การปรับปรุงพื้นผิวอย่างรวดเร็วของคาร์บอนนาโนฮอร์นแบบผนังเดี่ยวด้วยสารประกอบทองแดงโดยการฉายคลื่นไมโครเวฟ

นางสาวปาริฉัตร ทิพยางค์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2556

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)
เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ที่ส่งผ่านทางบัณฑิตวิทยาลัย
The abstract and full text of theses from the academic year 2011 in Chulalongkorn University Intellectual Repository(CUIR)
are the thesis authors' files submitted through the Graduate School.

RAPID SURFACE MODIFICATION OF SINGLE-WALLED CARBON NANOHORNS WITH COPPER COMPOUND BY MICROWAVE IRRADIATION

Miss Parichat Thipayang

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2013

Copyright of Chulalongkorn University

Thesis Title	RAPID SURFACE MODIFICATION OF SINGLE-WALLED CARBON NANOHORNS WITH COPPER COMPOUND BY MICROWAVE IRRADIATION
By	Miss Parichat Thipayang
Field of study	Chemical Engineering
Thesis Advisor	Associate Professor Tawatchai Charinpanikul, D.Eng

---

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Engineering

(Professor Bundhit Eua-arporn, Ph.D.)

THESIS COMMITTEE

.... Chairman

(Associate Professor Bunjerd Jongsomjit, Ph.D.)

....Thesis Advisor

(Associate Professor Tawatchai Charinpanikul, D.Eng)

.... Examiner

(Assistant Professor Varong Pavarajarn, Ph.D.)

.... External Examiner

(Kajornsak Faungnawakij, D.Eng)

ปาริฉัตร ทิพยางค์ : การปรับปรุงพื้นผิวอย่างรวดเร็วของคาร์บอนนาโนฮอร์นแบบผนังเดี่ยวด้วยสารประกอบทองแดงโดยการฉายคลื่นไมโครเวฟ (RAPID SURFACE MODIFICATION OF SINGLE-WALLED CARBON NANOHORNS WITH COPPER COMPOUND BY MICROWAVE IRRADIATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ธวัชชัย ชรินพาณิชกุล, 68 หน้า

วัสดุไฮบริดของวัสดุนาโนคาร์บอนกับอนุภาคโลหะขนาดนาโนมีแนวโน้มที่จะเป็นวัสดุที่ได้รับความสนใจโดยเฉพาะอย่างยิ่งวัสดุนาโนคาร์บอนชนิดใหม่ล่าสุด (คาร์บอนนาโนฮอร์นแบบผนังเดี่ยว) ไฮบริดกับโลหะที่มีค่าการนำไฟฟ้าที่สูงอย่างทองแดง ในกระบวนการสังเคราะห์วัสดุไฮบริดนั้น กระบวนการปรับปรุงพื้นผิวของคาร์บอนนาโนฮอร์นแบบผนังเดี่ยวมีความจำเป็นมากเนื่องจากคุณสมบัติความเฉื่อยด้านการทำปฏิกิริยาทางเคมีของแผ่นกราฟีน ด้วยการให้ความร้อนอย่างรวดเร็วและทั่วถึงของการฉายคลื่นไมโครเวฟนั้นสามารถนำมาช่วยในการปรับปรุงพื้นผิวของคาร์บอนนาโนฮอร์นแบบผนังเดี่ยว และช่วยในการไฮบริดคาร์บอนนาโนฮอร์นแบบผนังเดี่ยวกับอนุภาคทองแดงขนาดนาโนได้ จุดมุ่งหมายของการวิจัยนี้คือการใช้การฉายคลื่นไมโครเวฟในกระบวนการของการปรับปรุงพื้นผิวของคาร์บอนนาโนฮอร์นแบบผนังเดี่ยว เตาอบไมโครเวฟถูกใช้ในการให้ความร้อนแก่สารแขวนลอยระหว่างคาร์บอนนาโนฮอร์นแบบผนังเดี่ยวกับสารผสมของกรดซัลฟูริกกับกรดไนตริกด้วยกำลังและเวลาในการฉายคลื่นต่างๆกัน พบว่าการฉายคลื่นไมโครเวฟสามารถร่นระยะเวลาจากหน่วยชั่วโมงเป็นหน่วยวินาที ปริมาณกำลังในการฉายคลื่นไมโครเวฟเพียงเล็กน้อยก็เพียงพอต่อการปรับปรุงพื้นผิว ปริมาณประจุที่ผิวของคาร์บอนนาโนฮอร์นแบบผนังเดี่ยวที่ได้รับการปรับปรุงผิวแล้วและปริมาณอนุภาคทองแดงที่หุ้มคาร์บอนนาโนฮอร์นแบบผนังเดี่ยวเป็นหลักฐานของผลการทดลองนี้ นอกจากนี้ผลกระทบของความเข้มข้นของอนุภาคทองแดงในกระบวนการโพลีออลด้วยการฉายคลื่นไมโครเวฟจะถูกศึกษาและวิเคราะห์

ภาควิชา.........วิศวกรรมเคมี..........ลายมือชื่อนิสิต..

สาขาวิชา.......วิศวกรรมเคมี..........ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก......................................

ปีการศึกษา..........2556..............

5470967121: MAJOR CHEMICAL ENGINEERING

KEYWORDS: CARBON NANOHORNS/COPPER/SURFACE TREATMENT/ MICROWAVE

PARICHAT THIPAYANG: RAPID SURFACE MODIFICATION OF SINGLE-WALLED CARBON NANOHORNS WITH COPPER COMPOUND BY MICROWAVE IRRADIATION. ADVISOR: ASSOC.PROF.TAWATCHAI CHARINPANITKUL, D.Eng., 68 pp.

Hybrid material of carbonaceous materials and metallic nanoparticles turns into a promising material especially newest carbon nanostructure, single-walled carbon nanohorns (SWCNHs), hybridizes with high conductivity metal such as copper. To fabricate the hybrid material, surface modification of SWCNHs is necessary, owing to the chemical inertness of the graphene sheet. With fast and thorough heating, microwave irradiation could be employed for modifying surface property of SWCNHs and hybridizing SWCNHs with copper nanoparticles. The aim of this research was to implement microwave irradiation to a process of SWCNHs surface treatment. The microwave oven was employed to heat the suspension of SWCNHs with sulphuric acid and nitric acid mixture at different irradiation power and irradiation time. It was found that microwave irradiation can make a shorter process time from order of hour to order of second. Just a small irradiation power is enough for surface treatment. Surface polarity of acid treated SWCNHs and copper coating fraction of hybrid materials are an evidence for those results. The other effect, effect of copper concentration in microwave-polyol process was investigated and discussed.

Department: ……Chemical Engineering…… Student's Signature: ....

Field of Study: …Chemical Engineering……. Advisor's Signature: ……...............................

Academic Year: …………...2013……………..…

ACKNOWLEDGEMENTS

I am very thankful to my best thesis advisor and co-advisor, Assoc Prof. Tawatchai Charinpanitkul, Department of Chemical Engineering, Chulalongkorn University and Prof. Kunio Shinohara, Division of Materials Science and Engineering, Hokkaido University for introducing me to this interesting project, and for their encouragement and deep discussion throughout the course of this work. Furthermore, I am also thankful to Assoc Prof. Bunjerd Jongsomjit, Asst. Prof. Varong Pavarajarn and Dr. Kajornsak Faungnavakij for their comments and participation as my thesis committee.

I would like to thank Dr. Chantamanee Poonjarernsilp, Department of Chemical Engineering, Faculty of Engineering, Rajamangala University of Technology for very useful SWCNHs from her research.

I would like to acknowledge Assoc. Prof. Parkpoom Tengamnuay, Dr. Jittima Chatchawalsaisi and their staffs, Department of Pharmaceutics and Industrial Pharmacy, Chulalongkorn University for their kindly support for my work.

Moreover, I would like to praise Ms. Siriporn Monchayapisut, Ms. Pusanisa Patrachotesawate, Columbo team members and all members of Center of Excellence in Particle Technology for their help, suggestion, warm collaborations and friendship. I am also thankful to Ms. Piyaporn Harinputtasi, Ms. Nattakan Jungjittamat, Ms. Salisa Pungsuk and Mr. Pisut Sukkasem for their friendship and coursework support.

Finally, I would like to express my cordial and deep thanks to my family for their love and encouragement.

CONTENTS

Page

ABSTRACT (THAI) iv
ABSTRACT (ENGLISH) v
ACKNOWLEDGEMENTS vi
CONTENTS vii
LIST OF TABLES ix
LIST OF FIGURES x

CHAPTER

I INTRODUCTION

1.1 Motivation 1
1.2 Objectives of the research 3

1.3 Scope of the research

1.3.1 Synthesis of Single-walled carbon nanohorns (SWCNHs) 3
1.3.2 Investigation of microwave – assisted chemical modification method 4
1.3.3 Investigation of copper concentration effect on the characteristics of the prepared Cu/SWCNH composite 4
1.4 Procedure of the research 5
1.5 Expected benefit 5

II FUNDAMENTAL KNOWLEDGE AND LITERATURE REVIEWS

2.1 Single-walled carbon nanohorns (SWCNHs) 6
2.2 Fabrication of single-walled carbon nanohorns 7
2.3 Surface treatment 8
2.4 Microwave heating 9
2.5 Copper 10
2.6 Polyol process 11

2.7 Literature reviews

2.7.1 Synthesis of single-Walled Carbon Nanohorns (SWCNHs) 12
2.7.2 Surface modification by chemical treatment 14
2.7.3 Copper deposition on carbon nanohorns 15

III RESEARCH METHODOLOGY

3.1 Chemical agents 17
3.2 Equipments 18
3.3 Synthesis of single-walled carbon nanohorns (SWCNHs) by gas-injected arc-in-water (GI-AIW) method 19

Page

3.4 Single-walled carbon nanohorns surface modification using microwave-assisted chemical modification 20
3.5 Preparation of Copper/SWCNH hybrid material 21

3.6 Analytical items and instruments

3.6.1 Coating fraction of copper/SWCNH hybrid material 22
3.6.2 Uniformity of copper coating 23
3.6.3 Transmission electron microscopy (TEM) 23
3.6.4 Zetasizer 24
3.6.5 Fourier transform infrared spectroscopy (FTIR) 24
3.6.6 Raman spectroscopy 25
3.6.7 X-Ray Diffractometer (XRD) 26

IV RESULTS AND DISCUSSION

4.1 Synthesis of single-walled carbon nanohorns (SWCNHs) by gas-injected arc-in-water (GI-AIW) method 28

4.2 Microwave-assisted acid treatment for SWCNH surface modification

4.2.1 Effect of irradiation time on surface properties 31
4.2.2 Effect of irradiation power on surface properties 37

4.3 Copper/SWCNH hybrid material preparation

4.3.1 Effect of irradiation time at acid treatment on properties of copper/SWCNH hybrid material 41
4.3.2 Effect of irradiation power in acid treatment on properties of copper/SWCNH hybrid material 44
4.3.3 Effect of copper concentration on properties of copper/SWCNH hybrid material 47

V CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions 53
5.2 Recommendations for future work 54
REFERENCES 55

APPENDICES

APPENDIX A TEM MICROGRAPHS OF COPPER/SWCNH HYBRID MATERIAL 61
APPENDIX B CALCULATION FOR COATING FRACTION 66
APPENDIX C PUBLICATION 67
VITAE 68

LIST OF TABLES

Table **Page**

2.1 Properties of copper 11
3.1 Chemical agents for synthesizing single-walled carbon nanohorns, surface modification of single-walled carbon nanohorns and synthesizing copper/SWCNH hybrid material 17
3.2 Tropical Equipment for synthesizing single-walled carbon nanohorns, surface modification of single-walled carbon nanohorns and synthesizing copper/SWCNH hybrid material 18
4.1 Particle size and its deviation of SWCNHs and acid treated SWCNHs 36
4.2 I_D/I_G ratio in each step to synthesize copper/SWCNH hybrid material 52

LIST OF FIGURES

Figure **Page**

2.1 TEM images of a dahlia-like aggregate (a) a bug-like aggregate (b) and a seed-like aggregate (c)........ 7

2.2 Copper is … 10

2.3 TEM image of SWCNH/Pd hybrid materials which were synthesized by inserting Pd wire of (a) 0.3 mm, (b) 0.5 mm in diameter inside anode hole; (c) a close-up image of protruding horn in SWCNHs from the square mark in (a) and their molecular models 13

2.4 Schematic representation of copper nucleation and growth on MWCNT surface 16

3.1 Household microwave oven 18

3.2 Dimension of electrodes employed in gas-injected arc-in-water (GI-AIW) method 19

3.3 Schematic diagram of experimental set up for synthesis of single-walled carbon nanohorns (SWCNHs) by gas-injected arc-in-water (GI-AIW) method.. 20

3.4 Schematic diagram of experimental set up for microwave-assisted chemical modification........ 21

3.5 Schematic diagram of experimental set up for copper/SWCNH hybrid material 22

3.6 Transmission electron microscopy (TEM, Jeol JEM-2100)........ 23

3.7 Zetasizer (Zetasizer Nano ZS, Malvern Instrument Limited) 24

3.8 Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Scientific) 25

3.9 Raman spectroscopy (DXR SmartRaman, Thermo Scientific)........ 25

3.10 Typical Raman spectrum of carbonaceous material 26

Figure **Page**

3.11 X-Ray Diffractometer (XRD, Bruker D8 ADVANCE) 27

4.1 Typical TEM images of the SWCNHs synthesized by GI-AIW method (a) Low magnification image (b) High magnification image 28

4.2 Particle size distribution of typical sample of SWCNHs determined by DLS 29

4.3 The Raman spectra of (a) commercial MWCNTs and (b) synthesized SWCNHs 30

4.4 Zeta potential of acid treated SWCNHs samples with different irradiation time 32

4.5 FT-IR spectra of (a) pristine SWCNHs, (b) acid treated SWCNHs at 360 W for 30 sec, (c) acid treated SWCNHs at 360 W for 45 sec, (d) acid treated SWCNHs at 360 W for 60 sec and (e) acid treated SWCNHs at 360 W for 180 sec 33

4.6 Photographs of the dispersion solution of (a) pristine and acid treated SWCNHs (b) at 360W for 30sec, (c) 360 W for 45 sec (d) at 360 W for 60 sec and (e) at 360 W for 180 sec in de-ionize water immediately after sonication 34

4.7 Photographs of the dispersion solution in de-ionize water of (a) pristine and acid treated SWCNHs (b) at 360 W for 30 sec, (c) 360 W for 45 sec (d) at 360 W for 60 sec and (e) at 360 W for 180 sec after sonication (A) 1 day and (B) 1 month 35

4.8 Particle size distributions of SWCNHs before and after acid treatment at 360 W for 45 sec 36

4.9 Schematic of agglomeration in acid treated SWCNHs by intermolecular hydrogen bond 37

4.10 FT-IR spectra of (a) pristine SWCNHs, (b) acid treated SWCNHs at 90 W for 45 sec, (c) acid treated SWCNHs at 360 W for 45 sec, (d) acid treated SWCNHs at 600 W for 45 sec and (e) acid treated SWCNHs at 800 W for 45 sec 38

Figure **Page**

4.11 Photographs of the dispersion solution in de-ionize water of (a) pristine and acid treated SWCNHs (b) at 90 W for 45 sec, (c) 360 W for 45 sec (d) at 600 W for 45 sec and (e) at 800 W for 45 sec (A) after sonication immediately and (B) 1 month later 39

4.12 Raman spectra of (a) pristine SWCNHs and (b) acid treated SWCNHs at 90 W for 45 sec 40

4.13 TEM micrographs of Cu/SWCNH hybrid materials of (a) pristine SWCNHs and Cu/SWCNH hybrid materials with different irradiation time of acid treatment process: (b) 30 sec, (c) 45 sec and (d) 60 sec. 41

4.14 FT-IR spectra of (a) acid treated SWCNHs and (b) Cu/SWCNH hybrid materials fabricated with microwave irradiation at 360 W for 45 sec in acid treatment process. 42

4.15 The XRD profile of (a) pristine SWCNHs and Cu/SWCNH hybrid materials with different irradiation time of acid treatment process: (b) 30 sec, (c) 45 sec and (d) 60 sec. 43

4.16 The coating intensity of Cu/SWCNH hybrid material with different irradiation time 44

4.17 The uniformity of Cu/SWCNH hybrid material with different irradiation time ... 44

4.18 TEM micrographs of Cu/SWCNH hybrid materials of (a) pristine SWCNHs and Cu/SWCNH hybrid materials with different irradiation power of acid treatment process: (b) 90 W, (c) 360 W, (d) 600 W and (e) 800 W 45

4.19 The coating intensity of Cu/SWCNH hybrid material with different irradiation power 46

4.20 The uniformity of Cu/SWCNH hybrid material with different irradiation power. 47

4.21 TEM micrographs of Cu/SWCNH hybrid materials of (a) 15 wt%, (b) 30 wt% and (c) 60 wt% copper concentration 49

Figure **Page**

4.22 The XRD profile of Cu/SWCNH hybrid materials with different copper concentration: (a) 15 wt%, (b) 30 wt% and (c) 60 wt% 50

4.23 The coating intensity of Cu/SWCNH hybrid material with different copper concentration.. 51

4.24 The uniformity of Cu/SWCNH hybrid material with different copper concentration.. 51

4.25 Raman spectra of acid treated SWCNHs at 90 W for 45 sec and copper/SWCNH hybrid material that treated with 90 W for 45 sec and coated with 30 wt% copper precursor... 52

A.1 TEM micrographs of Cu/SWCNH hybrid materials of pristine SWCNHs with 60 wt% Cu 61

A.2 TEM micrographs of Cu/SWCNH hybrid materials at 360 W for 30 sec of acid treatment process with 60 wt% Cu 62

A.3 TEM micrographs of Cu/SWCNH hybrid materials at 360 W for 45 sec of acid treatment process with 60 wt% Cu 62

A.4 TEM micrographs of Cu/SWCNH hybrid materials at 360 W for 60 sec of acid treatment process with 60 wt% Cu 63

A.5 TEM micrographs of Cu/SWCNH hybrid materials at 90 W for 45 sec of acid treatment process with 60 wt% Cu 63

A.6 TEM micrographs of Cu/SWCNH hybrid materials at 600 W for 45 sec of acid treatment process with 60 wt% Cu 64

A.7 TEM micrographs of Cu/SWCNH hybrid materials at 800 W for 45 sec of acid treatment process with 60 wt% Cu 64

A.8 TEM micrographs of Cu/SWCNH hybrid materials at 90 W for 45 sec of acid treatment process with 15 wt% Cu 65

Figure **Page**

A.9 TEM micrographs of Cu/SWCNH hybrid materials at 90 W for 45 sec of acid treatment process with 30 wt% Cu 65

B.1 Image sample for Image processing measurement 66

B.2 Image sample for cropping copper and SWCNHs area 66

Chapter I

Introduction

1.1 Motivation

Since the discovery of the 3rd carbon's allotrope, Fullerenes, in 1985 [1] and the discovery of multi-walled carbon nanotubes in 1991 [2], various carbon nanostructures have been examined consecutively. In 1999, single-walled carbon nanohorns (SWCNHs), one of the revolutionary carbon nanostructures, were reported by Iijima [3]. Later an individual CNH which consists of many horn-shaped single-walled tubular graphene with a conical tip is also reported. Their unique conical structure has a large influence on their extraordinary properties, such as an extra large surface area of SWCNHs is good for adsorption of gas, carbon pentagon rings at the cap are affected to electronic properties etc [4]. To enhance ability of single-walled carbon nanohorns in various applications, it is synergetic mean to hybridize a functional group or other nanoparticles to their surface. The combination of at least two materials will provide pleasing properties from the materials. Metal-carbon nanohorn hybrid material is anticipated to be applied in electrochemical application, biosensing application and application for photovoltaic and photoelectrochemical cells. Meanwhile, metal-carbon nanohorn hybrid material is an engrossing candidate because of their synergetic characteristics [5, 6]

In order to hybridize metal nanoparticles on single-walled carbon nanohorns, it is necessary to pre-functionalize the surface of single-walled carbon nanohorns, owing to the chemical inertness of the graphene sheet [7]. There are several methods to oxidize carbon nanoparticles' surface such as HNO_3 acid oxidation [8], mixture of HNO_3 and H_2SO_4 acid oxidation [9], H_2O_2 oxidation [10], photo-oxidation [11], oxygen and ozone plasma [12, 13]. Generally, oxygen-containing group will decorate on the graphitic surface after they are subject to that surface treatment. The existence of those functional groups leads the carbon nanoparticles to be reactive in any chemical reaction and increase their stability in polar media [14]. In favor of performance-enhancing carbon nanohorns, pre-functionalize the surface of single-walled carbon nanohorns is a very influential step to synthesis metal/single-walled carbon nanohorn hybrid material. One of the most famous oxidation methods is acid oxidation. Simple and easy are the reason for widely using of acid oxidation. Acid Oxidation is tunable method for any purposes such as elimination of impurity, oxidation of graphene sheet etc. Difference acid type is supposed to difference result of oxidation [7]. Usually the method has involved the use of conventional unit operations, such as refluxing and heating. These kind of operations need to be carried over long period time. Moreover, these methods missed control and used large amounts of material and energy [15]. Nevertheless, as a rapid, uniform and more sufficient heating method, microwave irradiation is an attractive alternative.

