# FABRICATION, PURIFICATION AND CHARACTERIZATION OF MULTIWALL CARBON NANOTUBES

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

Faculty of Science
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FEBRUARY 2019

## DEDICATION

*Dedicated with my deepest love and affection to*

*My family and friends*

*For their supports and blessings*

*To my dearest husband Ahmad Fakhrurrazi*

*For his motivational support*

## ACKNOWLEDGEMENT

First and foremost, all praise to Allah, the Almighty, the Benevolent for His blessing and guidance, for giving me the inspiration to embark on this project and instilling in me the strength to see that, this research becomes reality. I would like to express my gratitude to all those who have helped in one way or another in the planning, brainstorming, writing, editing stages, and discussion for this research. I would like to specially thank to my supervisor Dr. Kashif Tufail Chaudhary for his continued guidance and support for this research and contributing in stimulating suggestions and encouragement, help me to coordinate this research. I would also like to express my sincere gratitute to my friends (especially Ruisheng Yang) for their research experiences and knowledges sharing and support in the field of nanomaterials research. They have created a very warm and friendly working atmosphere within the laboratory. I would also like to thank the scientific research officer.

A special thanks to my family. Words cannot express how grateful I am to my mother and father for all of the motivational support during my struggle. Your prayer for me help to sustain me thus far. I would also like to thank all of my friends who supported me in writing and incented me to strive towards my goal. At the end, I would like express appreciation to my beloved husband Ahmad Fakhrurrazi who was always be my support in the moments when there was no one to answer my queries.

# ABSTRACT

Multiwall carbon nanotubes (MWCNTs) have numerous potential applications which can be attributed to their outstanding electrical conductivity, mechanical strength and thermal conductivity. However, as-grown multiwall carbon nanotubes (a-MWCNTs) usually contain large amount of impurities or by-products in the form of carbonaceous and metal particles, which hinder and limit the technological implementation of MWCNTs. This study is focused on fabricating MWCNTs by arc discharge and developing an efficient purification route based on gas and liquid phase oxidation. The MWCNTs are fabricated by developing arc discharge carbon plasma between graphite rods by applying 20 V dc voltage and 100 A current at atmospheric pressure. The purification of as-grown MWCNTs is performed in two stages. In first stage, the as-grown MWCNTs are subjected to heat treatment at 750 $^{o}$C at atmospheric pressure. The second stage involves chemical oxidation using mixture of $HNO_3$ and $H_2O_2$ in different ratios via refluxing, sonication and drying processes. The role and impact of oxidizing agents such as $HNO_3$ and $H_2O_2$ are investigated in details and optimized. The synthesized and purified MWCNTs are characterized by thermogravimetric analysis (TGA), Raman spectroscopy, X-ray diffraction (XRD) and field emission electron microscopy (FESEM). The shift in the (002) peak towards lower angle in XRD spectra and low value of $I_D/I_G$ ratio from Raman spectra suggest improvement and increase in the presence of tubular structure for the chemically oxidized MWCNTs with $HNO_3$:$H_2O_2$ ratio of 3:0. A decrease in amorphous structures with no nanoparticles attached with nanotubes is observed for the MWCNTs samples treated by thermal and chemical oxidation for $HNO_3$:$H_2O_2$ ratio of 3:0 and 2:1 in the scanning electron microscopic images. Significant increase in the as-grown MWCNT density was observed from MWCNT samples thermally oxidized at temperature 750 $^{o}$C and chemically oxidized with $HNO_3$:$H_2O_2$ ratios of 3:0 and 2:1.

