time (Hours)	Concentration of acids
1	150	50	3:1	2	8
2	150	50	3:1	4	8
3	150	50	3:1	6	8
4	150	50	3:1	8	8
5	150	50	3:1	16	8
6	150	50	3:1	24	8
7	150	50	3:1	6	9
8	150	50	3:1	6	10
9	50	150	1:3	6	10

3.4 Characterization Methods

In this project, Fourier Transform Infrared Spectroscopy (FTIR), titration, Zeta Potential Measurement and Raman Spectroscopy were employed to characterize the CNTs.

3.4.1 Fourier Transform Infrared (FTIR)

FTIR spectroscopy is generally used to qualitatively analyse the functional groups (eg. Hydroxyl, carbonyl, aldehyde, carboxyl etc.) and evaluate the chemical structure of material (Ling et al., 2013). In this project, FTIR spectroscope (Model Thermo Fisher Scientific Nicolet iS10 FTIR Spectroscopy) was used to study the surface chemistry of the functionalized CNTs. The infrared absorption bands could identify specific molecular components and functional groups available on the sample.

Before analysis, functionalized CNTs were mixed with potassium bromide (KBr) in a weight ratio of 1:10. The mixture was the ground homogenize and pressed into pellet form (about 12.7 mm diameter and 1 mm thickness) at 4-ton pressure using manual hydraulic press. The purpose of mixing and homogenization of the CNTs sample with KBr was to ensure that the peaks can detected during the analysis. The pressed CNTs sample was carefully removed from cast and place in the FTIR sample holder. Next, the holder was placed inside the analysis chamber. The analysis was done using a program (OMNIC Spectra) attached to the system. The spectra were measured from wavelength of 4000 to 400 cm^{-1}.

3.4.2 Titration

The acid groups (eg. Carboxyl, lactones, lactols, and in some cases carbonyls) concentrations on the surface of the functionalized CNTs were quantitatively analysed by a simple back-titration method (Wepasnick et al., 2011). In this simple back-titration method, 250 mg of functionalized CNTs were placed in a 250 ml flask containing 100 ml of the sodium hydroxide (NaOH) solution with the concentration of 0.025 M. The flasks were sealed using paraffin film and shaken moderately in a water bath shaker (Model Memmert) for 24 hours at room temperature, to allow the CNTs to equilibrate with the NaOH solution. The solutions were then filtered using filter paper. 20 ml of filtrates were pipetted and added to 25 ml of 0.05 M hydrochloric acid (HCl) to neutralize the unreacted NaOH completely. At last, the solutions are back-titrated with 0.025 M standard NaOH solution to the neutral point of pH. Phenolphtalein is use as the pH indicator (Mostofizadeh, 2010). It was prepared by mixing 0.2 g phenolphthalein powder, 20 ml distilled water and 20 ml ethanol. The solution was then sonicated for 1 hour to ensure fully dissolved of phenolphthalein powder.

Titrations were performed in triplicate. In short, the quantity of total acid group concentrations was determined from the amount of NaOH used in the titration. The equation used to determine the quantity of total acid group concentrations is shown below in Equation 3.1 and 3.2:

$$[\mathrm{HCl}]V_{\mathrm{HCl}}=[\mathrm{std\ NaOH}]V_{\mathrm{std\ NaOH}}+([\mathrm{NaOH}]V_B-n_{SAG})\frac{V_A}{V_B} \tag{3.1}$$

$$n_{SAG}=[\mathrm{NaOH}]V_B-([\mathrm{HCl}]V_{\mathrm{HCl}}-[\mathrm{std\ NaOH}]V_{\mathrm{std\ NaOH}})\frac{V_B}{V_B} \tag{3.2}$$

Where [NaOH] and V_B are the concentration and volume of the sodium hydroxide mixed with the CNTs, providing the number of moles of sodium hydroxide that was available to the CNTs surface for reaction with the acid groups on the surface. n_{SAG} denotes the number of moles on the CNTs surface acid groups that reacted with the NaOH during mixing step. V_A is the volume of the solution taken from the V_B. [HCl] and V_{HCl} are the concentration and volume of the HCl added to the solution (A) taken from the original sample (B). This gives the number of moles of acid added to the solution (A), and available for reaction with the remaining NaOH.

The remaining moles of acid are then determined through the titration using [std NaOH] and $V_{std\ NaOH}$, the concentration and volume of the titrant in the back-titration. Thus, through the knowledge of the remaining moles of acid, leading to the amount of NaOH remaing after reaction, and by different (knowing the total amount of NaOH available initially) the amount of NaOH reacted with the surface acid groups, the number of moles of CNTs surface acid groups can be quantified. These equatio0n are based on the calculations from Oickle et al. (2009).

3.4.3 Zeta Potential Analysis

The stability of CNTs suspension was measured using Malvern Instruments Nano Series Zetasizer (model: ZEN 3600). Zeta potential and electrophoretic mobility of CNTs suspension is a measured parameter for various solvents and solution concentrations for selected solvent. The process of measurement consisted of place the sample in the cuvette, inserting the cuvette filled with sample in the zetasizer and setting the details in the zetasizer software follow standard operating procedure (SOP).

In brief, a sample about 1mL was injected into the cuvette using glass dropper. The cuvette used in this study was Dip Cell 1020 made from quartz materials. There is a need for proper handling during sample injection to avoid bubbles formation which will affect the count rate in the sample and inconsistent measurement. The sample was inserted in the instrument according to the instruction and the system was operated within few minutes based on the type of sample.

3.4.5 Raman Spectroscopy

The quality of the CNTs produced can be directly determined using Raman Spectroscopy. The analysis was run using Reinishaw in Via Raman Microscope at Science and Engineering Research Centre (SERC) in the range of 100-3200 cm^{-1} with laser excitation of 532 nm of argon laser at room temperature. Basically there are three peaks that exist in Raman Spectrum which are Radial Breathing Modes (RBM), D-band which refers to defective carbon network exist in the sample and G-band that refers to graphitized carbon network that exist in the sample. RBM that appeared in the range of 100-400 cm^{-1} is referring to the presence of SWCNTs. For D-band, the peak is in the range of 1200-1400 cm^{-1} and G-band peak appears in the range of 1500-1700 cm^{-1}. The degree of graphitization of the CNTs produced can be calculated using the ratio of intensity G-band over D-band (I_G/I_D). The higher the ratio subject to higher graphitized CNTs produced. The samples which consist of CNTs growth were directly placed in the equipment and three spots of CNTs growth from the samples were taken to observe the Raman spectrum and determined the ratio of I_G/I_D.