Recently, microwave-assisted treatment method has been widely examined for some application to synthesis of nanoparticles. In conventional methods (using water and oil as heating media), the precursor would be heated by the general mechanism of heat conduction and radiation. By the microwave-assisted method, the precursor is exposed to electromagnetic irradiation, which could provide fast and uniform heating [16]. Leelaviwat et al. [17] studied to apply microwave for polyol process (called microwave-polyol process) to synthesize copper/multi-walled carbon nanotubes. They found that microwave irradiation could reduce processing time from hours to minutes.

Among various metals, copper has attracted great attention. Copper is the element in column 1B of the periodic table as same as silver and gold that has high electrical and thermal conductivity. Among the three elements above, copper is the cheapest so it is applied in many industrials. So far, there are only few reports related to preparation of copper/carbon nanohorn hybrid materials. Therefore as a first step, pre-functionalize surface of carbon nanohorns using microwave irradiation in prior to preparation of copper/carbon nanohorn hybrid material is worth to investigate systematically.

In this work, microwave irradiation was applied to suspension of copper precursor and carbon nanoparticles which was subjected to acid treatment process for shortenings the processing time to prepare copper/single-walled carbon nanohorns hybrid material. Effects of microwave irradiation power and irradiation time on characteristics of copper/single-walled carbon nanohorns hybrid material have been experimentally investigated and discussed.

1.2 Objectives of the research

The objective of this research is to investigate a process of single-walled carbon nanohorn surface modification using microwave irradiation. The effect of experimental parameters, which are irradiation power and irradiation time on the characteristics of modified single-walled carbon nanohorns have been analyzed and discussed. Copper precursor concentration is also examined with an expectation that the copper concentration would testify effectiveness of surface modification.

1.3 Scope of the research

To accomplish the objective of this research, scope of the research was schemed as follows;

1.3.1 Synthesis of single-walled carbon nanohorns (SWCNHs)

The synthesis method is gas-injected arc-in-water (GI-AIW) method.

1.3.1.1. Arc current supplied to the anode is 80 A

1.3.1.2. Gas injected is N_2, Flow rate of N_2 is 5 L/min

1.3.1.3. The anode is a graphite rod (purity 99.9995%) of 3 mm in diameter and 100 mm in length. The cathode is also a graphite rod (purity 99.9995%) of 12 mm in diameter with a large hole of 8 mm diameter and 25 mm depth on one side, and two channels with 2 mm in diameter for injecting gas into the arc zone (refer to chapter 3.3).

1.3.1.4. The anode feeding speed is controlled by a step moter with a constant speed of 1.5 mm/s

1.3.1.5. Characteristics of the synthesized particles

- Morphology study by Transmission Electron Microscope (TEM)
- Analysis z-potential by zetasizer to compare degree of modification
- Characterize functional group (C-O, C=O and COOH) on SWCNHs by Fourier Transform Infrared (FT-IR) spectrometer

1.3.2 Investigation of microwave – assisted treatment method

After surface modification, Cu/SWCNH composite will be prepared by microwave - polyol process with irradiation time of 300s, irradiation power of 360 W and ethylene glycol as solvent. Mainly, the following parameter and variables have been examined

1.3.2.1 Effect of microwave - irradiation time, in a range of 30 – 180 second

1.3.2.2 Effect of microwave - irradiation power, in a range of 90 – 800 W

1.3.2.3 Characteristics of the surface modification particles

- Analysis z-potential by zetasizer to compare degree of modification
- Characterize functional group (C-O, C=O and COOH) on SWCNHs by Fourier Transform Infrared (FT-IR) spectrometer

1.3.2.4 Characteristics of the composite particle

- Morphology & deposited distribution study by Transmission Electron Microscope (TEM)
- Characterize chemical composition and physical properties by X-ray Diffractometer (XRD)

1.3.3 Investigation of copper concentration effect on the characteristics of the prepared Cu/SWCNH composite

1.3.3.1. Copper concentration has been varied in a range of 15 – 60%

1.3.3.2. Characteristics of the composite particle

- Morphology & deposited distribution study by Transmission Electron Microscope (TEM)
- Characterize chemical composition and physical properties by X-ray Diffractometer (XRD)

1.4 Procedure of the research

In this research, procedure was split into 9 sections as follows;

1.4.1 Literature survey and review

1.4.2 Preparation of experimental materials and setup

1.4.3 Synthesis of Single-walled Carbon nanohorns (SWCNHs) by gas-injected arc-in-water (GI-AIW) method

1.4.4 Characterization of SWCNHs properties by SEM ,TEM, Raman, Zetasizer and FT-IR

1.4.5 Preparation of SWCNHs surface modification and Cu/SWCNH composite

1.4.6 Characterization of surface-modified SWCNHs properties by Zetasizer and FT-IR

1.4.7 Characterization of Cu/SWCNH properties by TEM and XRD

1.4.8 Making discussion and conclusion of all experimental results

1.4.9 Writing thesis and preparing conference articles

1.5 Expected benefit

- Knowledge and understanding of SWCNH surface modification by microwave - assisted chemical modification method

Chapter II

FUNDAMENTAL KNOWLEDGE AND LITERATURE REVIEWS

Some fundamental knowledge and typical literatures related to single-walled carbon nanohorns, copper nanoparticles, surface modification and polyol process have been reviewed to grasp the updated situation of related research works. This chapter is separated into 7 parts; i.) Single-walled carbon nanohorns ii.) Fabrication of single-walled carbon nanohorns iii.) Surface modification iv.) Microwave heating v.) Copper vi.) Polyol process and vii.) Reviews of other previous research works

2.1 Single-walled carbon nanohorns (SWCNHs) [3, 4, 18]

Single-walled carbon nanohorns are a new type of carbon particles found in 1999 by S. Iijima [3]. Their shape is nearly spherical particle. Average diameter is around 80 to 100 nm. There has horn-shaped radiating from the center of the particle and horn-shaped tips have cone angles of about 20°. The diameters of individual single-walled carbon nanohorns are 1-2 nm at the horn tips and 4-5 nm in the tubule-body part.

Three types of single-walled carbon nanohorns, 'dahlia-like', 'bud-like', and 'seed-like' were found. 'dahlia-like' is the single-walled carbon nanohorns, protruding from the aggregate surface and the others two are developed inside the particle itself.

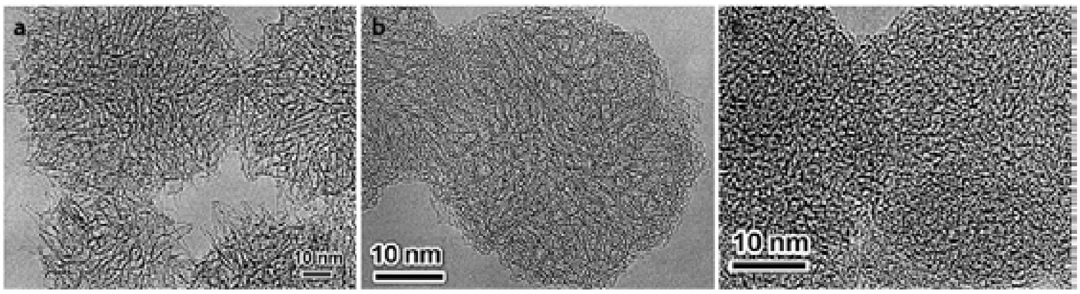


Figure 2.1 TEM images of a dahlia-like aggregate (a) a bug-like aggregate (b) and a seed-like aggregate (c) [3]

Single-walled carbon nanohorns and single-walled carbon nanotubes are made of single graphene sheets with hollow spaces inside. The diameter of single-walled carbon nanotubes is small therefore molecules would possibly be arranged in one-dimensional-like ordering, allowing detailed studies of their physics and chemistry in a highly constrained geometry. On the other hand, the diameter of single-walled carbon nanohorns is relatively large. Therefore, molecular movements, cluster formation and chemical reactions inside single-walled carbon nanohorns are conceptually three-dimensional-like, leading to useful applications in many aspects. For instance, a bundle of several nanohorns seems to be useful for holding catalysts or other materials.

2.2 Fabrication of single-walled carbon nanohorns

In order to fabricate single-walled carbon nanohorns, there are 2 main methods; CO_2 laser ablation and arc discharge.

1.) CO_2 laser ablation [3, 18, 19]

This technique makes use of CO_2 laser as an energy source for creating gas-phase carbon fragments. The laser is set in the reaction chamber with a vacuum pumping system. A piece of graphite rod that is a carbon source is laid in the chamber. The CO_2 laser is shooting to graphite rod target and then gas-phase carbon fragment is produced. In Ar ambient, the carbon fragment will form to single-walled carbon nanohorns. The purity of single-walled carbon nanohorns from this method is over than 90%. The main impurities are mixture structure of carbon nanoparticles and big chunks of graphitic particles.

The production capacity of this method is just about 10 g/day. Nowadays, there are many attempts to increase the production capacity. But the high production capacity comes with high investment cost because of high basic utility cost.

2.) Arc discharge [20, 21]

Arc discharge or 'arc in liquid' is recognized as one of cost effective methods. In some previous works, liquid nitrogen is used as 'liquid' to be a host of the arc plasma. For more cost reduction, water is used and introduces N_2 gas to the arc plasma area for excluding reactive gas.

Two graphite electrodes are immersed in de-ionized water. The arc discharge condition is carried out at a constant current around 30-80 A and a constant voltage around 30-50 V. The cathode has a large hole on one side for being as arc plasma area, and two small channels for injecting gas into the arc area. Single-walled carbon nanohorns are found as find powders floating on the water surface.

2.3 Surface treatment [18, 22, 23]

Surface characteristic of single-walled carbon nanohorns refers from their forming that tubule-part is pure-hexagon graphite while cone-part is pentagonal ring. The sidewalls of single-walled carbon nanohorns are defect-free therefore it is rather inert to chemical attack. With the same reason, single-walled carbon nanohorns are difficult to disperse in aqueous solution. The application of them is limited. Generation of functional groups is necessary.

Such surface functionalization enhances the reactivity, improves the specificity and provides possibility for further chemical modification, such as ion adsorption, metal deposition, and grafting reaction. Three main approaches to generate functional groups are i.) Surface groups generated through acid-induced oxidation of the carbon nanohorns surface. ii.) Direct addition to the carbon nanohorns sidewalls. iii.) Groups attached to polycyclic aromatic hydrocarbons that are immobilized to the carbon nanohorns surface through Van der Waals forces. There are several methods of the chemical treatment such as acid treatment, plasma treatment etc.

2.4 Microwave heating [24]

Dielectric heating could be applied by using high power of electromagnetic wave in radio frequency or microwave frequency pass through material. Any materials that possess a structure as dipolar molecules could be arranged by electromagnetic field following as electromagnetic field's direction. Because of such arrangement, each molecule is grazed and then thermal energy (heat) could be transmitted over the material. On the other word, thermal energy is transferred from wave to the material. Material that can be used in dielectric heating is any substances that respond to electromagnetic wave. Therefore, such material must have a structure as dipolar molecules. Material that has a structure as non-polar molecules such as air or glass can not absorb such thermal energy. Microwave will pass through the material by no heating or no any change. For metallic material, it reflects the wave so heat is not occurring. The efficient of dielectric heating is high because energy is transferred to the material directly. Another heating system transfer energy by convection or radiation from heat source.

2.5 Copper [25]

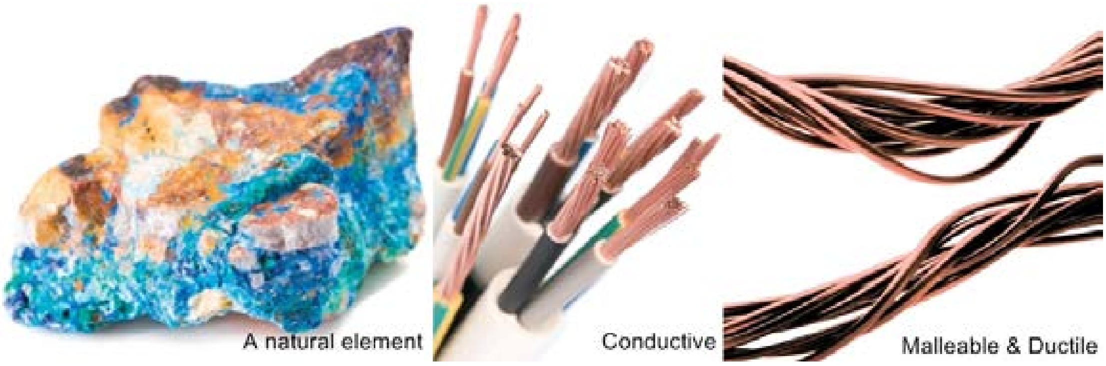


Figure 2.2 Copper is … (www.copper.org)

Copper, one of 94 spontaneously occurring elements on the Earth, is a metallic material with a reddish-orange color and metallic luster. Cu is its symbol, its atomic number is 29 and its atomic mass is 63.546. It is found in group 1B of the periodic table in the same group as silver and gold. With same group, some properties are similar. Copper is a soft, malleable and ductile metal. Because of its softness, the resistivity to transfer electron in metal at room temperature is relatively weak. So it partly explains that copper has high electrical conductivity and thus also high thermal conductivity. Although gold and silver have the highest conductivity, copper is a better conductor than most metals because copper is a large in number therefore cheaper material to use.

Copper forms many compounds with a couple of oxidation states. In general copper has 2 typical oxidation states; Cu^+ and Cu^{2+}, which are called cuprous and cupric, respectively. The properties of copper are shown in Table 2.1

Table 2.1 Properties of copper

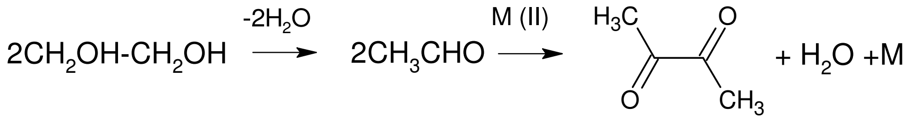
Properties	
Atomic number	29
Atomic mass	63.546 $g.mol^{-1}$
Density	8.9 $g.cm^{-3}$ at 20°C
Melting point	1083 °C
Boiling point	2595 °C
Vanderwaals radius	0.128 nm
Ionic radius	0.096 nm (+1) ; 0.069 nm (+3)
Isotopes	6
Electronic shell	[Ar]ff $3d^{10}$ $4s^{1}$
Energy of first ionization	743.5 $kJ.mol^{-1}$
Energy of second ionization	1946 $kJ.mol^{-1}$
Standard potential	+ 0.522 V (Cu^{+}/ Cu) ; + 0.345 V (Cu^{2+}/ Cu)
Electrical resistivity	16.78 nΩ·m at 20°C
Thermal conductivity	401 $W.m^{-1}.K^{-1}$

2.6 Polyol process [26, 27]

Polyol process is a process for preparation of fine powders of easily reducible metals such as copper, silver and nickel by reduction of inorganic compounds in liquid polyols (the compounds with numerous hydroxyl functional groups available for reactions). A relevant solid inorganic compound is suspended in a liquid polyol. The suspension is stirred and heated to a given temperature which can reach the boiling point of the polyol for the less easily reducible metals.

The general mechanism of the reaction occurred in the process has been investigated. The result shows that the reaction mentally carries on in two stages. In the first stage, the starting compound is converted to intermediate solid phase such as Cu_2O appears as an intermediate solid phase when CuO is reduced into Cu in ethylene glycol. In the second state, the intermediate solid phase is reduced to metal. The main aspect of this reaction stage is that the reduction reaction proceeds in the liquid state rather than in the solid state. Hence, the metal particles are acquired by nucleation and growth from the solution. The overall reaction can be schematized in equation 2.1.

For using ethylene glycol as polyol;



(2.1)

For applying microwave heating with this process (called microwave-polyol process), some properties of polyol needs to be considered. Dielectric constant (ε') represents the relative permittivity, which is a measure of the ability of a material to be polarized by an electric field. Among various polyols, ethylene glycol (EG) is mainly used because of its high dielectric constant and high reduction ability.

2.7 Reviews of other previous research works

The reviews of other previous research works is separated in 3 parts; i.) Synthesis of single-walled carbon nanohorns ii.) Surface modification by chemical treatment and iii.) Copper deposition on carbon nanohorns

2.7.1 Synthesis of single-walled carbon nanohorns (SWCNHs)

Sano [20] developed a new method to synthesize single-walled carbon nanohorns with cheaper operating cost than other methods. The method was arc-in-water method that injected gas into arc zone. After arc, single-walled carbon nanohorns floated on the water surface. More than 80% of product at water surface was single-walled carbon nanohorns. The key of the method was carbon vapor could leave arc zone rapidly and then form as single-walled carbon nanohorns in an inert zone containing N_2 gas.

Poonjarernslip et al. [21] synthesized single-walled carbon nanohorns hybridized with palladium (Pd) by N_2 gas-injected arc-in-water method. This method can synthesize hybrid material of Pd and single-walled carbon nanohorns in one step. Conditions of the method were following: Arc current 80 A with constant voltage 40 V, N_2 supply flow rate 5 L/min and anode raised up speed 1.5 mm/s. The cathode was a hollow graphite rod of 12 mm in diameter with a large hole of 8 mm diameter and 25 mm depth on one side, and two channels with 2 mm in diameter for injecting gas into the arc zone. The anode was a graphite rod of 3 mm in diameter. This condition can produce single-walled carbon nanohorns but for hybridized material with palladium, a palladium wire was need. It was inserted in the anode hole. Therefore during arc, arc zone had both carbon vapor and palladium vapor. After that two kinds of vapor underwent self-assembly to form hybrid material that had palladium inside of single-walled carbon nanohorns.

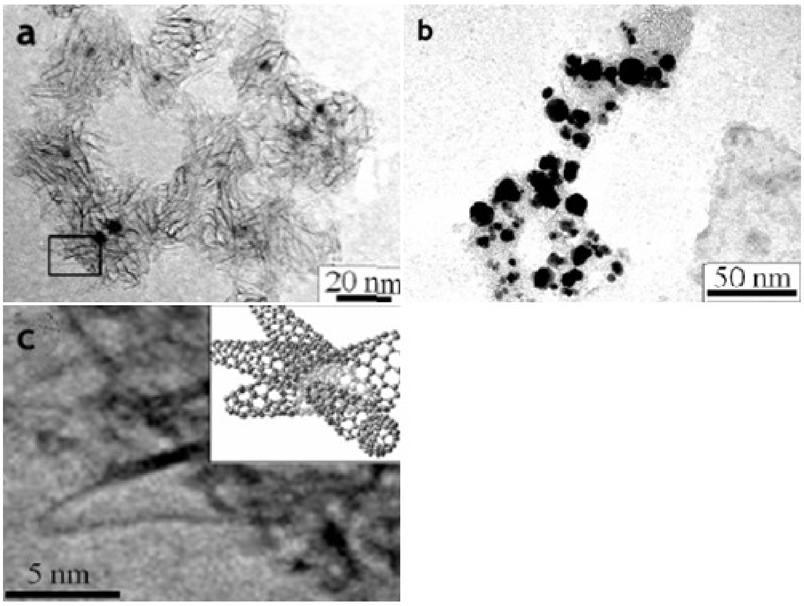


Figure 2.3 TEM image of SWCNH/Pd hybrid materials which were synthesized by inserting Pd wire of (a) 0.3 mm, (b) 0.5 mm in diameter inside anode hole; (c) a close-up image of protruding horn in SWCNHs from the square mark in (a) and their molecular models.