## ABSTRAK

Nanotiub karbon berbilang dinding (MWCNT) mempunyai banyak potensi penggunaan kerana kekonduksian elektrik yang luar biasa, kekuatan mekanikal dan kekonduksian terma. Walau bagaimanapun, MWCNT yang disediakan biasanya mengandungi banyak bendasing atau hasil sampingan dalam bentuk berkarbon dan zarah logam, yang menghalang dan menghadkan pelaksanaan teknologi MWCNT. Projek ini difokuskan pada pembuatan nanotiub karbon berbilang dinding dengan nyahcas arka dan membangunkan teknik penulenan yang cekap berdasarkan pengoksidaan fasa gas dan cecair. MWCNT direka dengan membangunkan nyahcas arka plasma karbon di antara rod grafit dengan menggunakan voltan arus terus 20 V dan arus 100 A pada tekanan atmosfera. Penulenan MWCNT yang disediakan dilakukan dalam dua peringkat. Pada peringkat pertama, MWCNT yang disediakan dikenakan rawatan haba pada 750 ºC pada tekanan atmosfera. Peringkat kedua melibatkan pengoksidaan kimia menggunakan campuran $HNO_3$ dan $H_2O_2$ dalam nisbah yang berbeza melalui proses refluks, sonik dan pengeringan. Peranan dan impak agen pengoksidaan $HNO_3$ dan $H_2O_2$ disiasat dengan teliti dan dioptimumkan. MWCNT yang disintesis dan ditulenkan dicirikan oleh analisis termograviti (TGA), spektroskopi Raman, pembelauan sinar-X (XRD) dan mikroskopi elektron pancaran medan (FESEM). Anjakan puncak (002) kearah sudut rendah pada spektrum XRD dan nilai rendah nisbah $I_D/I_G$ daripada spektrum Raman mencadangkan penambahbaikan dan kenaikan dalam kehadiran struktur bertiub untuk MWCNT yang dioksidakan secara kimia dengan nisbah $HNO_3:H_2O_2$ adalah 3:0. Pengurangan struktur amorfus dengan tiada zarah nano terlekat pada nanotiub diperhatikan pada sampel MWCNT yang dirawat secara terma dan pengoksidaan kimia dengan nisbah $HNO_3:H_2O_2$ 3:0 dan 2:1 dalam imej mikroskop pengimbas elektron. Kenaikan berkesan dalam ketumpatan MWCNT yang disediakan diperhatikan untuk sampel MWCNT yang dioksidakan secara terma pada suhu 750 ºC dan secara kimia dengan nisbah $HNO_3:H_2O_2$ 3:0 dan 2:1.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| CNTs | - Carbon nanotubes |
| SWCNTs | - Single wall carbon nanotubes |
| MWCNTs | - Multiwall carbon nanotubes |
| CVD | - Chemical vapour deposition |
| $O_2$ | - Oxygen gas |
| $CI_2$ | - Chlorine gas |
| $H_2O$ | - Water |
| $HNO_3$ | - Nitric acid |
| $H_2O_2$ | - Hydrogen peroxide |
| Co | - Cobalt |
| Ni | - Nickel |
| Cu | - Copper |
| CO | - Carbon monoxide |
| Fe | - Iron |
| CCVD | - Combustion chemical vapour deposition |
| DNA | - Deoxyribonucleic acid |
| $H_2S$ | - Hydrogen Sulfide |
| Ar | - Argon |
| HCl | - Hydrochloric acid |
| $SF_6$ | - Sulfur hexafluoride |
| $C_2H_2F_4$ | - Tetrafluoroethane |
| $CCI_4$ | - Carbon Tetrachloride |
| $H_2SO_4$ | - Sulfuric acid |
| $H_3PO_4$ | - Phosphoric acid |
| $CH_3COOH$ | - Acetic acid |

| | | |
|---|---|---|
| $KMnO_4$ | - | Potassium permanganate |
| $OsO_4$ | - | Osmium tetroxide |
| $K_2Cr_2O_7$ | | Potassium dichromate |
| FeO | - | Iron(II) oxide |
| DC | | Direct Current |
| SEM | | Scanning Electron Microscopy |
| TEM | | Transmission Electron Microscopy |
| FESEM | | Field Emission Scanning Electron Microscopy |
| XRD | | X-ray Powder Diffraction |
| TGA | | Thermogravimetric analysis |
| FTIR | | Fourier-transform infrared spectroscopy |
| HR-TEM | | High-resolution transmission electron microscopy |

## LIST OF SYMBOLS

| | | |
|---|---|---|
| Å | - | Angstrom Unit |
| °C | - | Degree Celsius |
| θ s | - | Angle in Degree |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of the Study

