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PREPARATION OF CARBON NANOTUBES DECORATED WITH COPPER NANOPARTICLES BY MICROWAVE TREATMENT

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
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ณัฐพร ลีลาวิวัฒน์ : การเตรียมท่อนาโนคาร์บอนที่ตกแต่งด้วยอนุภาคทองแดงระดับนาโน
โดยอาศัยการบำบัดด้วยไมโครเวฟ (PREPARATION OF CARBON NANOTUBES
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TREATMENT) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ธวัชชัย ชรินพาณิชกุล, 68 หน้า.

งานวิจัยนี้ศึกษาการเตรียมท่อนาโนคาร์บอนที่ตกแต่งด้วยอนุภาคทองแดงระดับนาโน ซึ่งเตรียมโดยเทคนิคการบำบัดด้วยไมโครเวฟ เตาอบไมโครเวฟถูกใช้เป็นแหล่งจ่ายคลื่นไมโครเวฟเพื่อใช้ในการสังเคราะห์คอมโพสิท โดยจะเป็นตัวจ่ายคลื่นไมโครเวฟให้แก่สารแขวนลอยที่มีท่อนาโนคาร์บอนกระจายตัวอยู่ในสารละลายผสมของคอปเปอร์(II)ซัลเฟต โซเดียมไฮดรอกไซด์และเอทิลีนไกลคอล ซึ่งเอทิลีนไกลคอลจะทำหน้าที่เป็นตัวรีดิวซ์ในการบำบัดด้วยไมโครเวฟ ในงานวิจัยนี้ได้ศึกษาผลกระทบของระยะเวลาในการให้ความร้อนด้วยคลื่นไมโครเวฟ ผลกระทบของกำลังไฟที่ใช้ที่มีผลต่อลักษณะอนุภาคคอมโพสิทที่สังเคราะห์ คลื่นไมโครเวฟมีบทบาทสำคัญต่อการเตรียมท่อนาโนคาร์บอนที่ตกแต่งด้วยอนุภาคทองแดงระดับนาโน อุณหภูมิถูกพบว่าเป็นตัวแปรสำคัญที่มีผลต่ออนุภาคที่สังเคราะห์ขึ้นได้ อุณหภูมิที่ใช้ในการสังเคราะห์ที่ 166 และ 194 องศาเซลเซียสเหมาะสมที่จะสังเคราะห์อนุภาคคอปเปอร์ออกไซด์และอนุภาคทองแดงระดับนาโนได้ตามลำดับ นอกจากนี้ ระยะเวลาในการให้ความร้อนด้วยคลื่นไมโครเวฟและผลกระทบของกำลังไฟที่ใช้ยังส่งผลถึงลักษณะของอนุภาคที่เกาะอยู่บนท่อนาโนคาร์บอนอีกด้วย อนุภาคคอปเปอร์ออกไซด์และอนุภาคทองแดงระดับนาโนจะสามารถกระจายตัวอย่างเป็นระเบียบและรวมเป็นกลุ่มก้อนอยู่บนท่อนาโนคาร์บอนได้ โดยขึ้นอยู่กับสภาวะที่ใช้ในการสังเคราะห์

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต...
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก...
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NATTAPORN LEELAVIWAT: PREPARATION OF CARBON NANOTUBES DECORATED WITH COPPER NANOPARTICLES BY MICROWAVE TREATMENT. ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng., 68 pp.