2.7.2 Surface modification by chemical treatment

Yu et al. [22] synthesized Pt deposited on carbon nanotubes. The researchers were interesting in chemical modification. The research compared kinds of oxidant between H_2SO_4-HNO_3 mixture and HNO_3 by use reflux time 5 hour. The results of TEM show that Pt can deposit on carbon nanohorns, modified by H_2SO_4-HNO_3 mixture better than those modified by HNO_3. After functional group checking, carbon nanohorns modified by H_2SO_4-HNO_3 mixture also found higher functional group number. The difference functional group was a sulfur-containing species.

Yu et al. [28] purified and functionalized multi-walled carbon nanotubes by oxidized with 65%HNO_3 at 40 °C for 40 min. Strong acid made defects and many kinds of functional group such as carboxylic acid and hydroxyl

Wang et al. [15] studied about using of microwave to rapid functionalize single-walled carbon nanotubes. They studied in amidation reaction. The conventional amidation reaction for single-walled carbon nanotubes has 3 steps with total reaction time at around 3 to 5 days. From this study, after applying microwave, the reaction step was reduced to 2 steps and the total reaction time was reduced to only 20 to 30 min. From FTIR result, carbonyl groups were occurred after treated with HNO_3 and then after reacted with 2, 6-dinitroaniline, amide linkages were occurred at the carbonyl groups.

Yoshida et al. [29] used microwave irradiation for chemical modification of carbon nanohorns. The research was study in finding minimum irradiances (irradiation time and irradiation power). The experiment was described as pour carbon nanohorns in glass tube and then gently place in microwave reactor. The result shows that carbon nanohorns after microwave irradiation had more oxygen-containing groups and 150 W/min was sufficient to oxidize carbon nanohorns.

2.7.3 Copper deposition on carbon nanohorns

Sun et al. [30] studied mechanism for preparing of copper power by polyol process. They used $CuSO_4 \cdot 5H_2O$ and NaOH mixed with ethylene glycol. The suspension was agitated and heated at speed 2 °C/min until it boiled. After that the suspension was kept temperature at 0.5 °C/min until its color changed to henna. Observation for reduction of cupric sulphate in ethylene glycol was color changing. Its color changed from Cambridge blue, deep blue, green, yellow, snuff, and henna, respectively. From XRD result of the solid after centrifuge, solid from deep blue sample had Na_2SO_4 with no copper compound. Solid from green to snuff sample found both Na_2SO_4 and Cu_2O and solid from henna sample found Cu instead of Cu_2O. It showed that the complex solution was reduced to cuprous oxide along with reaction time. The FTIR result showed that $CuSO_4 \cdot 5H_2O$ dissolve in ethylene glycol to form complex compound by Cu-O bond. After that the complex decomposed to cuprous oxide while ethylene glycol was partly changed to aldehyde in the beginning and in the end was oxidized to biacetyl.

Leelaviwat et al. [17] studied the effect of microwave irradiation time to fabricate copper/multi-walled carbon nanotubes hybrid material. They used mixture of $CuSO_4 \cdot 5H_2O$ and ethylene glycol with NaOH mixed with acid-treated multi-walled carbon nanotubes and then simple placed the mixture in household microwave. 360 W was used for this research and the irradiation time was varied from 1 to 9 min. From morphology of TEM, found that 1 min irradiation time could result in only small amount of copper decorated onto multi-walled carbon nanotubes. And after increasing the time longer than 1 min, more copper decorated on MWCNTs was found. At 7 and 9 min, agglomeration of copper was found. It showed that microwave irradiation time had an effect to form copper. From XRD result, 5 minute was enough for reduction of Cu^{2+} to Cu_2O and Cu. From all results, steps for forming of the copper onto multi-walled carbon nanotubes were following; i) Cu^{2+} precursor adsorb on surface of acid-treated multi-walled carbon nanotubes because of electrostatic attraction. And then ii.) Cu^{2+} was reduced with ethylene glycol and then copper nuclei grown up. iii.) Remained Cu^{2+} ion in system was reduced and grown on agglomerating Cu_2O and Cu.

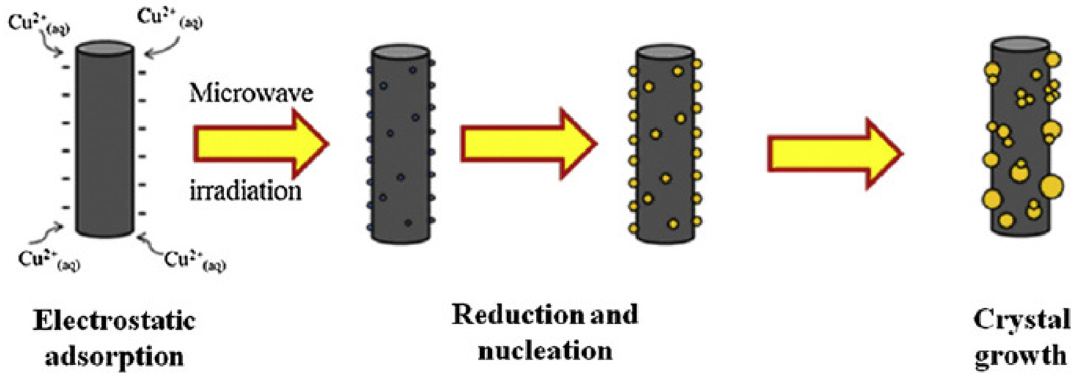


Figure 2.4 Schematic representation of copper nucleation and growth on MWCNT surface

Based on all literature reviews, there is a motivation that Cu/single-walled carbon nanohorn hybrid material could be considered as a novel research issue. However, processing time for preparing of cupper/ single-walled carbon nanohorns hybrids material should be shorter than conventional method by microwave irradiation.

Chapter III

RESEARCH METHODOLOGY

Based on our literature reviews, the following experimental procedures are designed for pursuing the research goal and objective. Experimental works would be separated into 3 parts; i.) synthesis of single-walled carbon nanohorns (SWCNHs) by gas-injected arc-in-water (GI-AIW) method, ii.) single-walled carbon nanohorns surface modification using microwave-assisted chemical modification and iii.) preparation of Copper/SWCNH hybrid material.

3.1 Chemical agents

Chemicals and raw materials required for synthesizing single-walled carbon nanohorns, modifying surface of single-walled carbon nanohorns and synthesizing copper/SWCNH hybrid material were listed in Table 3.1

Table 3.1 Chemical agents for synthesizing single-walled carbon nanohorns, modifying surface of single-walled carbon nanohorns and synthesizing copper/SWCNH hybrid material

Chemicals/Raw material	Manufacturer/Grade
Synthesis of single-walled carbon nanohorns	
Graphite rod	ALFA 99.9995%
Nitrogen gas (N_2)	TIG 99.99%
Single-walled carbon nanohorns surface modification	
Nitric acid (HNO_3)	J.T. Baker/Ar Grade 69-70%
Sulfuric acid (H_2SO_4)	QRëc/AR Grade 95-97%
Preparation of Copper/SWCNH hybrid material	
Copper(II) sulphate ($CuSO_4 \cdot 5H_2O$)	Asia Pacific Specially Chemicals /AR Grade
Ethylene glycol ($HOCH_2CH_2OH$)	QRëc/AR Grade 99.5%
Sodium hydroxide (NaOH)	Ajax Finechem/AR Grade

3.2 Equipments

The main and important equipment of this research is microwave oven. The microwave oven that was used is a simply household microwave oven. A model of household microwave oven for this research is LG MS-2127CW, which provides a maximum power of 800 W and frequency of magnetron operating at 2450 MHz.

Figure 3.1 Household microwave oven

Another equipment, tropical laboratory equipment used in this research were listed in Table 3.2

Table 3.2 Tropical Equipment for synthesizing single-walled carbon nanohorns, modifying surface of single-walled carbon nanohorns and synthesizing copper/SWCNH hybrid material

Equipments	Manufacturer
Ultrasonic bath	CREST 950 DAE
Hotplate stirrer	IKA RCT basic
Hot air oven	Memmert
Vacuum pump	GAST DOA-P504-BN
Filtration paper	WHATMAN Nylon membrane filter 0.2μm

3.3 Synthesis of single-walled carbon nanohorns (SWCNHs) by gas-injected arc-in-water (GI-AIW) method

Two graphite electrodes were immersed vertically in 2 L of de-ionized water. The arc discharge condition was carried out at a constant current at 80 A and a constant voltage at 40 V. The anode is a graphite rod (purity 99.9995%, ALFA) of 3 mm in diameter and 100 mm in length. The cathode is a graphite rod (purity 99.9995%, ALFA) of 12 mm in diameter with a large hole of 8 mm diameter and 25 mm depth on one side, and two channels with 2 mm in diameter for injecting gas into the arc zone. The dimension of electrodes was illustrated in Figure 3.2. The cathode was connected with gas supply tube and settled at top arm (fixed arm). The anode was settled at bottom arm (moving arm) and raised up vertically into cathode’s hole at a control speed at 1.5 mm/s. During the operation, nitrogen gas was supplied through the cathode at 5 L/min [21]. After the operation finished, sample was collected from the water surface and then dried in oven overnight before being characterized.

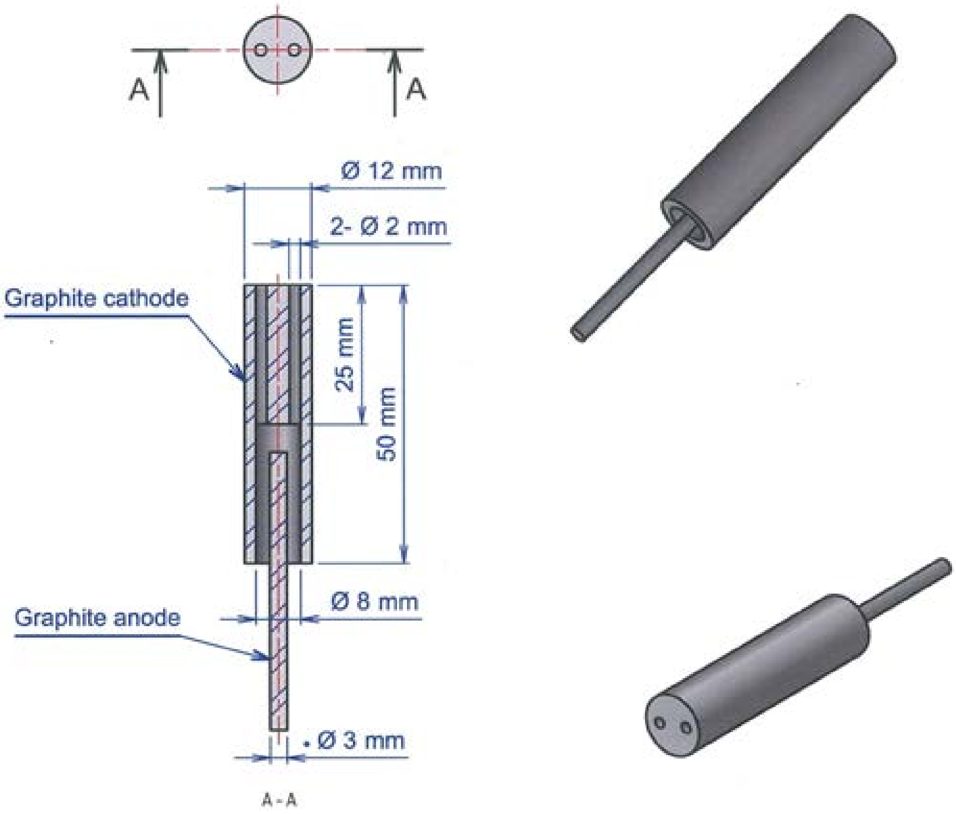


Figure 3.2 Dimension of electrodes employed in gas-injected arc-in-water (GI-AIW) method

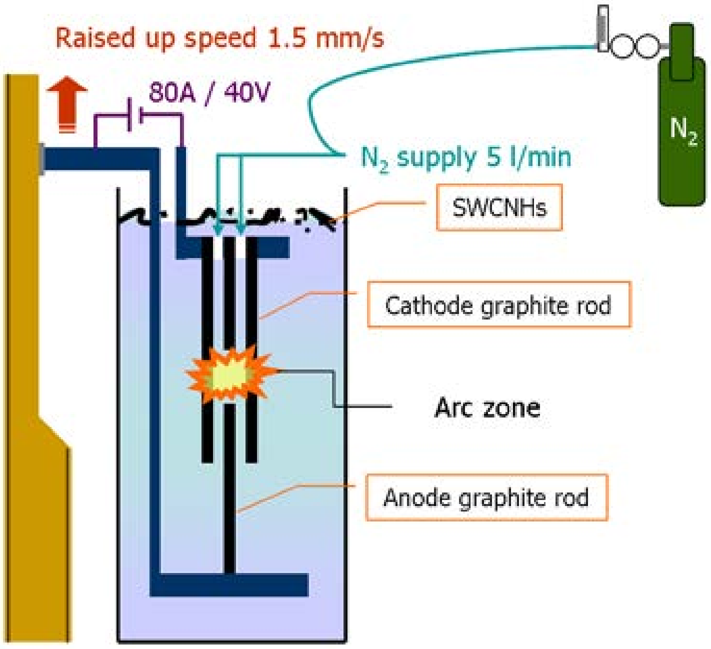


Figure 3.3 Schematic diagram of experimental set up for synthesis of single-walled carbon nanohorns (SWCNHs) by gas-injected arc-in-water (GI-AIW) method

3.4 Single-walled carbon nanohorns surface modification using microwave-assisted chemical modification

100 mg of pristine SWCNHs was sonicated into mixture of H_2SO_4 15 ml and HNO_3 5 ml. The dispersion was placed at the middle of a household microwave oven and heated at a given microwave irradiation power for a given time. The dispersion took from the oven was filtered and washed several time with de-ionized water until neutral. The obtained powder was dried in oven overnight at 100 °C before being characterized. The effect of microwave-irradiation time (30, 60, and 180 sec) and the effect of microwave-irradiation power (90, 360, 600 and 900 W) were investigated.

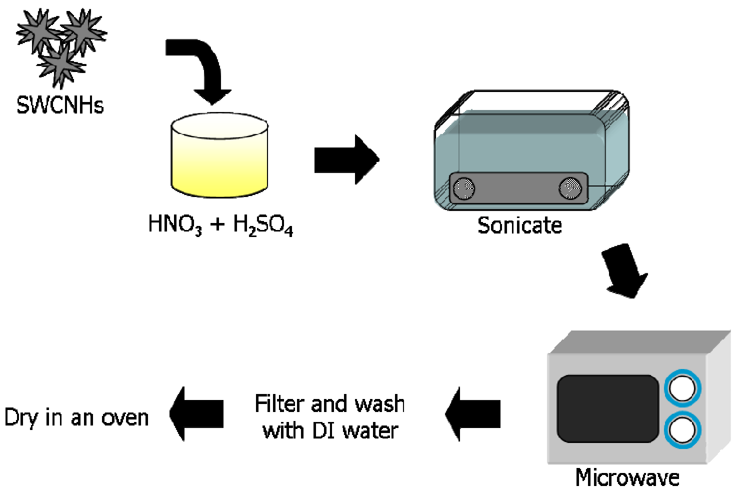


Figure 3.4 Schematic diagram of experimental set up for microwave-assisted chemical modification

3.5 Preparation of Copper/SWCNH hybrid material

$CuSO_4 \cdot 5H_2O$ was added into a mixture of ethylene glycol (EG) and NaOH by stirrer for 20 min. Then 50 mg of the acid-treated SWCNHs was added to 100 ml of the mixture of $CuSO_4$ in EG and NaOH in prior to ultrasonication. The dispersion was placed at the middle of a household microwave oven and irradiated with an input power of 360 W for 300 s [17]. The dispersion was taken from the oven, cooled down to room temperature, filtered, washed with several time of de-ionized water and dried in oven overnight. Effect of copper concentration, 15%, 30% and 60%, was investigated.

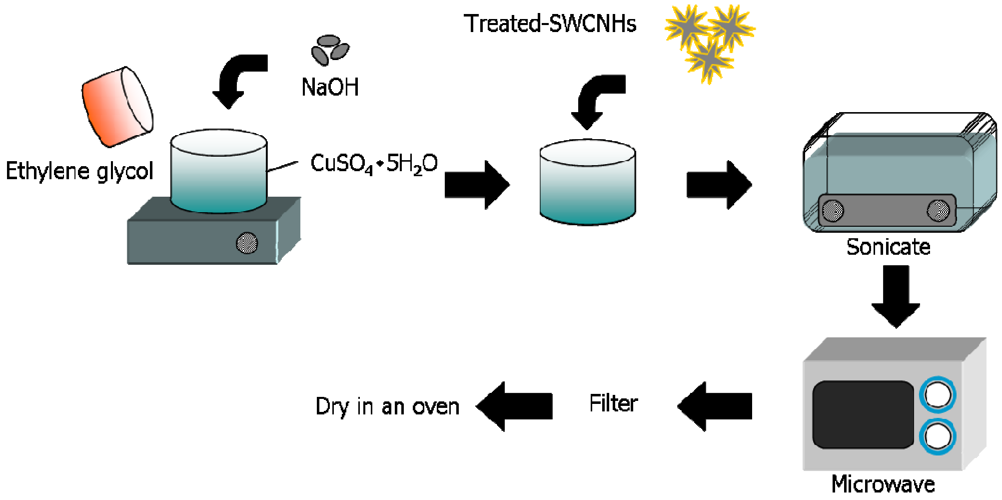


Figure 3.5 Schematic diagram of experimental set up for copper/SWCNH hybrid material

3.6 Analytical items and instruments

In this research, many analytical items and instruments were applied to characterize properties of synthesized material. Some detail and specifications of the equipments were described below.

3.6.1 Coating intensity of copper/SWCNH hybrid material

To analyze amount of copper loading onto SWCNHs' surface, image processing program was used. 'Image J' is the image processing program that selected. The program gave copper intensity, copper area and hybrid material area. The coating intensity is defined as the ratio of multiplication of copper intensity and copper area to hybrid material surface area as follow equation 3.1

$$
\begin{aligned}
Coating\_in.tensity &= \frac{Copper\_in.tensity \times Copper\_area}{4\pi r^2} \\
&= \frac{Copper\_in.tensity \times Copper\_area}{4(Hybrid\_material\_area)} \qquad (3.1)
\end{aligned}
$$

3.6.2 Uniformity of copper coating

Uniformity and coefficient of variation are statistic values. The coefficient of variation is defined as the ratio of standard deviation (SD) to average value ($\overline{\chi}$ of copper coating intensity as follow equation 3.2

$$\begin{aligned} Uniformity &= 1 - coefficient\_of\_\mathrm{var}iation \\ &= 1 - \frac{SD}{\overline{\chi}} \qquad (3.2) \end{aligned}$$

3.6.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was used to analyze morphology of single-walled carbon nanohorns and copper/SWCNH hybrid material. The TEM Jeol JEM-2100 model can operated in magnification range from x50 to x1,500,000. The analysis was done at Scientific and Technological Research Equipment Centre Foundation and Department of chemical, faculty of engineering, Chulalongkong University. A picture of the equipment was shown in Figure 3.7.

Figure 3.6 Transmission electron microscopy (TEM, Jeol JEM-2100)

3.6.4 Zetasizer

A potential on the surface of acid treated single-walled carbon nanohorns was measured by Zetasizer (Zetasizer Nano ZS, Malvern Instrument Limited) at National Metal and Materials Technology Center. He-Ne laser source was used. De-ionized water was used as dispersion medium. A picture of the equipment was shown in Figure 3.8.

Figure 3.7 Zetasizer (Zetasizer Nano ZS, Malvern Instrument Limited)

3.6.5 Fourier transform infrared spectroscopy (FTIR)

The functional groups on the surface of synthesis sample were determined by Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Scientific) using KBr pellets at Center of Excellence in Particle Technology, Chulalongkorn University. The spectrometer collected spectra from 400 cm^{-1} to 4000 cm^{-1} with resolution of 2 cm^{-1} and number of scans 64. A picture of the equipment was shown in Figure 3.9.

