



UNIVERSITI PUTRA MALAYSIA

***THEORETICAL AND EXPERIMENTAL MODELS OF CATALYSTS FOR
SELECTIVE SYNTHESIS OF METALLIC SINGLE-WALLED CARBON
NANOTUBES AND THEIR ELECTROCHEMICAL CAPACITANCE***

DANLAMI UMAR ZURU

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By

DANLAMI UMAR ZURU

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

May 2017

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DEDICATION

This research work is dedicated to my late parents, Mr. and Mrs. Umar Ajaye, for setting the right footing towards my educational career, may Almighty ALLAH forgive all your sins, accept your good deeds and grant you *al-jannah firdaus*, amen.



Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

THEORETICAL AND EXPERIMENTAL MODELS OF CATALYSTS FOR SELECTIVE SYNTHESIS OF METALLIC SINGLE WALLED CARBON NANOTUBES AND THEIR ELECTROCHEMICAL CAPACITANCE

By

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May 2017

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A major challenge in the field of carbon nanotubes (CNTs) synthesis via Chemical Vapour Deposition (CVD) method is lack of established theoretical model for the selection and design of metal/support catalysts to grow single wall carbon nanotubes (SWCNTs) of desired electronic types. This has limited the application of these materials in electronics, specifically as electrodes for supercapacitor. In the current report, Theoretical Model 1 (DH1) was proposed and developed via kinetic theory, by correlating decompositions of carbon precursors with active metal electrons and applied in the selection of carbon feedstock and metal catalyst matrix. Theoretical Model 2 (DH2) was a proposed modification of the Extended Tight Binding (ETB) model equations, developed by introducing circumferential and axial distortions to diameter and chiral angles of SWCNTs, respectively, which was then applied in predicting the selection and design of metal/support catalyst matrix. Outcomes of these models conformed with advances in heterogeneous catalysis and CNT synthesis, and were employed in the design and preparation of four $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst samples each, with compositions A (11, 8), B (10, 4), C (10, 7) and D (8, 8) where (n, m) are the chiral index of each SWCNT. This was achieved via impregnation of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ precursor salts, calcined at 450°C . Optimized parameters of the CVD processes for the synthesis of the corresponding CNTs were achieved at 1000°C working temperature, 0.5 g catalyst loading and 30 min pyrolysis of $\text{C}_6\text{H}_{14}/\text{N}_2$ feedstock. Field Emission Scanning Electron Microscopy (FESEM) images of the catalyst samples showed spherical nano sized particles and resulting Energy Dispersive Spectroscopy (EDS) indicated the presence of only Fe, Al, and O elements. X-ray Diffraction (XRD) analysis revealed $\alpha\text{-Fe}_2\text{O}_3$ phases in which Al_2O_3 were incorporated, with average crystallite size of 27 nm. BET surface area analysis of catalysts A, B, C and D revealed surface area ($\text{m}^2 \text{g}^{-1}$) of 170, 205, 172 and 153, respectively, with average pore diameter of 4 nm, suggesting mesoporosity. Transmission Electron Microscopy (TEM) and FESEM images of the as-grown CNTs shows densely entangled bundles, while High Resolution Transmission Electron

Microscopy analysis (HR-TEM) confirmed arrangement of SWCNTs in the bundles. XRD analysis indicated peaks of highly graphitized carbon atoms, Fe_3C , FeN and Al_4C_3 , suggesting that CNT growth might have occurred on reduced metal atoms, as predicted in DH2. Raman analysis of the CNT samples revealed that the Radial Breathing Modes (RBMs), diameter and energy band gaps of the samples were in conformity with those of ETB model. Fourier Transformed Infra-Red (FT-IR) analysis of the four samples confirmed the stretching and bending vibrations of amide carbonyl ($-\text{C}=\text{ONHR}$) and carboxylic ($-\text{COOH}$) functional groups, respectively, in all the samples, indicating that the samples were successfully functionalized.