In this work, microwave irradiation treatment has been used for the preparation of carbon nanotubes decorated with copper nanoparticles. A household microwave oven was employed for providing microwave irradiation to a suspension of MWCNTs dispersed in a solution of copper precursor which was $CuSO_4 \cdot 5H_2O$. As a reducing agent, ethylene glycol (EG) was introduced to copper ions which were dispersed in MWCNTs suspension subject to microwave treatment. Effect of microwave irradiation power and irradiation time on morphology of the Cu/MWCNT composite was examined and reported. It was found that microwave irradiation plays a important role in the formation of the products; temperature was also found to be important in the reaction. At 166 and 194 ^{o}C was suitable for preparing Cu_2O and Cu nanoparticles, respectively. The microwave irradiation power and irradiation time also affect the morphology of the products. With the change of the reaction conditions, it is found that Cu_2O and Cu nanoparticles on the surface of MWCNTs can be uniformly and agglomerated deposited on the surface of MWCNTs. The possible formation mechanism of Cu/MWCNT composite is also discussed.

Department: Chemical Engineering Student‟s signature:……………………… .
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CONTENTS

CHAPTER

Page

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

Figure **Page**

CHAPTER I

INTRODUCTION

Carbon nanotubes (CNTs) have drawn a great deal of attention from many researchers since their discovery [1, 2]. CNT can be described as a graphene sheet rolled up into a nanoscale tube (which is called “single-walled carbon nanotube”, SWCNT), or with additional graphene tubes around the core of a single-walled carbon nanotube (which is called “multi-walled carbon nanotube, MWCNT) [1]. It is well known that CNTs have excellent mechanical and electrical characteristics, such as high tensile strength, high elastic modulus, high thermal conductivity and electrical conductivity. Meanwhile, recent studies have shown that metal-loaded CNTs exhibit remarkable improvements in the CNT properties without compromising on their density and processability. In this respect, copper (Cu) appears to be a promising metal for loading on CNTs since it has good thermal and electrical conductivities (secondly only to silver) and has long been investigated for use in electronic devices[3].

There are many investgations reporting that several metal-loaded CNTs, e.g. Au/CNTs, Pt/CNTs, and Cu/CNTs, could be prepared by means of different techniques, including metal-vapor deposition, chemical-reduction deposition in the solution phase, arc discharge, electroless deposition, and microwave-polyol process. The microwave-polyol process has been applied in the preparation of metal-loaded CNTs as it is a simple-and-fast method that allows formation and simultaneous loading of nano-scale particles of metals on CNTs. In this process, polyalcohol, or “polyol”, is employed as solvent and reducing agent to cause or promote the reduction of a metal precursor to a desired metal compound or elemental metal, whereas microwave irradiation is utilized as an attractive way for supplying energy to reactions involved for the synthesis of nanoparticles due to its rapid, uniform and effective heating method. A conceptual diagram of the preparation of metal-loaded CNTs by microwave-polyol process is shown in Figure 1.1.

In this research work, the microwave-polyol process will be applied for the preparation of Cu-loaded MWCNTs composite, which could be potentially useful for some novel thermal and electrical conduction applications. To develop the understanding of this process, the effects of operating parameters, which are microwave irradiation power, irradiation time and initial feed compositions will be investigated and discussed based on morphological observation and internal structure analysis using SEM, TEM, XRD and FT-IR.