Figure 3.8 Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Scientific)

3.6.6 Raman spectroscopy

Crystallinity of single-walled carbon nanohorns was distinguished by Raman spectroscopy (DXR SmartRaman, Thermo Scientific) at Center of Excellence in Particle Technology, Chulalongkorn University. A picture of the equipment was shown in Figure 3.10.

Figure 3.9 Raman spectroscopy (DXR SmartRaman, Thermo Scientific)

Raman spectroscopy is a useful technique for identifying sp^2 and sp^3 hybridized carbon atoms. Figure 3.11 illustrates typical Raman spectrum of carbonaceous material. The D-mode, appears at approximately 1350 cm^{-1}, is caused by disordered structure carbon. The G-mode, appears at approximately 1583 cm^{-1}, is referred to sp^2 carbon systems [31, 32].

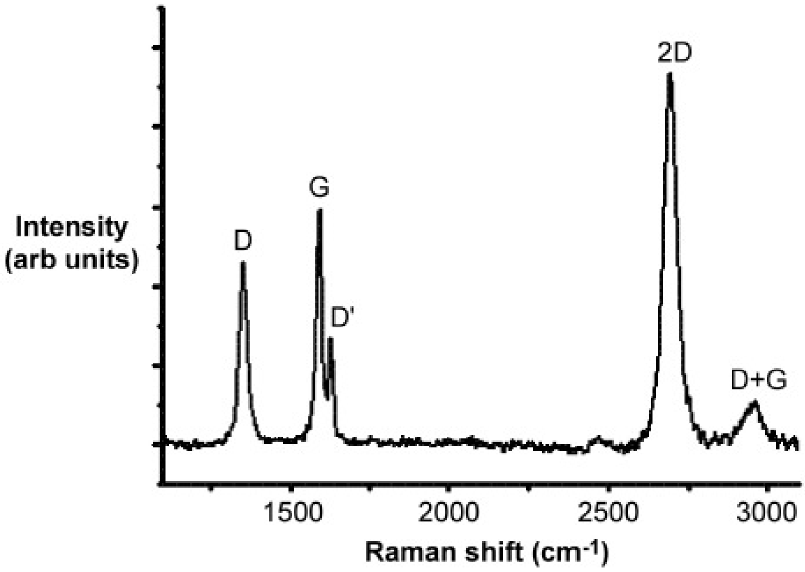


Figure 3.10 Typical Raman spectrum of carbonaceous material [31]

3.6.7 X-Ray Diffractometer (XRD)

Crystal structure and chemical component of copper/SWCNH hybrid material were characterized by X-Ray Diffractometer (XRD, Bruker D8 ADVANCE) at Scientific and Technological Service, Faculty of science, Chulalong University. The scanning angle is started from 5° to 80°. A picture of the equipment was shown in Figure 3.12.

Figure 3.11 X-Ray Diffractometer (XRD, Bruker D8 ADVANCE)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of single-walled carbon nanohorns (SWCNHs) by gas-injected arc-in-water (GI-AIW) method

In order to synthesize hybrid material of copper nanoparticles and SWCNHs, preparation of SWCNHs was concluded as the first step. Gas-injected arc-in-water (GI-AIW) method was selected because of its advantages on low- operating cost and providing SWCNHs with high purity. The synthesized product was characterized to confirm their properties.

Figure 4.1 reveals typical TEM images of the single-walled carbon nanohorns synthesized by GI-AIW method. These images show that SWCNHs make up of agglomeration of many single-walled horns. SWCNH agglomerates exhibit nominal size ranged from 60 to 100 nm. Other kinds of carbon nanoparticles, such as multi-walled carbon nanotubes were not found. The synthesized product has high purity.

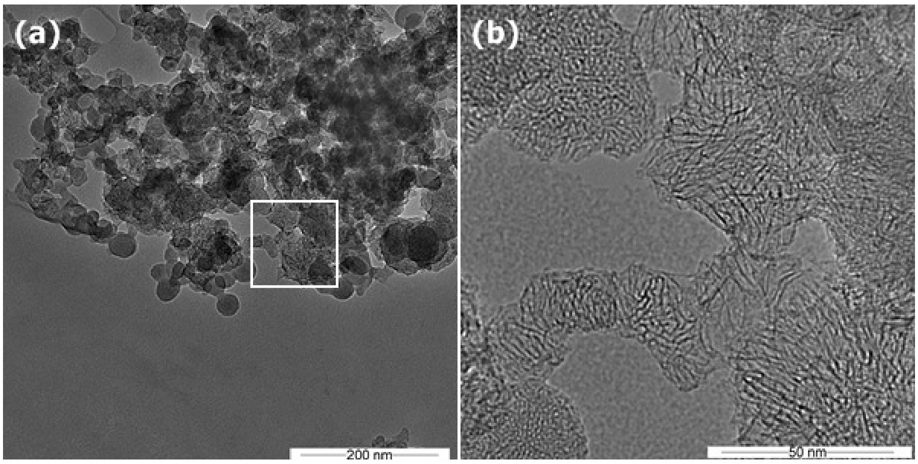


Figure 4.1 Typical TEM images of the SWCNHs synthesized by GI-AIW method

(a) Low magnification image (b) High magnification image

Particle size distribution (PSD) of the synthesized product was determined by dynamic light scattering (DLS). Figure 4.2 presents the particle size distribution ranges from 50 to 340 nm, with a peak at 122 nm. Both TEM result and the DLS result reveal that the synthesized SWCNHs tend to form agglomerate with nominal size in several hundred of nanometers.

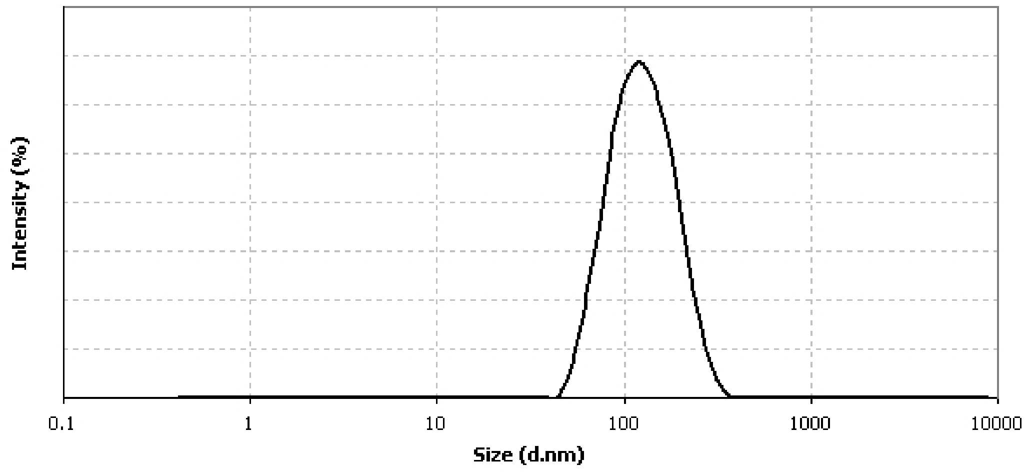


Figure 4.2 Particle size distribution of typical sample of SWCNHs determined by DLS

Because another unique property of SWCNHs is crystallinity, Raman spectroscopy was then employed for further analysis. Figure 4.3 exhibits the Raman spectra of the synthesized SWCNHs in comparison with commercial multi-walled carbon nanotubes (MWCNTs). Typical signals of Raman spectrum in carbonaceous material are described as follows; The D-band, appears at Raman shift of 1350 cm^{-1}, the G-band, appears at 1583 cm^{-1}, the D′-band, appears at 1620 cm^{-1}, and the 2D-band appears at 2680 cm^{-1} [31, 32].

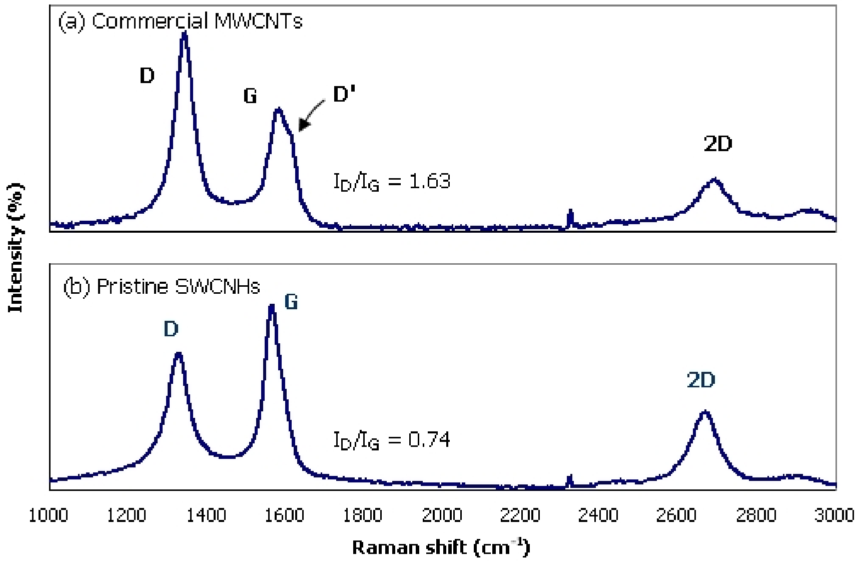


Figure 4.3 The Raman spectra of (a) commercial MWCNTs and (b) synthesized SWCNHs

The D′-band is one of the Raman shift that identify the difference between CNHs and CNTs. Kaneko et al. reported CNHs has only single peak of G-band but the G-band of CNTs can split into two peaks, G-band and D′-band [33]. Similarly, this experimental result shows that the synthesized product has only a single of G-band. Therefore, it could be implied that the synthesized product is CNHs with high purity. For confirmation of the number of wall of the product, the 2D-band is used. The shape of 2D-band is much different in single-layer graphene. Higher intense and sharper are character of single-layer graphene comparing with multi-layer graphene. From figure 4.3, 2D-band of synthesized product is much more intense and sharper than that of commercial MWCNTs. From above results can confirm that the synthesized product is SWCNHs.

4.2 Microwave-assisted acid treatment for SWCNH surface modification

In general, reactive surface of SWCNHs would affect preparation of hybrid material. It is indispensable for modifying the surface of SWCNHs. Study in applying microwave for acid oxidation, two effects were selected, irradiation time and irradiation power. Firstly, irradiation time was preferred. To investigate the effect of irradiation time, the irradiation power was settled at 360 W and irradiation time was varied from 30 sec to 180 sec. Subsequently, the properties of acid treated SWCNHs were distinguished.

4.2.1 Effect of irradiation time on surface properties

Figure 4.4 exhibits surface polarity of both pristine and acid treated SWCNHs. The surface polarity was determined by zeta potential value that measured by Zetasizer. Reference line in the figure represents the zeta potential value of acid treated SWCNHs which treated by conventional method. The conventional method generally spends 3 hours for ultrasonication [22]. It could be observed that, the acid treated SWCNHs reveal higher negative polarity than that of pristine SWCNHs. The longer treatment time would provide the higher negative polarity. Based on our experimental results, the microwave-assisted method with a treatment time of 45 sec could provide the SWCNHs with the same polarity level as that of the conventional method which spent treatment time of 3 hours. However, with a irradiation time longer than 45 sec, the surface polarity of the acid treated SWCNHs would reach an equilibrium which results in the saturated zeta potential value. These results would suggest that there is an optimal condition of irradiation time which could provide an equilibrated polarity on the surface of acid treated SWCNHs.

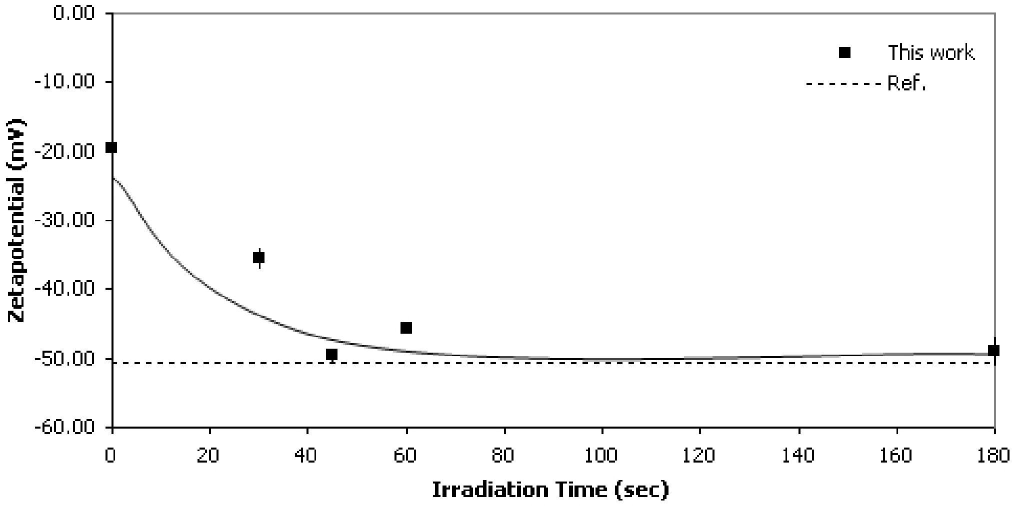


Figure 4.4 Zeta potential of acid treated SWCNHs samples with different irradiation time

The zeta potential analysis would suggest that surface properties of acid treated SWCNHs would change with regard to treatment condition. Therefore, FT-IR is employed to identify the presence of some radicals on the SWCNH surface. As could be observed in figure 4.5, comparison of FT-IR spectra of pristine and acid treated SWCNHs with different irradiation time present some typical peaks at approximately 1081, 1416, 1584, 1735, 2872 and 2928 cm^{-1}. The peak at approximately 1081 cm^{-1} represents C-O stretching bond, the peak at approximately 1416 cm^{-1} for O-H bending bond, the peak at approximately 1584 cm^{-1} for C=C stretching bond originated from structure of carbon nanohorns, the peak at approximately 1735 cm^{-1} for C=O stretching bond of carboxylic acid and both peaks at 2872 and 2928 cm^{-1} for CH_2/CH_3 stretching bond [34]. Such comparison of pristine and acid treated SWCNHs suggests that the CH_2/CH_3 stretching bond disappears upon the acid treatment and there are additional functional groups onto the surface of the acid treated SWCNHs. The additional functional groups (hydroxyl, carboxylic and carbonyl groups) have a good polarizability which affect to hydrophilicity.

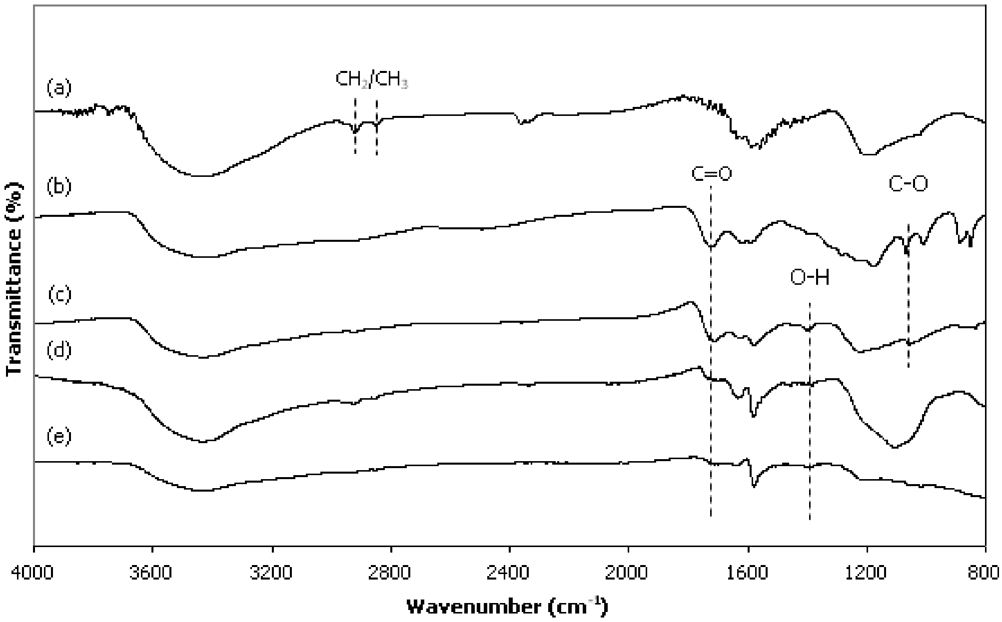


Figure 4.5 FT-IR spectra of (a) pristine SWCNHs, (b) acid treated SWCNHs at 360 W for 30 sec, (c) acid treated SWCNHs at 360 W for 45 sec, (d) acid treated SWCNHs at 360 W for 60 sec and (e) acid treated SWCNHs at 360 W for 180 sec

To confirm of dispersion ability, one of the reachable methods is dispersion of powder sample in a polar media then study on the powder sample nature in a polar media [7, 35]. Figure 4.6 exhibits photographs of the dispersion of the pristine and the acid treated SWCNHs in de-ionize water immediately after sonication. It could be observed that only the colloidal dispersion of pristine SWCNHs could not be dispersed into de-ionize water. The samples of acid treated SWCNHs dispersion are well dispersed, suggesting that the presence of functional groups on the surface of acid treated SWCNHs could enhance their dispersibility and concequently result in lower agglomeration.

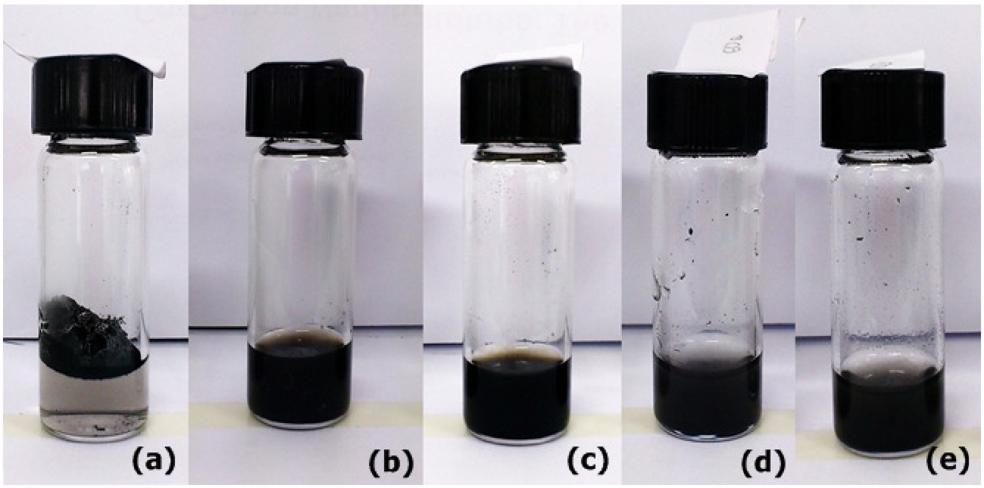


Figure 4.6 Photographs of the dispersion solution of (a) pristine and acid treated SWCNHs (b) at 360 W for 30 sec, (c) 360 W for 45 sec (d) at 360 W for 60 sec and (e) at 360 W for 180 sec in de-ionize water immediately after sonication

After leaved quiescently for one day, the colloid dispersion of acid treated SWCNHs irradiated at 360 W for 60 sec and 180 sec settle down as shown in figure 4.7(A). Figure 4.7(B) shows the dispersion after leaved for 1 month later. It should be noted that the acid treated SWCNHs with irradiation at 360 W for 30 sec and 45 sec show better dispersibility in de-ionize water. Regarding to all results (zeta potential, FT-IR and water dispersibility) it would be advocated that the acid treated SWCNHs would possess better hydrophilicity, which would be beneficial to a process of hybridizing with Cu nanoparticles.