Highest electrochemical abilities of the SWCNT samples were observed in 0.1 M KCl electrolyte, tested from -1.0 to 1.0 V potential window and from scan rate of 0.01 to 0.2 V s^{-1} . Specific capacitance (F g^{-1}) of 242, 207, 284 and 259 were recorded for SWCNTs A4, B4, C4 and D4, respectively. All samples showed stable pseudocapacitive cyclic voltammograms, straight charge-discharge profiles, sustained 1000 cycle test and enhanced current-potential responses which suggested good potential for pseudocapacitor electrodes.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**PEMODELAN TEORI DAN EKSPERIMEN PEMANGKIN BAGI SINTESIS
KARBON NANOTIUB BERCIRI LOGAM DAN KAPASITANS
ELEKTROKIMIANYA**

Oleh

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Cabaran utama dalam sintesis karbon nanotub (CNTs) melalui Kaedah Penganapan Wap Kimia (CVD) adalah kelemahan model teori sedia ada bagi pemilihan dan reka bentuk pemangkin logam/sokongan untuk penghasilan karbon nanotub berdinggi tunggal dengan sifat elektronik yang diperlukan. Ini telah menghadkan penggunaan bahan ini dalam sektor elektronik, khususnya sebagai elektrod di dalam superkapasitor. Dalam laporan ini, Model Teori 1(DH1) telah dicadangkan dan dibangunkan melalui teori kinetik, dengan menghubungkan penguraian prekursor karbon dengan elektron logam aktif dan digunakan dalam pemilihan bahan suapan karbon dan matrik logam pemangkin. Model Teori 2 (DH2) adalah pengubahsuaian yang dicadangkan untuk model persamaan ikatan ketat (ETB), yang dibangunkan dengan memperkenalkan herotan lilitan dan paksi terhadap diameter dan sudut kiral SWCNT, yang kemudiannya digunakan dalam meramalkan pemilihan dan reka bentuk matrik pemangkin logam/sokongan. Model-model yang terhasil ini bertepatan dengan perkembangan dalam bidang pemangkinan heterogen dan sintesis CNT, digunakan dalam mereka bentuk dan penyediaan empat sampel pemangkin $\text{Fe}_2\text{O}_3 / \text{Al}_2\text{O}_3$ iaitu A (11, 8), B (10, 4), C (10, 7) dan D (8, 8), dimana (m, n) adalah indeks kiral setiap SWCNT. Ini dicapai melalui pengisitepuan garam pelopor $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dan $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dan pengkalsinan pada suhu 450°C . Parameter optimum bagi proses CVD untuk sintesis CNTs yang berkaitan dicapai pada suhu 1000°C , muatan pemangkin 0.5 g dan 30 min pirolisis suapan $\text{C}_6\text{H}_{14}/\text{N}_2$. Imej mikroskopi pengimbasan elektron pancaran medan (FESEM) sampel pemangkin menunjukkan zarah bersaiz nano-sfera dan analisis spektroskopi penyerakan tenaga (EDS) menunjukkan kehadiran unsur Fe, Al, dan O sahaja. Analisis pembelauan sinar-X mendedahkan fasa $\alpha\text{-Fe}_2\text{O}_3$ di mana Al_2O_3 dipadukan bersama, dengan purata saiz kristal 27 nm. Analisis luas permukaan BET pemangkin A, B, C, dan D menunjukkan masing-masing mempunyai luas permukaan ($\text{m}^2 \text{g}^{-1}$) 170, 205, 172 dan 153, dengan purata diameter liang 4 nm, menunjukkan mesoporisiti. Imej mikroskopi pancaran elektron (TEM) dan FESEM menunjukkan SWCNT terikat padat secara berkelompok, manakala analisis