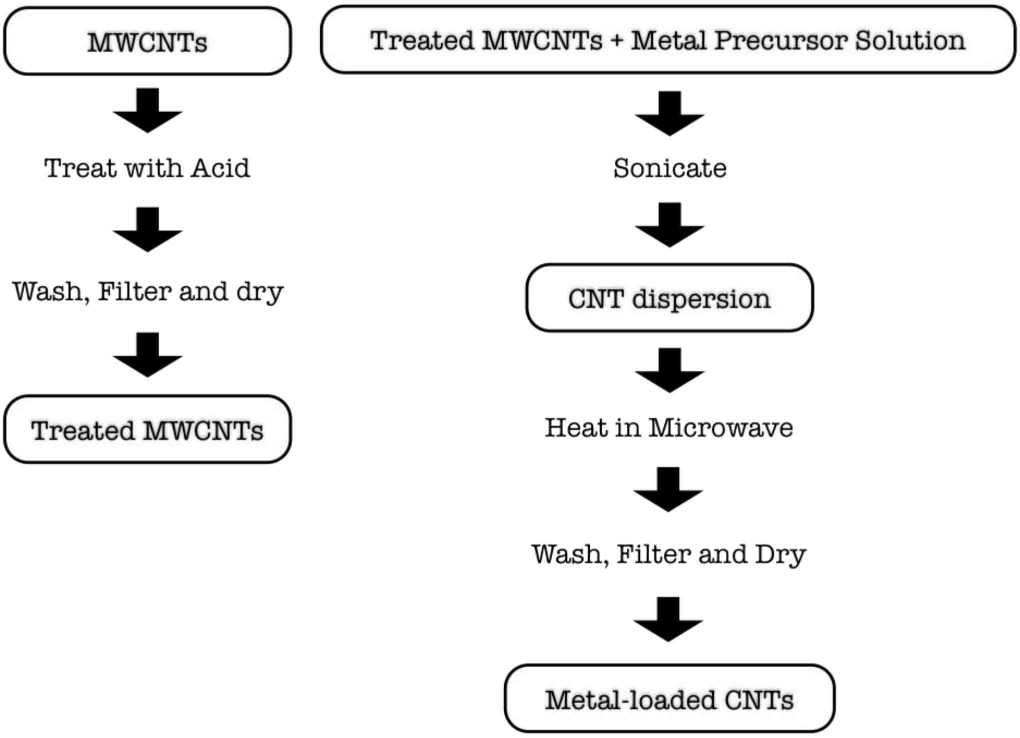


Figure 1.1 Conceptual diagram of preparation of metal-loaded CNTs by microwave-polyol process

1.2 Objectives of research

1.2.1 To apply the microwave treatment method for preparing Cu/MWCNT composite.

1.2.2 To investigate the effect of preparation parameters on the characteristics of the synthesized Cu particles and the prepared Cu/MWCNT composite.

1.3 Scope of research

1.3.1 Investigation of the effect of preparation parameters on the characteristics of the synthesized Cu particles:

  1.3.1.1 Irradiation time is 1, 3, 5, 7 and 9 min.
  1.3.1.2 Microwave-irradiation power is 360, 600 and 800 W.

1.3.2 Investigation of the effect of preparation parameters on the characteristics of the prepared Cu/MWCNT composite:

  1.3.2.1 MWCNTs are about 15-20 nm in diameter.
  1.3.2.2 Irradiation time is 1, 3, 5, 7 and 9 min.
  1.3.2.3 Microwave-irradiation power is 360, 600 and 800 W.
  1.3.2.3 Mass of copper precursor is 0.114 and 0.233 g.

1.3.3 Characteristics of the prepared composite:

  1.3.3.1 Analysis of surface morphology by Scanning Electron Microscope (SEM)
  1.3.3.2 Analysis of internal structure by Transmission Electron Microscope (TEM)
  1.3.3.3 Elemental analysis using energy dispersive X-ray spectroscopy (EDS) (as an integrated feature of the SEM)
  1.3.3.4 Analyses of chemical composition and physical properties by X-ray Diffractometer (XRD)
  1.3.3.5 Analysis of functional elements by Fourier Transform Infrared (FT-IR) spectrometer
  1.3.3.6 Analysis of zeta potential by zetasizer (Malvern Nano – ZS)

1.4 Benefits obtained from this work

1.4.1 Comprehensive understanding of formation of Cu particles in the microwave-polyol process for obtaining controlled formation of Cu particles with uniformity in size

1.4.2 Comprehensive understanding of loading of Cu particles on MWCNTs surface in the microwave-polyol process for obtaining controlled formation of Cu particles with high dispersion on the MWCNTs surface.