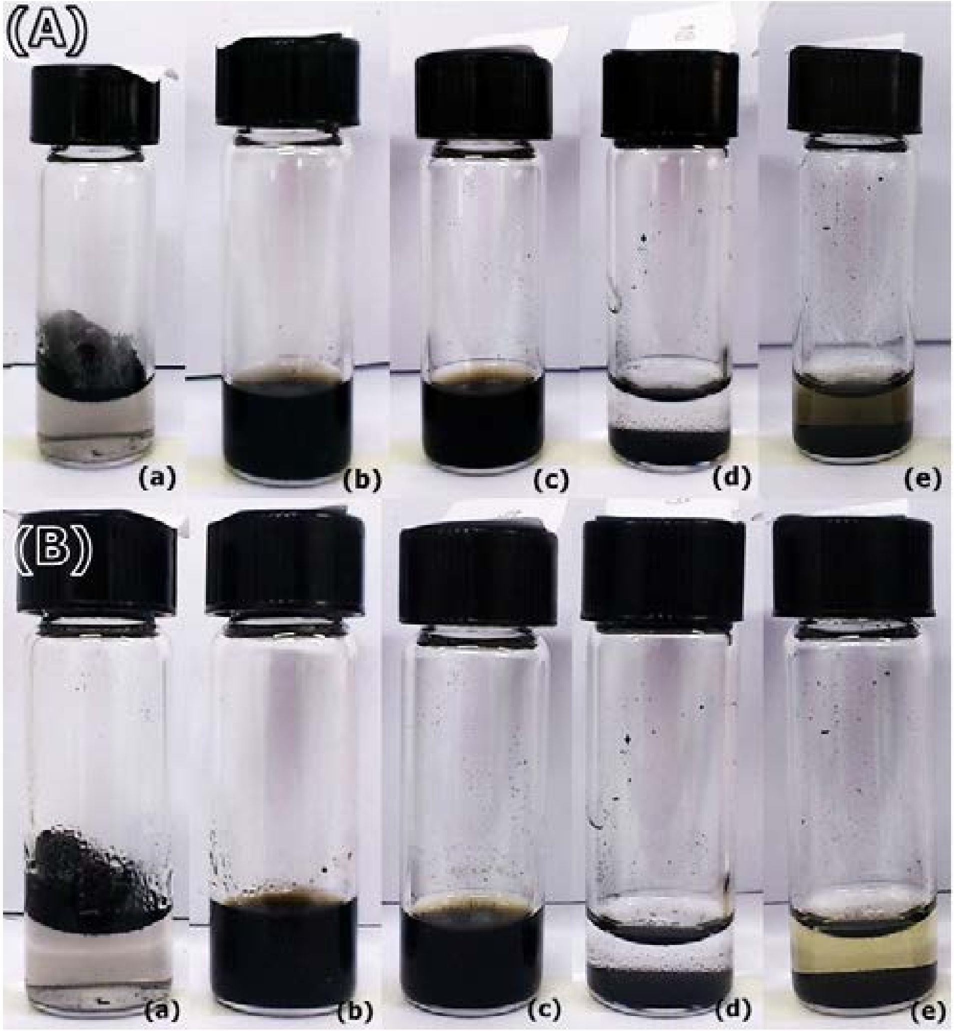


Figure 4.7 Photographs of the dispersion solution in de-ionize water of (a) pristine and acid treated SWCNHs (b) at 360 W for 30 sec, (c) 360 W for 45 sec (d) at 360 W for 60 sec and (e) at 360 W for 180 sec after sonication (A) 1 day and (B) 1 month

Figure 4.8 shows particle size distribution before and after of acid treatment SWCNHs at 360 W for 45 sec. The size distribution after acid treatment of SWCNHs is shifted to bigger particle size. Average particle size of pristine SWCNHs is approximately 120 nm and that of acid treated SWCNHs at 360 W for 45 sec is approximately 257 nm. For longer irradiation time, it could be observed that standard deviation (SD) of particle size become larger as shown in table 4.1. It suggests that SWCNHs after acid treated with longer irradiation is easy to agglomerate. It might because of intermolecular hydrogen bonding between COOH groups as exhibited in figure 4.9 [36, 37].

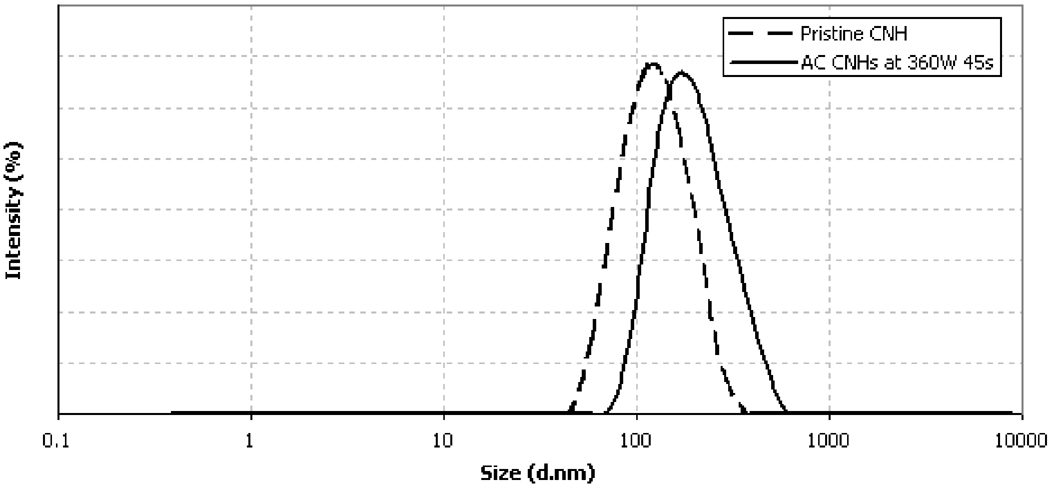


Figure 4.8 Particle size distributions of SWCNHs before and after acid treatment at 360 W for 45 sec

Table 4.1 Particle size and its deviation of SWCNHs and acid treated SWCNHs

Sample name	Particle size (d.nm)			
	1	2	3	Average
Pristine SWCNHs	118.40	119.60	120.50	119.50 ±1.05
Acid treated SWCNHs at 360 W for 45 sec	258.80	252.30	243.00	251.37 ±7.94
Acid treated SWCNHs at 360 W for 60 sec	649.70	592.30	691.60	644.53 ±49.85
Acid treated SWCNHs at 360 W for 180 sec	525.20	506.30	422.50	484.67 ±54.66

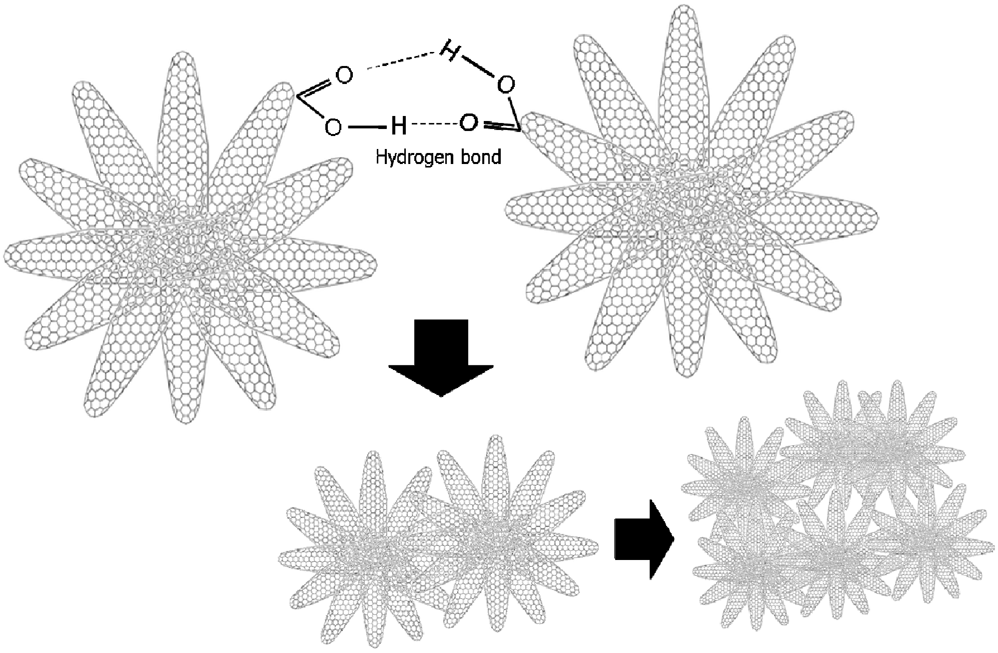


Figure 4.9 Schematic of agglomeration in acid treated SWCNHs by intermolecular hydrogen bond

4.2.2 Effect of irradiation power on surface properties

From the study in effect of irradiation time in section 4.2.1 advises that longer irradiation time purpose higher negative polarity. However, over surface treatment affect to worse dispersibility. Due to the results, irradiation time of 45 sec is selected for the study in second effect. The second effect for our research in microwave-assisted acid treatment process is effect of irradiation power. To interrogate the effect of irradiation time, the irradiation time was settled at 45 sec and irradiation power was varied from 90 W to 800 W. The irradiation power in this research means total irradiation power which supply to experimental system in the irradiation time of 45 sec.

FT-IR was employed to characterized functional group on the surface of acid treated SWCNHs with different irradiation power as shown in figure 4.10. The results match with the results of the study in effect of irradiation time. The CH_2/CH_3 stretching peaks are faded away and three new peaks are shown up. Three new peaks are the peak of C=O stretching, O-H bending and C-O stretching that appear at approximately 1735, 1416 and 1081 cm^{-1} respectively [22]. Comparing four spectra of acid treated SWCNHs with irradiation power of 90 W, 360 W, 600 W and 800 W, there are not significant different in peak position of each spectra. It should be note that just small irradiation power of 90 W is enough for treatment the surface of SWCNHs.

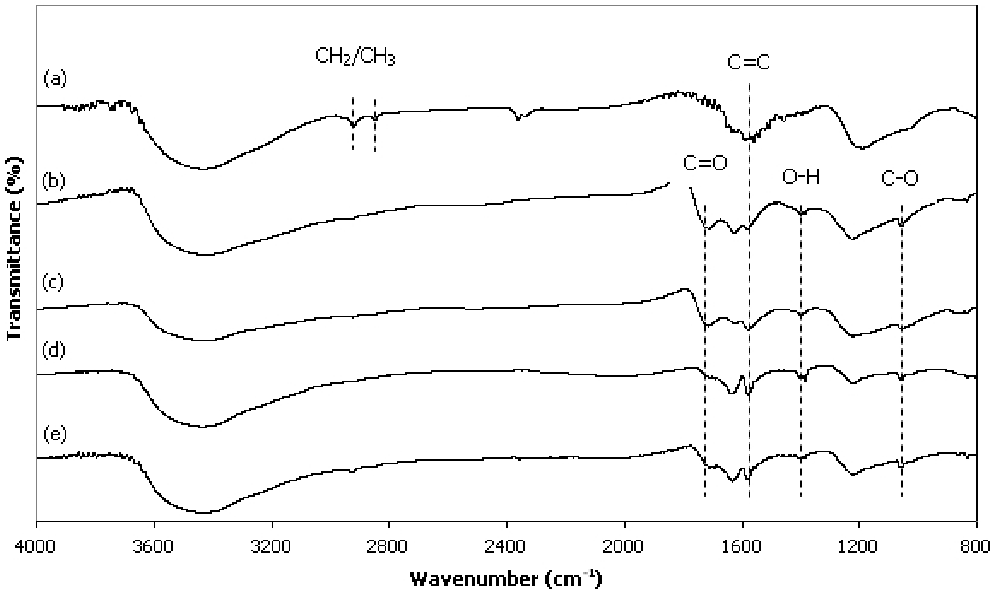


Figure 4.10 FT-IR spectra of (a) pristine SWCNHs, (b) acid treated SWCNHs at 90 W for 45 sec, (c) acid treated SWCNHs at 360 W for 45 sec, (d) acid treated SWCNHs at 600 W for 45 sec and (e) acid treated SWCNHs at 800 W for 45 sec

Figure 4.11 displays photographs of the colloidal dispersion of pristine SWCNHs and acid treated SWCNHs with different irradiation power after sonication immediately and 1 month later. As could be observed in figure 4.11(A), all different power conditions of acid treated SWCNHs are well disperse in water. Even though the dispersions were left for 1 month, there is no coagulation in any sample as seen in figure 4.11(B). The results are in good agreement with FT-IR results which small irradiation power is required for surface treatment of SWCNHs.

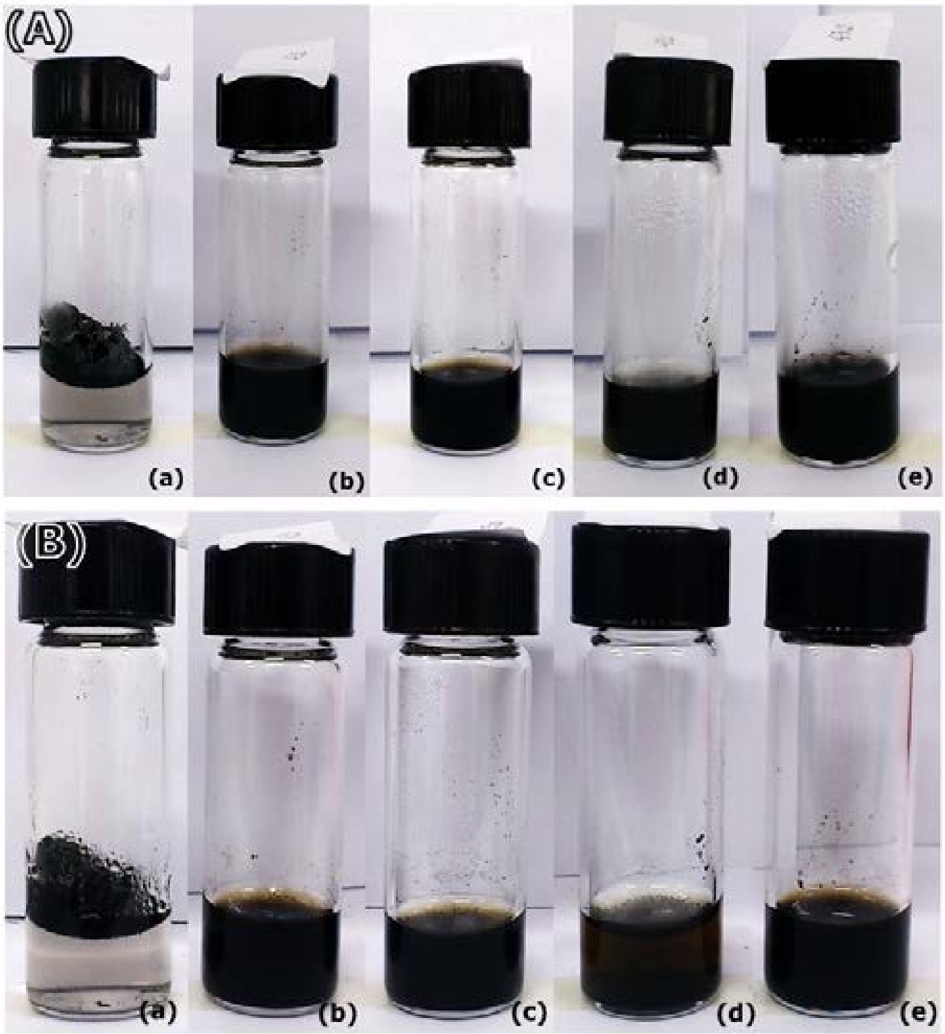


Figure 4.11 Photographs of the dispersion solution in de-ionize water of (a) pristine and acid treated SWCNHs (b) at 90 W for 45 sec, (c) 360 W for 45 sec (d) at 600 W for 45 sec and (e) at 800 W for 45 sec (A) after sonication immediately and (B) 1 month later

Figure 4.12 depicts Raman spectra of pristine SWCNHs and acid treated SWCNHs at 90 W for 45 sec. The Raman was applied for confirmation of crystallinity after acid treatment. As evident from the figure, the ratio between intensity of D-band and that of G-band (I_D/I_G) are not significant different. I_D/I_G of pristine SWCNHs and acid treated SWCNHs at 90 W for 45 sec is 0.74 and 0.80 respectively. It seems that acid treatment could not destroy the crystallinity of SWCNHs.

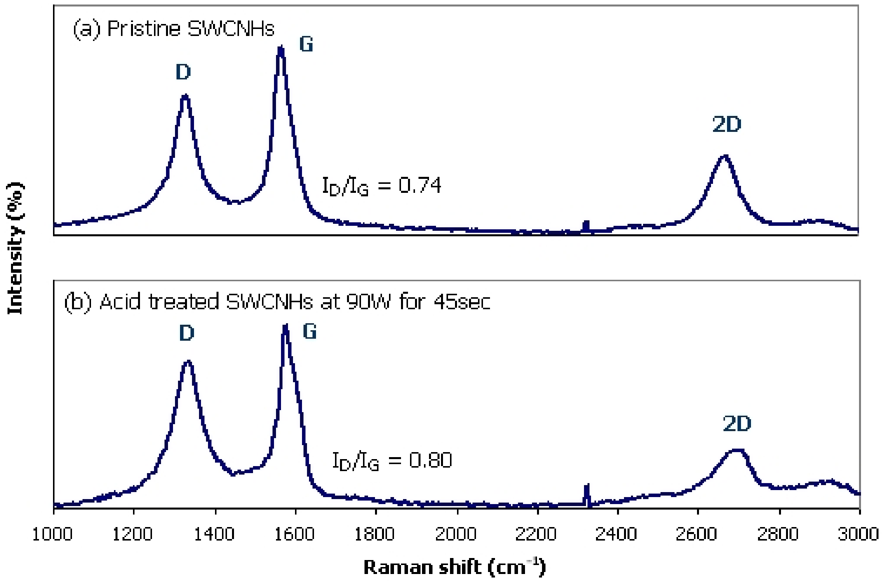


Figure 4.12 Raman spectra of (a) pristine SWCNHs and (b) acid treated SWCNHs at 90 W for 45 sec

4.3 Copper/SWCNH hybrid material preparation

In previous section, the effects of irradiation time and irradiation power on the surface properties of SWCNHs were investigated. In this section, the effects on properties of copper/SWCNH hybrid material were examined. Acid treated SWCNHs, which were treated with different conditions, were hybridized with copper precursor by microwave-polyol process. The condition of microwave for hybridizing of copper and SWCNHs was set at 360 W for 5 min. The copper concentration for the study is 60 wt%. Subsequently the properties of copper/SWCNH hybrid material were distinguished.

4.3.1 Effect of irradiation time at acid treatment on properties of copper/SWCNH hybrid material

Figure 4.13 shows TEM micrographs of copper/SWCNH hybrid material with different irradiation time of acid treatment process. It could be inspected in figure 4.13(a), copper cluster can partially coat on SWCNHs. With irradiation time longer than 45 sec, almost of SWCNHs surface are coated with clusters of copper nanoparticles.

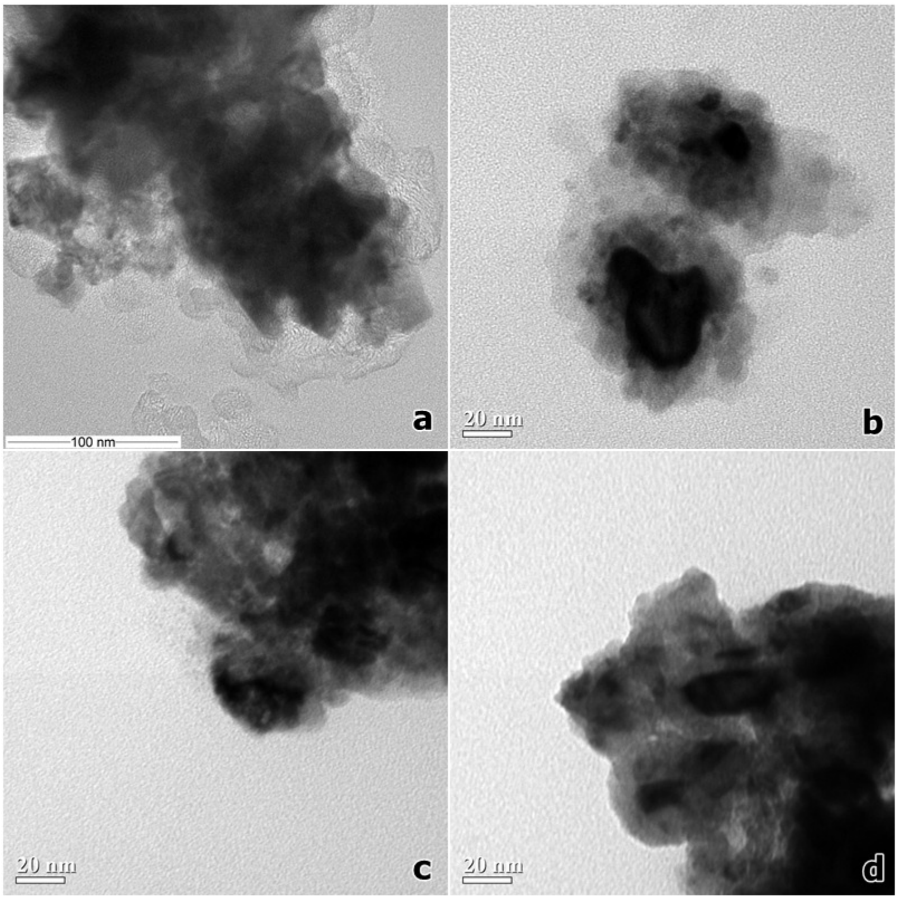


Figure 4.13 TEM micrographs of Cu/SWCNH hybrid materials of (a) pristine SWCNHs and Cu/SWCNH hybrid materials with different irradiation time of acid treatment process: (b) 30 sec, (c) 45 sec and (d) 60 sec.