resolusi tinggi mikroskopi pancaran elektron (HR-TEM) mengesahkan susunan secara berkelompok dengan ruang untuk setiap SWCNT. Analisis XRD menunjukkan kehadiran puncak atom karbon yang bergrafit, Fe_3C , FeN dan Al_4C_3 dengan purata saiz kristal 17.4 nm, membuktikan pertumbuhan CNT berlaku melalui atom logam terturun, seperti yang diramalkan dalam DH2. Analisis Raman sampel CNT mendedahkan bahawa Mod Pernafasan Radial (RBMs), diameter dan tenaga ruang jalur sampel sepadan dengan model ETB yang lain. Analisis Infra-merah Transformasi Fourier (FT-IR) daripada mengesahkan kewujudan getaran regangan dan lenturan kumpulan berfungsi amide dan karbonil ($-\text{C}=\text{ONHR}$) dan karbosilik ($-\text{COOH}$), dalam semua sampel, menunjukkan bahawa sampel tersebut telah berjaya ditambah kumpulan berfungsi.

Kebolehan elektrokimia tertinggi sampel SWCNT dicerap di dalam elektrolit 0.1 M KCl pada tingkat keupayaan di antara -1.0 hingga 1.0 V dan kadar imbasan 0.01 to 0.2 V/s. Kapasitans spesifik (F g^{-1}) dengan nilai 242, 207, 284 dan 259 direkodkan untuk SWCNT A4, B4, C4 dan D4. Semua sampel menunjukkan kitar voltammogram yang stabil, profil cas-discas yang lurus, kestabilan pada 1000 ujian kitaran dan peningkatan respons arus-keupayaan menunjukkan potensi yang baik sebagai elektrod pseudo kapasitor.

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I certify that a Thesis Examination Committee has met on 8 May 2017 to conduct the final examination of Danlami Umar Zuru on his thesis entitled "Theoretical and Experimental Models of Catalysts for Selective Synthesis of Metallic Single-Walled Carbon Nanotubes and their Electrochemical Capacitance" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
CNTs	Carbon Nanotubes
CV	Cyclic Voltammetry
CVD	Chemical Vapour Deposition
DH1	Theoretical Model 1
DH2	Theoretical Model 2
ECP	Electrically Conducting Polymer
EDLC	Electrochemical Double Layer Capacitor
EDS	Electron Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
ES	Electrochemical Supercapacitor
ESR	Equivalent Series Resistance
ETB	Extended Tight Binding
FESEM	Field Emission Scanning Electron Microscopy
FETs	Field-Effect Transistors
FT-IR	Fourier Transformed Infra-Red
HR-TEM	High Resolution Transmission Electron Microscopy
IEA-PVPS	International Energy Agency-Photovoltaic Power Systems
IEA-PVPS	International Energy Agency-Photovoltaic Power Systems.
IHP	Inner Helmholtz Plane
MWCNTs	Multi Wall Carbon Nanotubes
OBES	Office of Basic Energy Sciences

OHP	Outer Helmholtz Plane
RBM	Radial Breathing Mode
SETs	Single-Electron Transistors
SWCNTs	Single-Walled Carbon Nanotubes
TEM	Transmission Electron Microscopy
TGA/DTG	Thermogravimetric Analysis/Derivative Thermal Gravimetry
XRD	X-Ray Diffraction



CHAPTER 1

INTRODUCTION

1.1 Research Background

The need for energy storage has invoked the need for intensive research in search of suitable and efficient materials to augment the use of batteries and conventional capacitors as energy storing devices in the field of electronics. Supercapacitors have been reported as promising candidates for this purpose because they possess several advantages over conventional capacitors such as high power density, very long life, quick mode of operation and excellent reversibility (Burke & Miller, 2000 P. 519). They are reported to store electrical energy many folds greater than electrolytic capacitors. A supercapacitor can store electric energy in two ways: electrostatically via charge adsorption between the surface of a conductive electrode and an electrolyte, usually referred to double-layer capacitance, and through electron transfer which is achieved by redox reactions, a process known as pseudocapacitance (Conway, 1999, P. 67). These excellent electrochemical properties of supercapacitors made them suitable for various applications, including consumer applications where they stabilize the power supply for fluctuating loads such as laptop computers and portable media player; in industries to provide back up or emergency shutdown power to low-power equipment such as RAM, SRAM and PC cards; in medicine where they are used to deliver power energy for shocking the heart (IEA-PVPS, 2011, P. 124). This might be the reason why research advances are ongoing in the field of electronics, in search of suitable materials that may find application in the design of electrodes for supercapacitors.