Carbon Nanotubes (CNTs) are the center of attention since discovery of CNTs by Ijima in 1991 [1]. CNTs possess unique chemical, physical, electrical, mechanical and thermal characteristics which are strongly dependent on the nano size, tubular structure and high aspect ratio of length to diameter**.** The carbon nanotubes are categorized in two categories as single walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNT is made of a single graphene sheet rolled up around in form a cylinder, whereas MWCNTs contain concentrically nested cylinders with an interlayer spacing of 3.4 A$^\circ$ with diameter usually in the order of 10 to 20 nm [2]. The outstanding properties make CNTs as potential material for the different technological applications such as nano-sensors, nano-composite materials [3], nanoelectronic devices, as catalyst supports [4], hydrogen storage [5] and optical devices. CNTs are also excellent material for electrochemistry application [6].

The CNTs are grown by different synthetic routes such as arc discharge plasma, laser ablation, chemical vapour deposition (CVD) and etc. [1]. Regardless of synthesis route, during fabrication of

CNTs, the powders of carbonaceous particles such as fullerene, amorphous carbon, nanocrystalline graphite, multi-walled graphite and metallic catalyst also exist along with tubular structures [7]. These carbonaceous particles act as impurities and hinder the accurate analysis of CNTs characteristics as well as limit the best performance of CNTs for technological applications. As-prepared material, contains variety of impurities leads to a weakness of the device or material. Most of the advanced technological applications of CNTs are highly dependent on the purity of the materials. These impurities are desired to be removed and an effective purification is required to remove all by-products and at the same time maintaining the original physical structure of CNTs in order to exploit the full potential of CNTs properties.

A number of purification techniques have been developed which involves chemical and physical processes and mainly depend on nanotube stability and morphologies (single-walled or multi-walled), synthesis techniques, types of impurities [8] and carbon source as well as types of catalyst used [9]. Commonly used purification techniques are gas phase oxidation, electrochemical oxidation and liquid phase oxidation [10]. Furthermore, the synthesis methods for SWCNTs require metal catalyst. However, for the production of MWCNTs, only the arc discharge method does not involve any metal catalyst and does not yield any metallic impurities [11].

The purification techniques can be divided into two main parts, which are chemical and physical purifications. The chemical techniques involve separation process of the synthesis products, depend on their reactivity which commonly produce unavoidable defects along the tubes and at the tube ends of the pentagonal structure. Some extraordinary damages to the CNTs structure and morphology can be yielded by these techniques. The examples of chemical purification techniques are oxidation by heating, acids and oxidizing agents, alkali treatment and annealing in inert gases. Besides that, the physical techniques for example filtration, ultrasonication, centrifugation and size-exclusive chromatography are able to separate the impurities according to their sizes. These techniques are actually less effective and more complex although they are quite mild and tubes are not damaged badly. Basically, physical methods can work to remove and separate the unwanted impurities like aggregate, nanocapsules and amorphous carbon [11].

The gas phase and liquid phase conditions are the most usually used in chemical purification technique involving oxidation of as-synthesized CNTs. The gas phase condition commonly uses air, $O_2$, $Cl_2$, $H_2O$ and etc. For liquid phase condition generally refers to oxidation using strong acids solution and electrochemical oxidation [10]. Gas phase oxidation technique generally employes ball milling process which flavin mononucleotide (FMN) is helically self assembled around MWNTs through non-covalent interactions without introducing defects in MWCNTs [12]. The removal of carbonaceous impurities without vigorously producing sidewall defects is a major challenge [10]. The amorphous carbon, polyhedral carbon and metal impurities can be effectively removed by chemical-based purification according to a large amount of CNTs. Gas phase purification is able to make the caps of CNTs opened without increasing considerable more sidewall defects or functional groups. Incompatible of volumetric ratio of liquid phase oxidation yields defects and functional groups especially on CNTs side wall and causes different types of CNTs cutting [10].

In arc discharge method, MWCNTs are produced by controlling the growth conditions such as the pressure of inert gas in the discharge chamber and the arcing current. Based on this method, the nanotubes commonly bound together by strong Van der Waals interactions and tight bundles. The advantageous of arc discharge method is the grown MWCNTs possess very straight tubular structure, high crystalline and does not involve metal catalyst during synthesis process and also yield fewer defects than MWCNTs produced by other methods. Typically, the arc discharge process produces large amounts of by-product such as polyhedral carbon and amorphous carbon [11].