The surface of hybrid material was indicated by FT-IR. As depicted in figure 4.14, FT-IR spectra of acid treated SWCNHs with irradiation power of 360 W for 45 sec, exhibit a peak at 1735 cm^{-1}, which is C=O stretching bond of carboxylic acid. Nevertheless, the peak could not be observed in the sample of Cu/SWCNH hybrid material. Meanwhile, there is a new peak of Cu-O stretching appears at 626 cm^{-1} for the copper/SWCNH hybrid material fabricated under the same microwave irradiating condition [38].

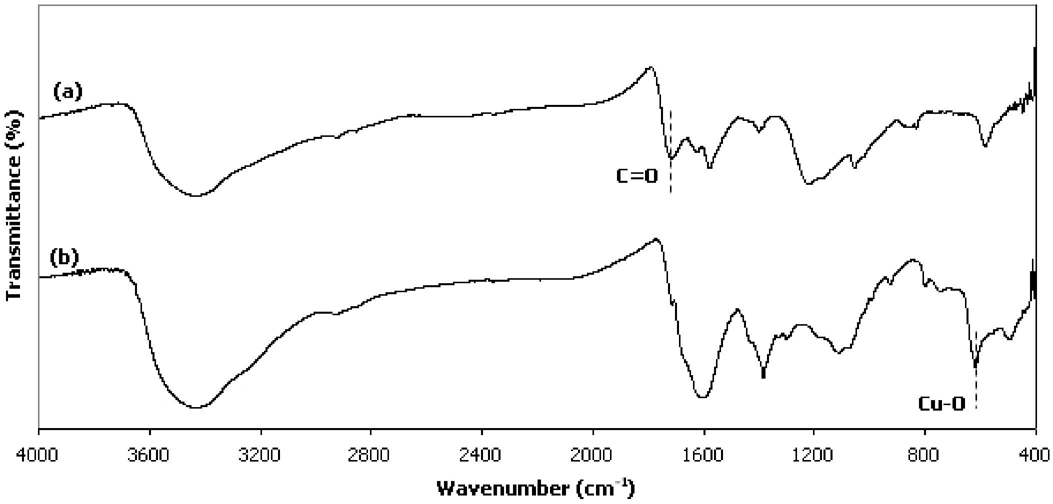


Figure 4.14 FT-IR spectra of (a) acid treated SWCNHs and (b) Cu/SWCNH hybrid materials fabricated with microwave irradiation at 360 W for 45 sec in acid treatment process.

The XRD pattern in figure 4.15 illustrates the diffraction profile of pristine SWCNHs and copper/SWCNH hybrid material with different irradiation time at acid treatment process. The identically peak for carbon appear at approximately 26.5°. Common peaks of copper compound are defined as follow; peaks at approximately 43.42° and 50.54° represent the (111) and (200) plane of the face centered Cu, respectively. Peaks at approximately 35.98° and 39.26° represent the (111) and (200) plane of cupric oxide (CuO) respectively. Peaks at approximately 36.42°, 42.34° and 61.52° represent the (111), (200) and (220) plane of cuprous oxide (Cu_2O) respectively [39, 40]. As evident from the figure, all three diffraction profiles of hybrid materials with irradiation time 30, 45 and 60 sec at acid treatment process manifest the presence of cuprous oxide and copper. The results are qualitatively similar to those of earlier microwave-polyol process studies. Leelaviwat et al. found that the reduction of Cu precursor with irradiation power 360 W for 5 min could provides Cu but the Cu is easy to oxidize to form Cu_2O during synthesis [17].

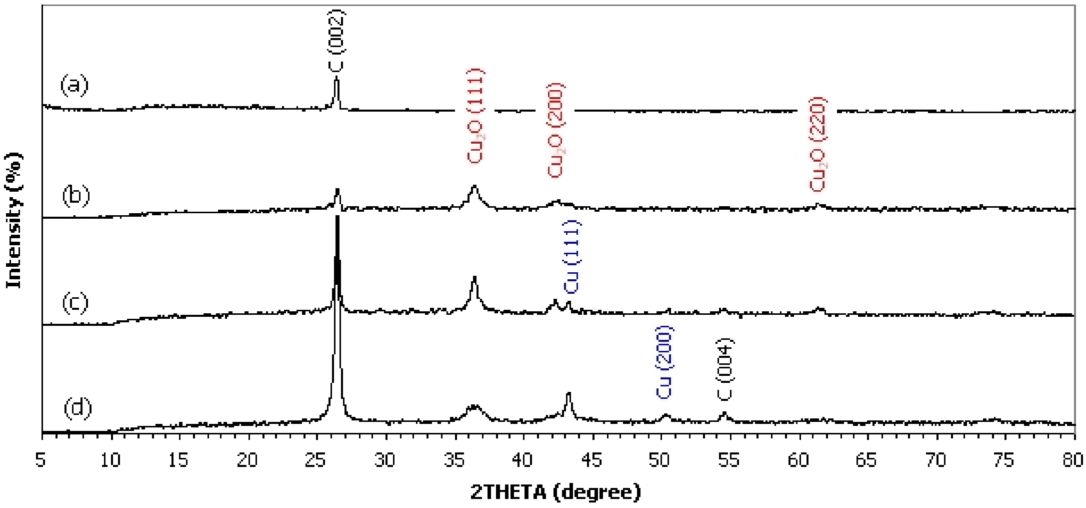


Figure 4.15 The XRD profile of (a) pristine SWCNHs and Cu/SWCNH hybrid materials with different irradiation time of acid treatment process: (b) 30 sec, (c) 45 sec and (d) 60 sec.

To corroborate amount of copper compound coating on SWCNHs surface, image processing technique is also employed. TEM image, not only provide morphology of the particle but also provide different image intensity because of different electron transmission ability in different type and thickness of specimen. Volume and area of Cu nanoparticles and SWCNHs are analytically extracted from TEM images using software of Image J. The coating intensity of Cu nanoparticles on the surface of SWCNHs which are irradiated by microwave for 30, 45 and 60 sec is depicted in figure 4.16. It appears that the coating intensity is increasing by increasing of irradiation time. Similarly trend with uniformity results in figure 4.17, long irradiation time obtains a high uniformity. These results are good agreement with zeta potential after acid treatment results. The high contents of negative polarity would increase possibility of Cu^{2+} ion to anchor onto the surface of acid treated SWCNHs. With irradiation time of 60 sec a higher coating intensity and uniformity could be achieved, supporting the idea that growth process of Cu nanoparticle clusters on the surface of SWCNHs could be enhanced by a longer stimulating time.

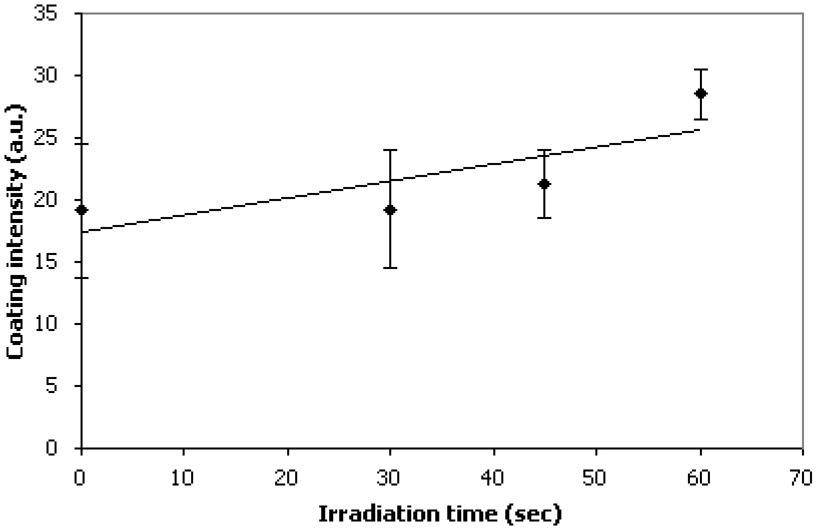


Figure 4.16 The coating intensity of Cu/SWCNH hybrid material with different irradiation time

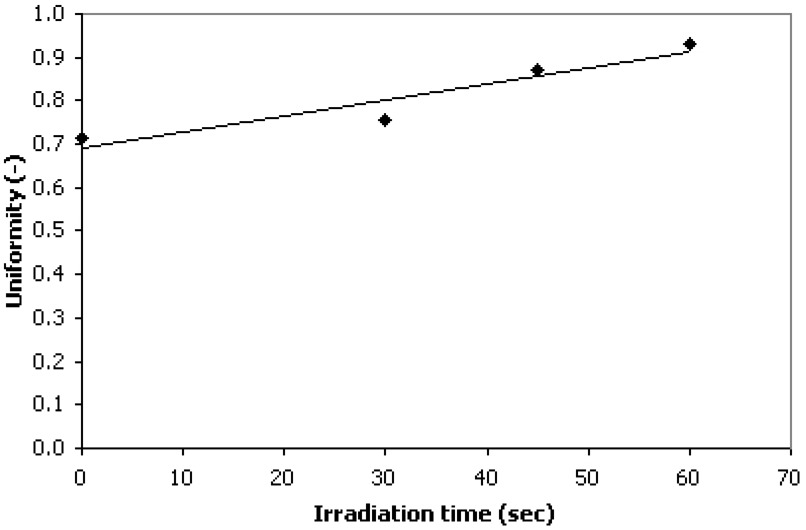


Figure 4.17 The uniformity of Cu/SWCNH hybrid material with different irradiation time

4.3.2 Effect of irradiation power in acid treatment on properties of copper/SWCNH hybrid material

Morphology of copper/SWCNH hybrid materials with acid treatment by different irradiation power was characterized by TEM as shown in figure 4.18. As evident from the figure, only in figure 4.18(a) can observe SWCNHs without copper coating. Figure 4.18(b) – 4.18(e) display copper cluster coat all over the surface of SWCNHs. However, there is not significant difference in each different irradiation power. The results strongly confirm FT-IR result as previous discussion.

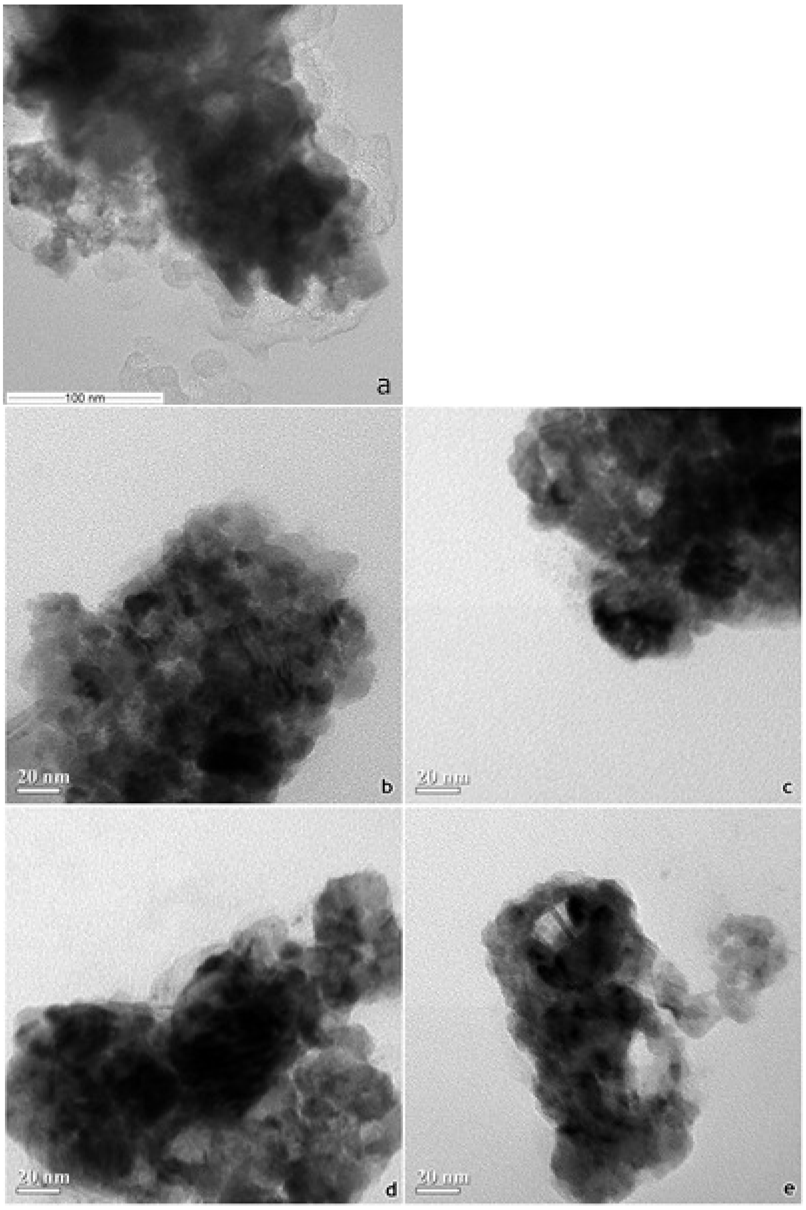


Figure 4.18 TEM micrographs of Cu/SWCNH hybrid materials of (a) pristine SWCNHs and Cu/SWCNH hybrid materials with different irradiation power of acid treatment process: (b) 90 W, (c) 360 W, (d) 600 W and (e) 800 W

TEM images of copper/SWCNH hybrid materials were analyzed by image processing method to determine amount of copper cluster coat on the surface of SWCNHs. Figure 4.19 illustrates coating intensity of Cu nanoparticles on the surface of SWCNHs which are irradiated by microwave at 90 W, 360 W, 600 W and 800 W. It can be seen from the figure that coating intensity of copper/SWCNH hybrid material that without acid treatment shows lower intensity than that of hybrid materials that apply acid treatment even if applies only low power (90 W). Comparisons in each irradiation power, It should be note that all four irradiation powers have almost the same level of coating intensity or just a bit difference. Figure 4.20 displays uniformity of Cu nanoparticles on the surface of SWCNHs which are irradiated by microwave at 90 W, 360 W, 600 W and 800 W. It seems like the uniformity value slow increases follow increasing of irradiation power. From all results (effect on surface properties results and effect on hybrid material properties), irradiation power has much lower effect to treat the surface of SWCNHs while irradiation time has more effect. It might because molecules of ion in sulfuric acid and nitric acid mixture are small so just small power is required.

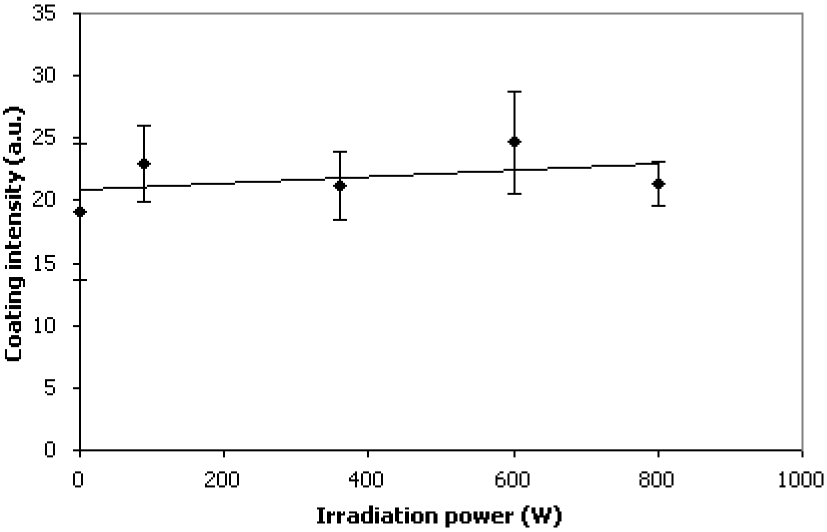


Figure 4.19 The coating intensity of Cu/SWCNH hybrid material with different irradiation power

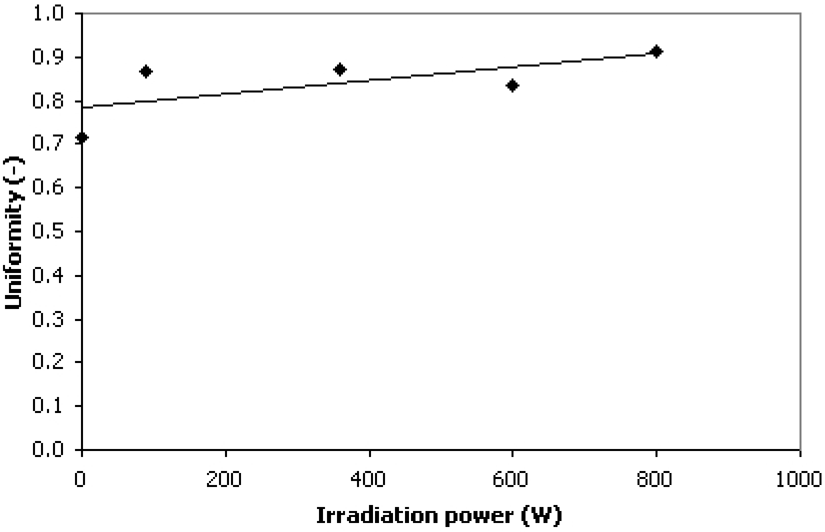


Figure 4.20 The uniformity of Cu/SWCNH hybrid material with different irradiation power

4.3.3 Effect of copper concentration on properties of copper/SWCNH hybrid material

The reactions for polyal process when ethylene glycol was used are proposed by Fievet et al. [26]. Metallic particles (M) are created by reduction as following mechanisms.

$$CH_2OH\text{-}CH_2OH \rightarrow CH_3CHO + H_2O \qquad (4.1)$$

$$2nCH_3CHO + 2M^{n+} \rightarrow 2M + 2nH^+ + nCH_3COCOCH_3 \qquad (4.2)$$

According to basic kinetic theory, to get more metallic particles in the right side of equation 4.2, it is necessary to increase M^{n+} in the left side of the equation. Thus concentration of metallic procurer should have an effect to synthesize metallic particles. The same reaction should occur during synthesize copper/SWCNH hybrid material. So the selected effect for the study is effect of copper precursor concentration on properties of copper/SWCNH hybrid material.

From section 4.3.2, irradiation power seems to be low effect to treat surface of SWCNHs. Owing to the results from section 4.2 and 4.3, 45 sec and 90 W are selected for this section evaluation. The condition of microwave for treatment of SWCNHs surface was set at 90 W for 45 sec. Similarly with the study in effect of irradiation time and irradiation power, the acid treated SWCNHs were hybridized with copper by microwave-polyol process. The condition of microwave for hybridizing of copper and SWCNHs was set at 360 W for 5 min. The copper concentration was varied from 15 wt% to 60 wt%. Subsequently the properties of acid treated SWCNHs and copper/SWCNH hybrid material were characterized.

Figure 4.21 illustrates TEM micrographs of copper/SWCNH hybrid materials with different copper concentration. The micrograph of copper/SWCNH hybrid material with 15 wt% copper concentration can observed that plenty of SWCNHs are not coated by copper precursor as shown in figure 4.21(a). Barely of SWCNHs in figure 4.21(b) are not covered with copper precursor and almost all surface of SWCNHs in figure 4.21(c) are coated. As expected, copper concentration has an effect on the properties of copper/SWCNH hybrid material.