Among the various forms of carbon materials, carbon nanotubes (CNTs) have been receiving outstanding considerations as promising materials for nanotechnology, since their discovery in 1991, by Iijima. A CNT is a cylindrical tube of hexagonal matrix formed by rolling a graphene sheet: it is called single wall carbon nanotube (SWCNT) if it consists of one tube and multi wall carbon nanotube (MWCNT), if it has more than two walls. A SWCNT can exhibit metallic or semiconducting character, depending on a unique chiral index (n, m) , which determines the thermal, optical, mechanical, electronic and magnetic properties of the material. They are generally one-dimensional carbon materials with excellent mechanical properties, and are therefore applied in composite materials to enhance physical and chemical properties such as toughness, durability, conductivity and strength; their sensing abilities enabled them have potential applications in environmental, medical and agricultural studies; they also possess good electrical conductivity and pore sizes suitable for storing electrolyte ions, which made them attractive in the field of electronics (Azam & Rosle, 2013, P. 3905; Jiang, Meng & Wu, 2011, P. 155). It is therefore evident that these materials (CNTs) affect all part of our lives: health, transport, media, communication and environment. These unique properties possessed by CNTs have invoked the need for intensive research in order to exploit and explore their synthesis, characterization and applications through theoretical

and experimental means. However, despite all research advances in the field of CNT synthesis, the problem of producing these essential materials in mass, with the desired electronic properties, using a low-cost method, is still a persistent challenge (Kumar & Ando, 2010, P. 3749).

Currently, Chemical Vapour Deposition (CVD) method of CNT synthesis is regarded as the best of the three methods, others being laser ablation and arch discharge methods. The former method is said to be easy in handling and the most economical for large scale production of CNTs (Ward, Wei & Ajayan, 2003, P. 721); most efficient for yielding pure and quantitative CNT products and the most suitable in terms of CNT architecture, purity and yield (Jacques, 2009, P. 68). Among the various material parameters involved in this process, the catalyst and the precursor carbon source are the most influential; the metal catalysts mostly used are nano particles of nickel (Ni), iron (Fe) and cobalt (Co), mainly because they serve as better media for effective carbon solubility and diffusion (Ding et al., 2008, P. 465); common carbon precursors include methane, ethane, propane, butane, pentane, hexane, ethylene, benzene, methanol, ethanol, sucrose, kerosene (dodecane) and tripropylamine (Kumar & Ando, 2010, P. 3751). Their molecular structures play a very significant role on the structural architecture of CNTs, for instance, methane and benzene can form straight and curved CNTs, respectively. (Schneider et al., 2008, P. 1773; Maruyama et al., 2010, P. 4097).

The unique optical and electronic properties exhibited by SWCNTs made them more attractive materials for future electronics than MWCNTs and theoretical results has confirm that metallic SWCNTs can carry electric current density many folds greater than metals. Therefore, recent advances in the field of selective synthesis of these carbon materials are receiving greater attention and were mostly achieved through manipulation of the catalyst shape and composition (Yang et al., 2014, P. 524).