## 1.2 Problem Statement

MWCNTs have numerous potential applications including biomaterials, multifunctional composites and electronic components attributed to their outstanding electrical conductivity, mechanical strength and thermal conductivity [13]. Despite of CNTs preparation route, different types of impurities are produced as by-product which mainly depend on the synthetic routes. In all MWCNTs growing techniques, by-products or impurities are generally in the form of carbonaceous particles such as nanocrystalline graphite, amorphous carbon and fullerenes, produced in large quantity along with the MWCNTs [14]. The presence of impurities or by-products hinder and limit the technological applications of MWCNTs. Therefore, these impurities are required to be removed in order to exploit the full potential of the MWCNTs. An effective purification technique is required to eliminate such contaminations by keeping intact the original physical structure of MWCNTs. The liquid phase oxidation is an effective technique to remove carbonaceous impurities from MWCNTs sample. Liquid phase oxidation is based on oxidative etching process that is capable to eliminate unstable carbon atoms such as amorphous carbon and carbon particles easier as compared to MWCNTs due to their higher oxidation reaction rate [11].

The removal of amorphous carbon particles from CNTs surface is proven using the strong oxidizing agents as $HNO_3$ and $H_2O_2$. This strong oxidizing agent removes the carbonaceous impurities and enhances thermal stability of carbon nanotubes through thermogravimetric analysis [15]. Nitric acid is one of most preferable reagent, which is used for purification of CNT due to mild oxidation nature and capable to remove amorphous carbon selectively. Moreover, it is nontoxic and inexpensive, has the ability to remove metal catalysts and no secondary impurities are produced. Hydrogen peroxide ($H_2O_2$) is also a mild, cost-effective and green oxidant agent which is capable to attack the carbon surface [8].

Therefore, this research focuses on the fabrication of MWCNTs by arc discharge method and the optimization of an efficient purification route based on liquid phase and gas phase oxidation processes in order to remove the carbonaceous impurities present in the synthesized MWCNTs. The selective oxidative etching process eliminates impurities more easily as compared to CNTs due to the higher oxidation reaction rate of CNTs [16].

## 1.3 Objectives

The main objective of this study is to fabricate of multiwalled carbon nanotubes (MWCNTs) by arc discharge and optimize an efficient purification route based on liquid phase and gas phase oxidation. The specific objectives are:

1. To fabricate MWCNTs by arc discharge method.
2. To purify the fabricated MWCNTs by gas phase oxidation and liquid phase oxidation using oxidizing agents such as $HNO_3/H_2O_2$ with different volumetric ratios.
3. To characterize the purified samples based on TGA, Raman Spectroscopy, XRD and FESEM.

## 1.4 Scope of Study

The MWCNTs were fabricated using arc discharge method in ambient environment at atmospheric pressure for dc voltage 20V and current 100A. The purification of MWCNTs was performed using gas phase and liquid phase oxidation. The gas phase oxidation was performed by heating grown MWCNTs sample at 750$^{o}$C for 60 minutes, followed by the chemical oxidation i.e. refluxing, washing and drying. The $HNO_3$ and $H_2O_2$ were used as oxidizing agents to study the impact of acidic solution on purification for different volume ratios of 3:0, 2:1, 1:1, 1:2 and 0:3. The refluxing process was performed at 100°C to110 °C and refluxing time 6 hours for all different volume ratios of $HNO_3$/$H_2O$. The MWCNTs were dried at 100°C for 30 minutes after washing. The as-prepared and purified sample of MWCNTs were characterized by XRD, FESEM, Raman spectroscopy and TGA in order to study and identify the morphology, structural changes and content of impurities under different refluxing conditions.

## 1.5 Significance of Study

This research contributes significantly towards the technological implementation of MWCNTs especially for photovoltaic applications. The development of efficient purification mechanism will help to exploit full potential of MWCNTs in different technological applications of enormous fields such as electronics, optoelectronics, medical and many more. The role and impact of the investigated refluxing parameters are valuable to optimize the purification process of MWCNTs synthesized by arc discharge technique.

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