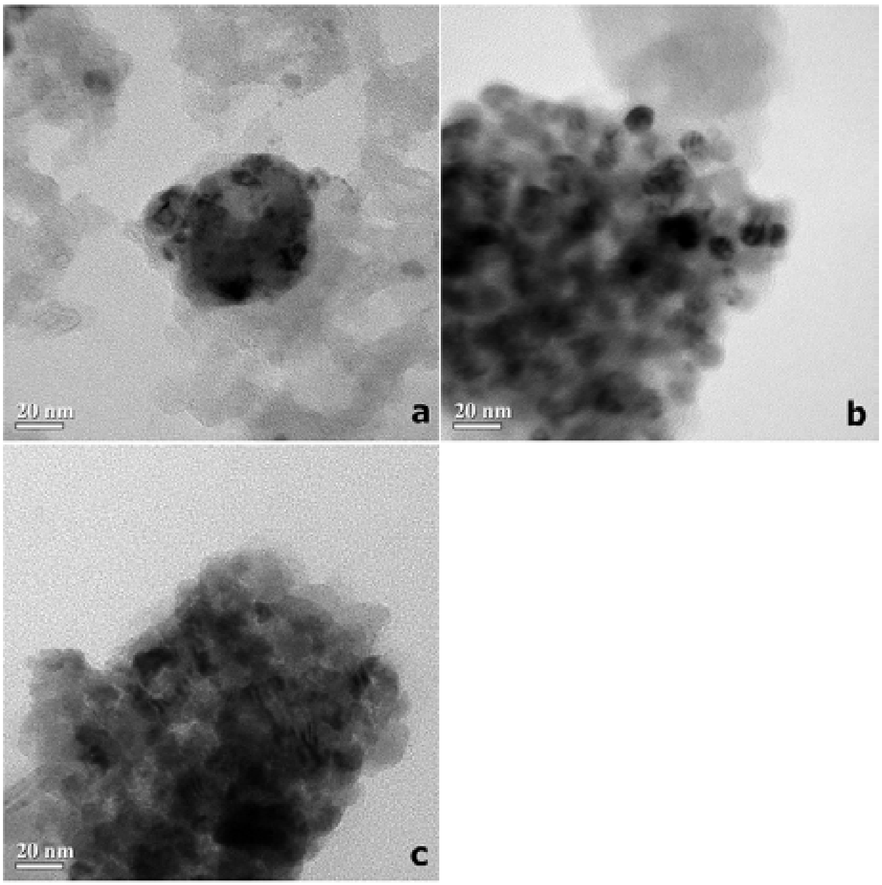


Figure 4.21 TEM micrographs of Cu/SWCNH hybrid materials of (a) 15 wt%, (b) 30 wt% and (c) 60 wt% copper concentration

Figure 4.22 presents XRD spectra of copper/SWCNH hybrid materials with different copper concentration. XRD results provide copper, cupric oxide and cuprous oxide peak in all three spectra. It should suggest that copper concentration do not have an effect on reduction mechanism.

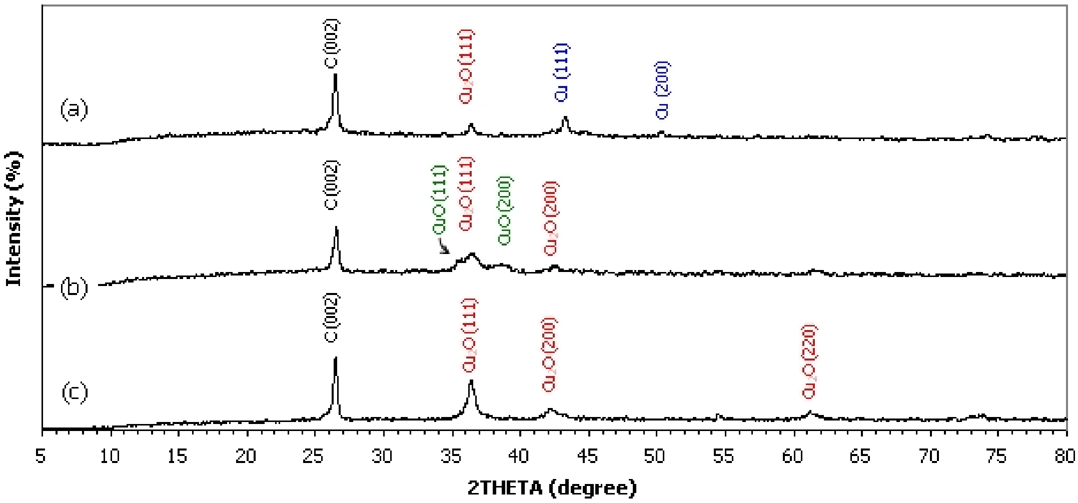


Figure 4.22 The XRD profile of Cu/SWCNH hybrid materials with different copper concentration: (a) 15 wt%, (b) 30 wt% and (c) 60 wt%

Similarly analytical method to determine copper coating over SWCNHs was employed. Figure 4.23 exhibits coating intensity of copper/SWCNH hybrid material with different copper concentration. As previous prediction, copper concentration has an effect on the properties of copper/SWCNH hybrid material. High concentration gains high coating intensity. It is might because higher concentration may increase opportunity to meet copper precursor with the functional groups on the surface of SWCNHs. Uniformity results also show the same tend with coating intensity as depicted in figure 4.24. Uniformity of 15 wt% concentration reveals only 0.49 while that of 60 wt% concentration reveals 0.87.

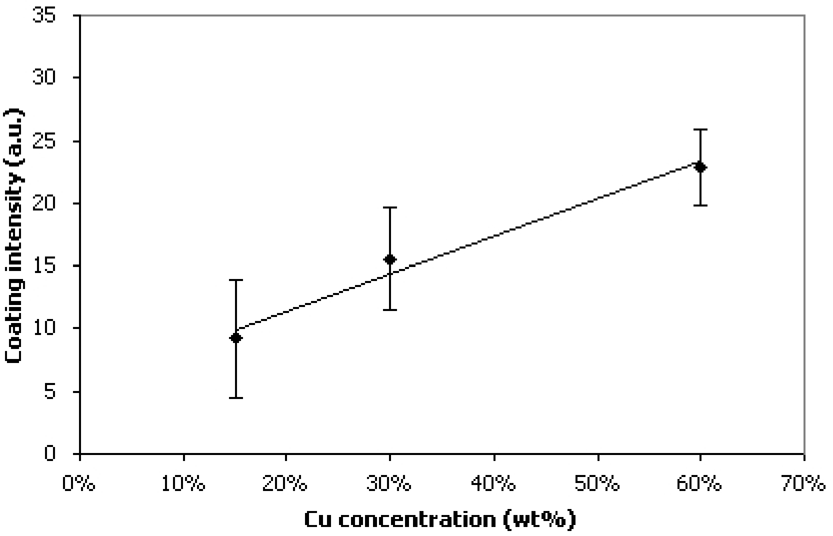


Figure 4.23 The coating intensity of Cu/SWCNH hybrid material with different copper concentration

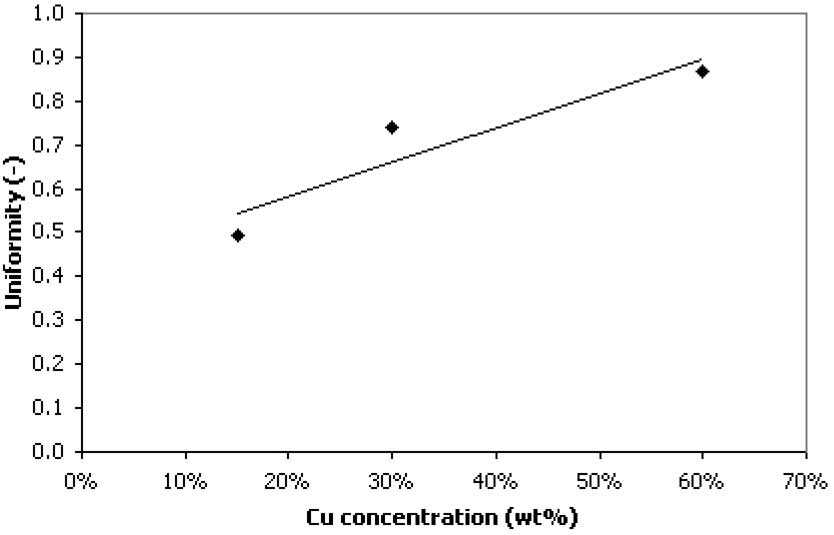


Figure 4.24 The uniformity of Cu/SWCNH hybrid material with different copper concentration

To confirm the structure of SWCNHs after hybridized with copper nanoparticles, Raman spectroscopy was applied. Figure 4.25 illustrates Raman spectra of acid treated SWCNHs at 90 W for 45 sec and copper/SWCNH hybrid material that treated with 90 W for 45 sec and coated with 30 wt% copper precursor. As could be observed, D-band of hybrid material is increased. It should be considered that D-band is represented the disorder of sp^2 structure so bonding between copper nanoparticle and SWCNHs should cause the increasing of D-band intensity [41]. Table 4.2 is summarized I_D/I_G ratio in each step to synthesize copper/SWCNH hybrid material.

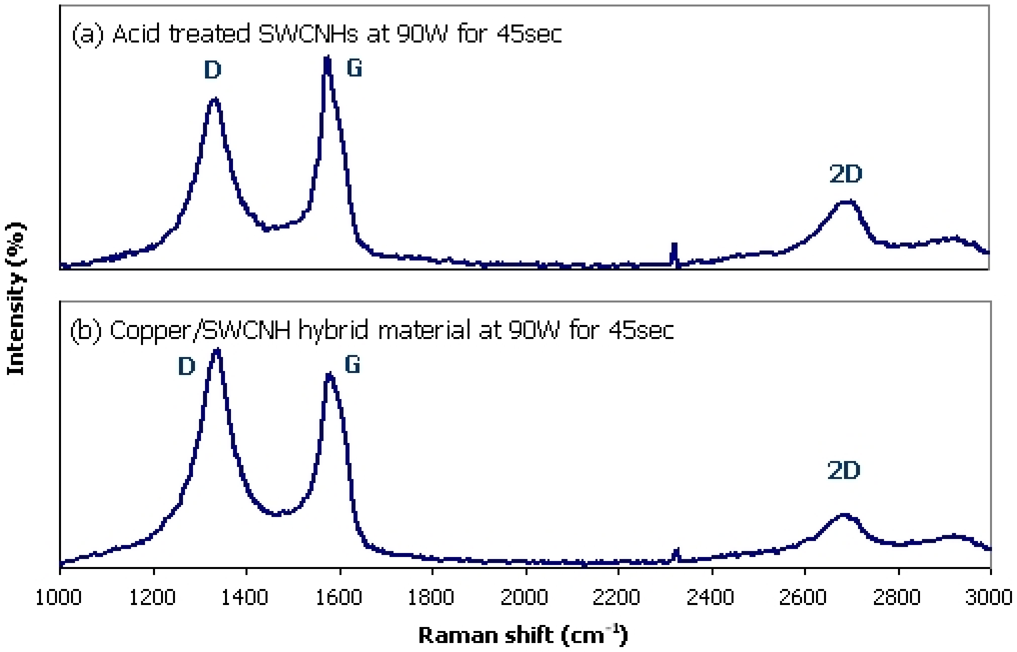


Figure 4.25 Raman spectra of acid treated SWCNHs at 90 W for 45 sec and copper/SWCNH hybrid material that treated with 90 W for 45 sec and coated with 30 wt% copper precursor

Table 4.2 I_D/I_G ratio in each step to synthesize copper/SWCNH hybrid material

Sample name	Surface treatment	Cu concentration (wt%)	I_D/I_G
Pristine SWCNHs	-	-	0.74
Acid treated SWCNHs	90 W for 45 sec	-	0.80
Cu/SWCNH hybrid material	90 W for 45 sec	30wt%	1.13

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The framework of this research is to introduce a process of single-walled carbon nanohorns surface modification using microwave irradiation. Synthesized SWCNHs from gas-injected arc-in-water method were treated to modify surface polarity by microwave-assisted acid treatment. Then acid treated SWCNHs were hybridized with copper nanoparticles by microwave-polyol process.

In surface modification process, we found that microwave irradiation can make a shorter process time from order of hour to order of second. Irradiation time has a high effect to modify the SWCNHs surface. Longer irradiation provides more negative polarity on the surface of SWCNHs. However, over irradiation affects badly to dispersibility in polar media. In the view point of studying in effect of irradiation power, just small irradiation power is required. It might be the molecules of ion in the mixture of sulfuric acid and nitric acid are too small then small power is required as penetration power. This research therefore indicates that surface modification of SWCNHs is the important process to fabricate the hybrid material of copper nanoparticles and SWCNHs. Amount of negative polarity on the surface of SWCNHs plays an important role to decoration of copper onto their surface. In microwave-polyol process, as expectation, concentration of copper precursor has an effect on coating of copper onto SWCNHs. Higher concentration gains more coating intensity and better uniformity.

In conclusion, the microwave-assisted surface modification of SWCNHs for hybridization with copper nanoparticles is successful as rapid method. The microwave irradiation power of 90 W and the microwave irradiation time of 45 sec could lead to the increased polarity of SWCNHs surface.

5.2 Recommendations for future work

The present work just focused on how to apply the microwave application to modify the surface of SWCNHs. Therefore, there are still many investigation items for next study. The recommendations for future work are list as follow;

1. There are barely researches works with the applications of copper/SWCNH hybrid material. To confirm ability of the material, it is necessary to investigated.
2. SWCNHs become a useful material so the synthesized method needs to improve in term of yield improvement or losing yield investigation.
3. There are 3 steps for fabrication of copper/SWCNH hybrid material in this work. Finding shorter step is better way to minimize cost and time.

REFERENCES

[1] Kroto H. W., J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley. C60: Buckminsterfullerene. Nature 318 (1985): 162-163

[2] Iijima S. Helical microtubules of graphitic carbon. Nature 354 (1991): 56-58

[3] Iijima S., et al. Nano-aggregates of single-walled graphitic carbon nano-horns. Chemical Physics Letters 309 (1999): 165-170

[4] Zhu S. and G. Xu. Single-walled carbon nanohorns and their applications. Nanoscale 2 (2010): 2538-2549

[5] Lai H., J. Li, Z. Chen and Z. Huang. Carbon nanohorns as a high-performance carrier for MnO2 anode in lithium-ion batteries. ACS Appl Mater Interfaces 4 (2012): 2325-2328

[6] Zhao Y., J. Li, Y. Ding and L. Guan. Single-walled carbon nanohorns coated with Fe2O3 as a superior anode material for lithium ion batteries. Chemical Communications 47 (2011): 7416-7418

[7] Datsyuk V., et al. Chemical oxidation of multiwalled carbon nanotubes. Carbon 46 (2008): 833-840

[8] Andrade N. F., et al. Temperature effects on the nitric acid oxidation of industrial grade multiwalled carbon nanotubes. Journal of Nanoparticle Research 15 (2013):

[9] He R. U. I., et al. Effects of Ultrasonic Radiation Intensity on the Oxidation of Single-Walled Carbon Nanotubes in a Mixture of Sulfuric and Nitric Acids. Nano 08 (2013): 1350040

[10] Martín O., et al. An efficient method for the carboxylation of few-wall carbon nanotubes with little damage to their sidewalls. Materials Chemistry and Physics 140 (2013): 499-507

[11] Lu F., et al. Surface oxidation of single-walled carbon nanotube paper with oxygen atoms. Journal of Adhesion Science and Technology 27 (2013): 208-215

[12] Morales-Lara F., et al. Functionalization of Multiwall Carbon Nanotubes by Ozone at Basic pH. Comparison with Oxygen Plasma and Ozone in Gas Phase. The Journal of Physical Chemistry C 117 (2013): 11647-11655

[13] McEvoy N., H. Nolan, N. Ashok Kumar, T. Hallam and G. S. Duesberg. Functionalisation of graphene surfaces with downstream plasma treatments. Carbon 54 (2013): 283-290

[14] Gong H., S.-T. Kim, J. D. Lee and S. Yim. Simple quantification of surface carboxylic acids on chemically oxidized multi-walled carbon nanotubes. Applied Surface Science 266 (2013): 219-224

[15] Wang Y., Z. Iqbal and S. Mitra. Microwave-induced rapid chemical functionalization of single-walled carbon nanotubes. Carbon 43 (2005): 1015-1020

[16] Motshekga S. C., S. K. Pillai, S. Sinha Ray, K. Jalama and R. W. M. Krause. Recent Trends in the Microwave-Assisted Synthesis of Metal Oxide Nanoparticles Supported on Carbon Nanotubes and Their Applications. Journal of Nanomaterials 2012 (2012): 1-15

[17] Leelaviwat N., et al. Microwave-induced fabrication of copper nanoparticle/carbon nanotubes hybrid material. Current Applied Physics 12 (2012): 1575-1579

[18] Masako Yudasaka S. I., Vincent H. Crespi. Single-Wall Carbon Nanohorns and Nanocones. CARBON NANOTUBES: TOPICS IN APPLIED PHYSICS 111 (2008): 605-629

[19] Azami T., et al. Large-Scale Production of Single-Wall Carbon Nanohorns with High Purity. The Journal of Physical Chemistry C 112 (2008): 1330-1334

[20] Sano N. Low-cost synthesis of single-walled carbon nanohorns using the arc in water method with gas injection. Journal of Physics D: Applied Physics 37 (2004): L17-L20

[21] Poonjarernsilp C., et al. Single-step synthesis and characterization of single-walled carbon nanohorns hybridized with Pd nanoparticles using N2 gas-injected arc-in-water method. Carbon 49 (2011): 4920-4927

[22] Yu R., et al. Platinum Deposition on Carbon Nanotubes via Chemical Modification. Chemistry of Materials 10 (1998): 718-722

[23] Trojanowicz M. Analytical applications of carbon nanotubes: a review. TrAC Trends in Analytical Chemistry 25 (2006): 480-489

[24] Metaxas A. C. Foundations of electroheat: A unified approach.:Chichester: Wiley., 1996

[25] Hammond C. R. The Elements, in Handbook of Chemistry and Physics. 81st edition.CRC Press, 2004

[26] Fievet F., J. P. Lagier, B. Blin, B. Beaudoin and M. Figlarz. Homogeneous and heterogeneous nucleations in the polyol process for the preparation of micron and submicron size metal particles. Solid State Ionics 32–33, Part 1 (1989): 198-205

[27] Tsuji M., M. Hashimoto, Y. Nishizawa, M. Kubokawa and T. Tsuji. Microwave-assisted synthesis of metallic nanostructures in solution. Chemistry 11 (2005): 440-452

[28] Yu Y., et al. Sonication assisted deposition of Cu2O nanoparticles on multiwall carbon nanotubes with polyol process. Carbon 43 (2005): 670-673

[29] Yoshida S. and M. Sano. Microwave-assisted chemical modification of carbon nanohorns: Oxidation and Pt deposition. Chemical Physics Letters 433 (2006): 97-100

[30] Sun J., Y. Jing, Y. Jia, M. Tillard and C. Belin. Mechanism of preparing ultrafine copper powder by polyol process. Materials Letters 59 (2005): 3933-3936

[31] Ferrari A. C., et al. Raman Spectrum of Graphene and Graphene Layers. Physical Review Letters 97 (2006): 187401

[32] Pimenta M. A., et al. Studying disorder in graphite-based systems by Raman spectroscopy. Physical Chemistry Chemical Physics 9 (2007): 1276-1290

[33] Kaneko K A. M., Yamamoto M, Ohba T, Miyamoto JI, Kim DY, Tao Y, Yang CM, Urita K, Fujimori T, Tanaka H, Ohkubo T, Utsumi S, Hattori Y, Konishi T, Fujikawa T, Kanoh H, Yudasaka M, Hata K, Yumura M, Iijima S, Muramatsu H, Hayashi T, Kim YA, Endo M. Fundamental Understanding of Nanoporous Carbons for Energy Application Potentials. Carbon Letter 10 (2009): 177-180

[34] Ros T. G., A. J. van Dillen, J. W. Geus and D. C. Koningsberger. Surface Oxidation of Carbon Nanofibres. Chemistry – A European Journal 8 (2002): 1151-1162

[35] Avilés F., J. V. Cauich-Rodríguez, L. Moo-Tah, A. May-Pat and R. Vargas-Coronado. Evaluation of mild acid oxidation treatments for MWCNT functionalization. Carbon 47 (2009): 2970-2975

[36] Zhang J., et al. Effect of Chemical Oxidation on the Structure of Single-Walled Carbon Nanotubes. The Journal of Physical Chemistry B 107 (2003): 3712-3718

[37] Zeng L., L. Zhang and A. R. Barron. Tailoring Aqueous Solubility of Functionalized Single-Wall Carbon Nanotubes over a Wide pH Range through Substituent Chain Length. Nano Letters 5 (2005): 2001-2004

[38] T. Petrov I. M.-D., O. Chauvet, R. Nikolov, I. Denev. SEM AND FT-IR SPECTROSCOPY STUDY OF Cu, Sn AND Cu-Sn NANOPARTICLES. Journal of the University of Chemical Technology and Metallurgy 47 (2012): 197-206

[39] LI L.-P. Z., H.-Y.; PANG, J.-S.; LIN, J. Fabrication and performance of carbon coated copper nanoparticles. Materials Science-Poland 28 (2010): 181-187

[40] Ellner M., K. Kolatschek and B. Predel. On the partial atomic volume and the partial molar enthalpy of aluminium in some phases with Cu and Cu3Au structures. Journal of the Less Common Metals 170 (1991): 171-184

[41] Sheng G., et al. Adsorption of copper(II) on multiwalled carbon nanotubes in the absence and presence of humic or fulvic acids. J Hazard Mater 178 (2010): 333-340

APPENDICES

APPENDIX A

TEM MICROGRAPHS OF COPPER/SWCNH HYBRID MATERIAL

TEM images of copper/SWCNH hybrid material in any magnifications of all conditions are listed.