1.2 Statement of Research Problems

The structural architecture of SWCNTs were reported to depend on their chirality index (n, m), which determines their diameter and chiral angle. Authors are unanimous that the most determinant parameter for chirality control of SWCNT growth is the catalyst nano particles; therefore, modern researches were based on the epitaxial model of SWCNT growth, which attributed chirality growth control to the crystal structure and thermal stability of the catalyst nano particles. This model therefore, recommends that the catalyst nano particles must be in solid crystalline form and of high thermal stability. A breakthrough in the selective synthesis of (12, 6) SWCNTs was reported by Yang et al., (2014), in which molecular clusters of $W_{39}Co_6O_x$ were used to prepare nano particles of W-Co catalyst supported on SiO_2/Si substrates and synthesis of (12, 6) SWCNTs were achieved via CVD pyrolysis of ethanol (P. 526). Raman RBM of the as-grown SWCNTs conformed with RBM of (12, 6) SWCNTs. The authors attributed the success of selective growth to the enhanced structural similarities between the atomic arrangement of the catalyst nano particles and the

circumference (diameter) of the (12, 6) SWCNT. Stability of the nano-sized catalyst particles during reaction processes was attributed to high thermal stability (2400°C) of W-Co alloy. This work was complemented two years later by An et al., (2016) who selectively grow (12, 6) SWCNTs with Co-W catalyst prepared by magnetron sputtering of W and Co metals on SiO₂ followed by annealing at 400°C in air (P. 14525). Here, selective synthesis was attributed to the formation of an intermediate structure of Co₆W₆C as revealed by in-plane transmission electron microscopy, while stability of the catalyst was due to anchoring nature of W.

However, despite advances in this field, the ultimate aim of obtaining a desired type of SWCNT by structural growth control of chirality through manipulation of catalyst composition, shape and structure has posed a major challenge for over 20 years (Yang et al., 2014, P. 530). There are two main reasons for this difficulty (1) it has not been possible to prepare identical nano particles of catalyst of the same sizes, compositions or shapes (2) it is even more challenging to control the stability of these nano-sized particles at higher temperatures of growth processes. This has necessitated the need for new innovative approaches, different from attribution of chirality to catalyst crystal sizes, in order to solve the problem of SWCNT chirality control growth (Liu, Wu, Gui, Zheng, & Zhou, 2017, P. 38).

It was based on this persistent challenge that Theoretical Model 2 of the current report was a proposed attempt to correlate the magnitudes of the chirality index (n, m) of each SWCNT directly to the weight percent fractions of the metal/support catalyst matrix, respectively, which may be used to select and design suitable metal/support catalyst to selectively grow SWCNTs of desired chirality, without the use of tedious *in situ* experimental control..

1.3 Research Aim and Objectives

The aim of this research work is to selectively synthesize metallic SWCNTs of the types A (11, 8), B (10, 4), D (10, 7) and E (8, 8), via CVD method, and evaluate their capacitances. To achieve this aim, the following specific objectives were designed:

1. Development of Theoretical Model 1 (DH1) using the kinetic theory of gases and its applications in the selection of carbon precursor/metal catalyst matrix.
2. Development of Theoretical Model 2 (DH2), a comparative study with the Extended Tight Binding (ETB) results, and its application in the selection and design of Metal / Support catalyst matrix.
3. Application of DH1 and DH2 in the design and preparation of sample catalysts with compositions A (11, 8), B (10, 4), C (10, 7) and D (8, 8) by chemical impregnation method, and their analysis using X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Electron Dispersive Spectroscopy (EDS), Thermogravimetric Analysis (TGA) and BET surface area analysis.

- 4 Synthesis of the corresponding CNTs of the types A (11, 8), B (10, 4), D (10, 7) and E (8, 8) via thermal CVD process and characterization of the as-grown CNTs using XRD, FESEM, EDS, Transmission Electron Microscopy (TEM), High-Resolution Transmission Electron Microscopy (HR-TEM), TGA and Raman analyses.
- 5 Evaluation on the effects of catalyst loading, working temperature and pyrolysis time on the structure of the as-grown CNTs.
- 6 Comparison of the electronic properties of the as-grown CNTs with those established by the Extended Tight Binding (ETB) Model, based on Raman spectroscopy analysis.
- 7 Evaluation of the electrochemical properties of the CNTs using Cyclic Voltammetry (CV) analysis and galvanostatic charge-discharge tests.



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