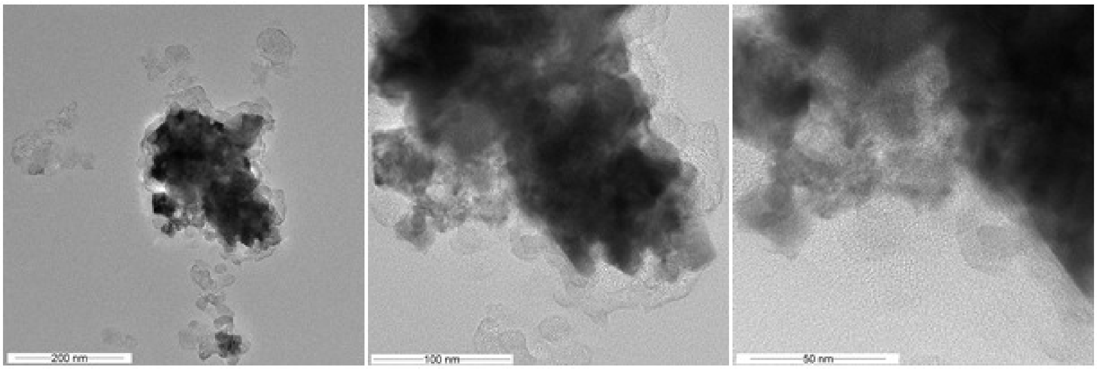


Figure A.1 TEM micrographs of Cu/SWCNH hybrid materials of pristine SWCNHs with 60 wt% Cu

1. Effect of irradiation time on properties of copper/SWCNH hybrid material

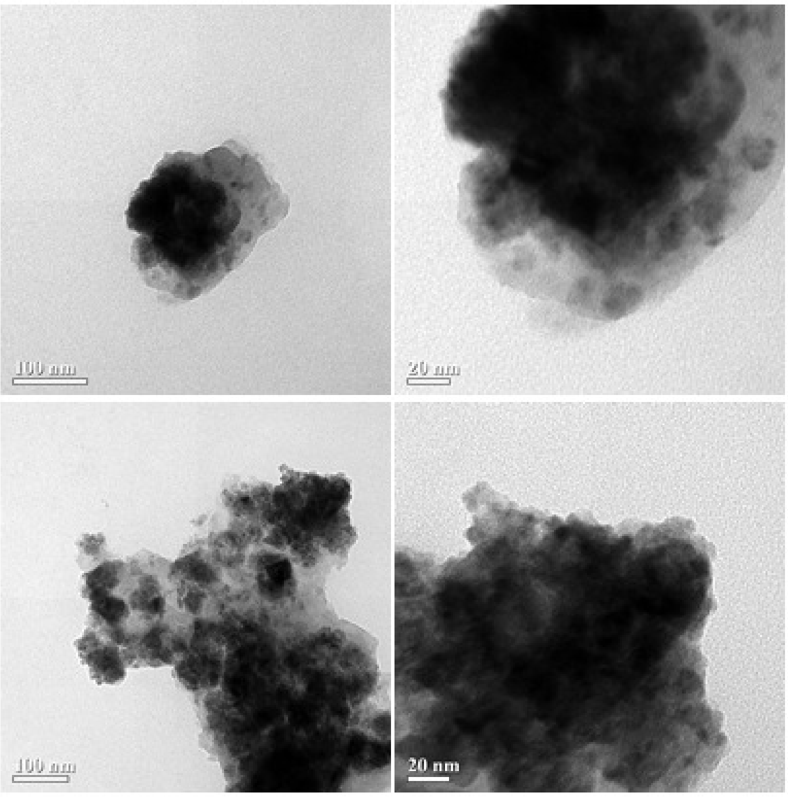


Figure A.2 TEM micrographs of Cu/SWCNH hybrid materials at 360W for 30sec of acid treatment process with 60 wt% Cu

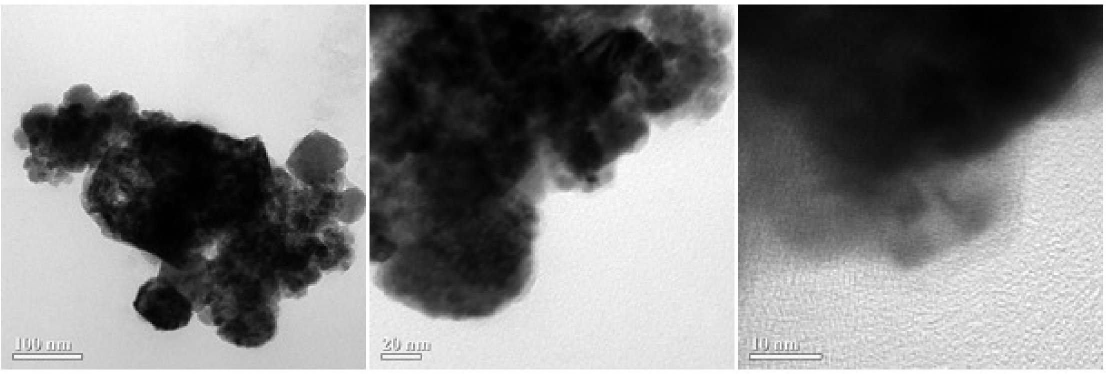


Figure A.3 TEM micrographs of Cu/SWCNH hybrid materials at 360W for 45sec of acid treatment process with 60 wt% Cu

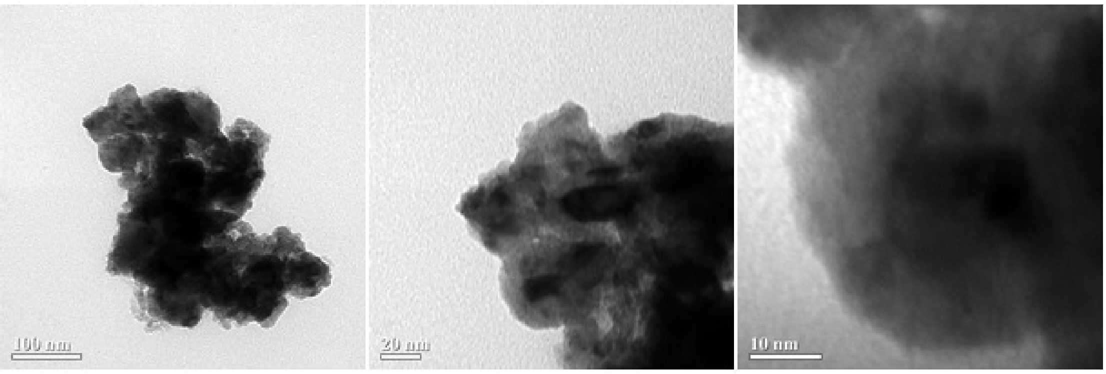


Figure A.4 TEM micrographs of Cu/SWCNH hybrid materials at 360W for 60sec of acid treatment process with 60 wt% Cu

2. Effect of irradiation power on properties of copper/SWCNH hybrid material

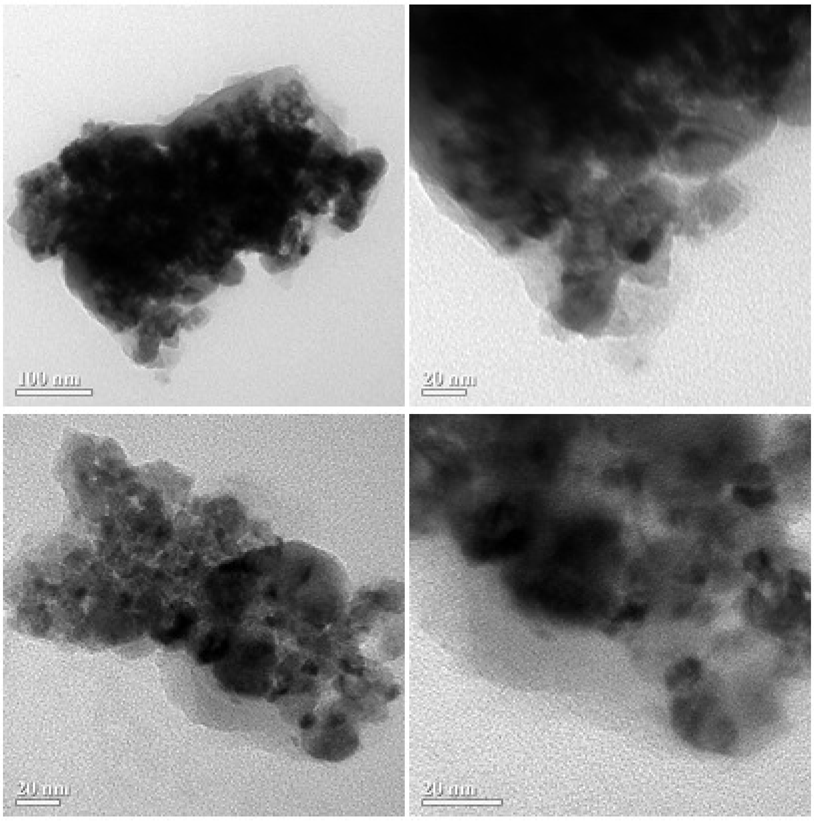


Figure A.5 TEM micrographs of Cu/SWCNH hybrid materials at 90W for 45sec of acid treatment process with 60 wt% Cu

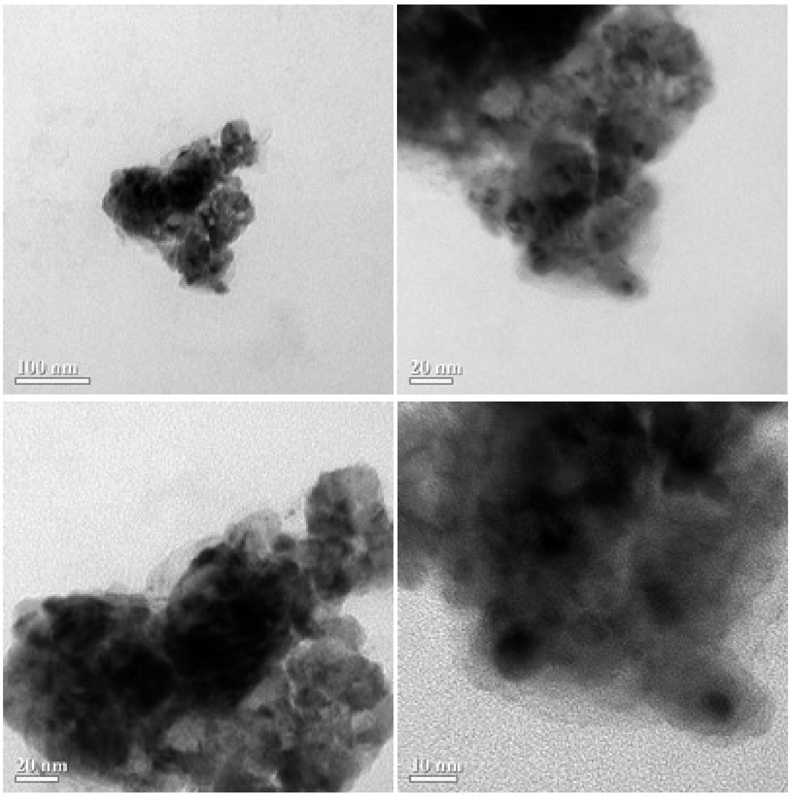


Figure A.6 TEM micrographs of Cu/SWCNH hybrid materials at 600W for 45sec of acid treatment process with 60 wt% Cu

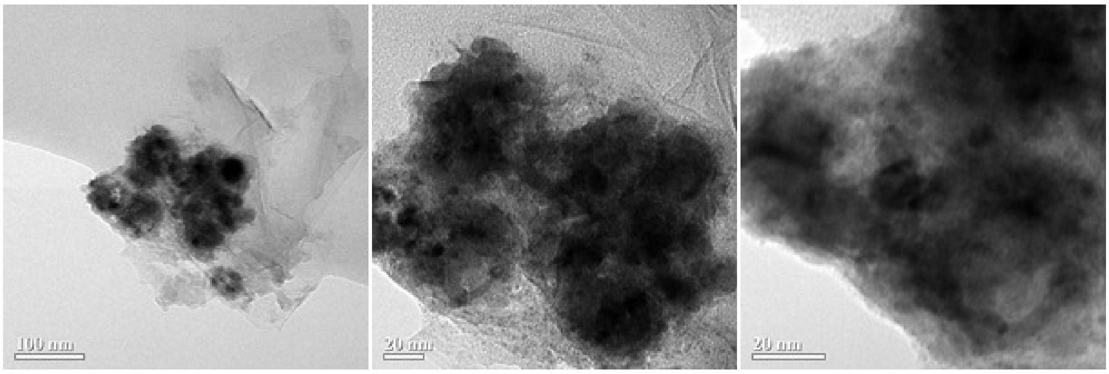


Figure A.7 TEM micrographs of Cu/SWCNH hybrid materials at 800W for 45sec of acid treatment process with 60 wt% Cu

3. Effect of copper concentration on properties of copper/SWCNH hybrid material

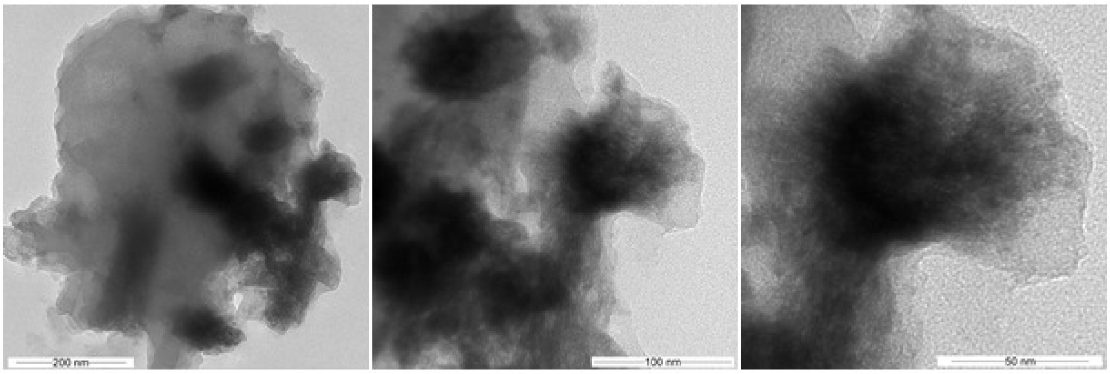


Figure A.8 TEM micrographs of Cu/SWCNH hybrid materials at 90W for 45sec of acid treatment process with 15 wt% Cu

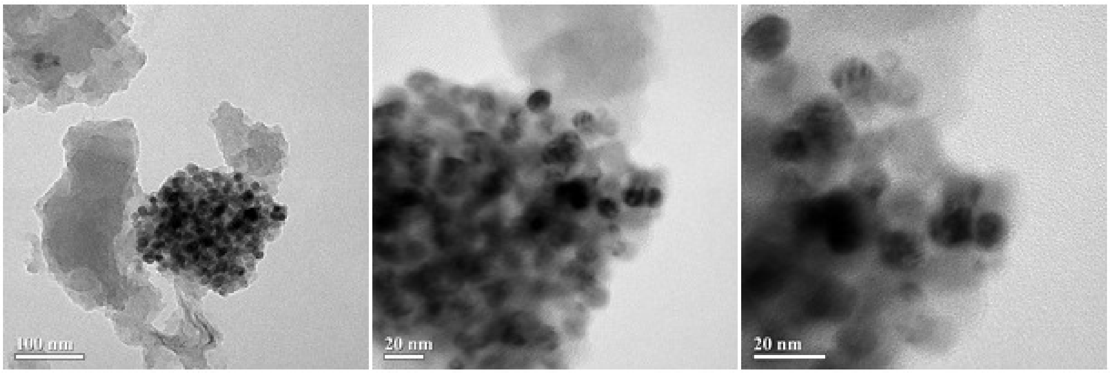


Figure A.9 TEM micrographs of Cu/SWCNH hybrid materials at 90W for 45sec of acid treatment process with 30 wt% Cu

APPENDIX B

CALCULATION FOR COATING FRACTION

The way for calculate the coating fraction is described step by step as following.

Step 1 Select TEM image that applied from 100,000x magnification and open it by Image J.

Step 2 From the image, 3 different color levels were noticed. Measure intensity of the color that represented SWCNHs

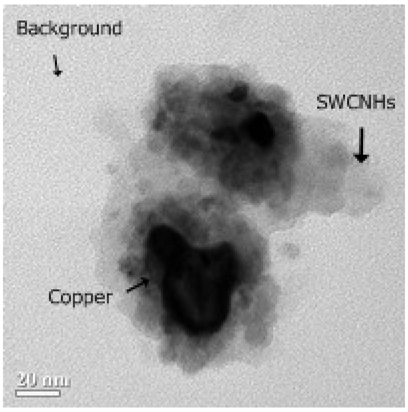


Figure B.1 Image sample for Image processing measurement

Step 3 Crop copper area from the image and measure intensity and area. Actual intensity of copper is equal to measured intensity minus with background intensity. Copper volume is equal area multiply by copper intensity.

Step 4 Crop copper combined with SWCNHs area from the image and measure area.

Step 5 Calculate following as equations in chapter 3

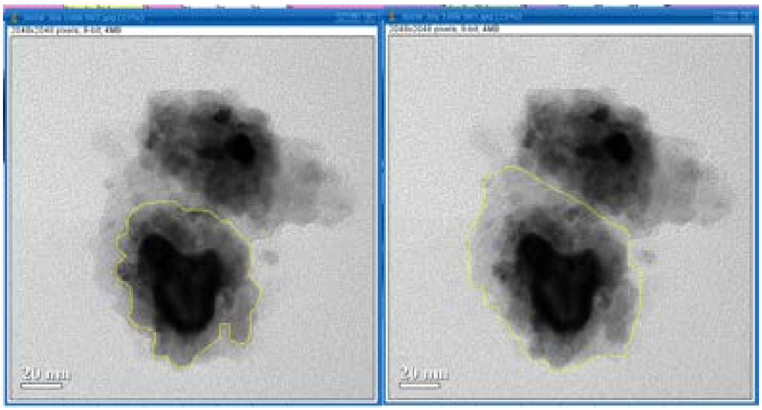


Figure B.2 Image sample for cropping copper and SWCNHs area

APPENDIX C

PUBLICATION

Proceeding:

Parichat Thipayang, Kunio Shinohara, Chantamanee Poonjarernsilp, and Tawatchai Charinpanitkul, Fabrication of copper/single-walled carbon nanohorn hybrid material by microwave irradiation. Proceeding of Pure and Applied Chemistry International Conference 2013 (PACCON 2013), Chonburi, Thailand, January 23-25, 2013

VITAE

Miss Parichat Thipayang was born on April 1st, 1984. In 2006, she graduated in chemical technology from faculty of science, Chulalongkorn University. After graduated, she worked as production supervisor in production department for Thai Kansai Paint Co.,Ltd from June, 2006 to April, 2007. Then she worked as senior engineer in process engineering department for AGC Electronics (Thailand) Co.,Ltd from May, 2007 to February, 2012. In 2011, she enrolled in master course of chemical engineering at faculty of engineering, Chulalongkorn University.