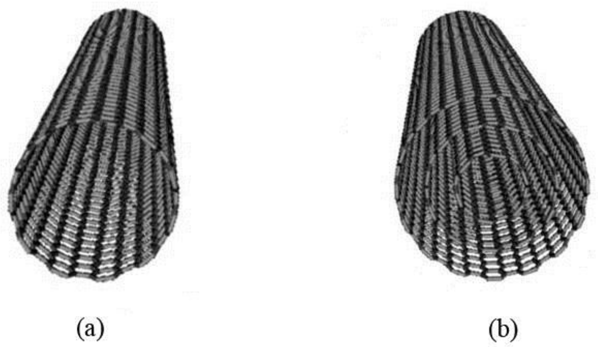
CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Carbon Nanotubes [1, 4, 5]

Carbon nanotubes (CNTs) are molecular-scale tubes of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibres known, and have remarkable electronic properties and many other unique characteristics. For these reasons, they have attracted huge academic and industrial interest, with thousands of papers on nanotubes being published every year. Commercial applications have been rather slow to develop, however, primarily because of the high production costs of the best quality nanotubes.

CNTs can be described as a graphite sheet rolled up into a nanoscale tube (which is called “single-walled carbon nanotube” (SWCNT)), or with additional graphene tubes around the core of a SWCNT (which is called “multi-walled carbon nanotube (MWCNT)) as shown in Fig. 2.1 (a) and (b), respectively. These CNTs have diameters in the range between fractions of nanometers and tens of nanometers and lengths up to several centimeters with both their ends normally capped by fullerene-like structures.



(a)

(b)

Figure 2.1 Structures of (a) SWCNTs and (b) MWCNTs.
(itech.dickinson.edu)

Recently, CNTs with relatively short lengths have been attracting strong attention because such CNTs are expected to provide connectors and components in molecular electronic devices and have rich chemistry. CNT walls are not reactive, but their fullerene-like tips are known to be more reactive, so end functionalization of CNTs is used relatively often to generate functional groups (e.g., -COOH, -OH, or -C=O). Non-covalent sidewall functionalization of CNTs can be based on weak interactions (e.g., hydrogen bonding, π-π stacking, electrostatic forces, van der Waals forces and hydrophobic interactions). This can be used to attach small molecules or biochemically active molecules (e.g., for protein immobilization), or to wrap polymer chains onto the sidewall of CNTs.

They exhibit extraordinary strength and unique electrical properties. Information of attraction properties of CNTs could be briefly summarized as follows,

- Strength property

Carbon nanotubes are one of the strongest and stiffest materials known, in terms of tensile strength and elastic modulus, respectively. This strength results from the covalent sp2 bonds formed between the individual carbon atoms. A multi-walled carbon nanotube was tested to have a tensile strength of 63 GPa . In comparison, high-carbon steel has a tensile strength of approximately 1.2 GPa. Further, CNTs have very high elastic modulus, on the order of 1 TPa.

- Electrical property

Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. In theory, metallic nanotubes can have an electrical current density more than 1,000 times greater than metals such as silver and copper.

- Thermal property

All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction," but good insulators laterally to the tube axis. It is predicted that carbon nanotubes will be able to transmit up to 6000 watts per meter per Kelvin at room temperature; comparing to copper, a metal well-known for its good thermal conductivity, which only transmits 385 watts per meter per Kelvin.

From these properties, carbon nanotubes have potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science. Recent examples of applications include the use of carbon nanotubes as:

- gas storage components of argon, nitrogen, and hydrogen
- AFM probes and field emission sources
- high power electrochemical capacitors
- electronic nanoswitches
- chemical sensors
- magnetic data storage (e.g. iron filled nanotubes)
- nanocomposites with polymer, metal and etc.
- catalyst supports
- drug delivery systems

Chemical treatment of CNTs

Because of their hydrophobic nature, carbon nanotubes tend to agglomerate hindering their dispersion is solvents or viscous polymer melts. Unsurprisingly, the resulting aggregates reduce the mechanical performance of the final composite. Effort has been directed at modifying the surface of the carbon nanotube to reduce the hydrophobicity and improve interfacial adhesion to a bulk polymer through chemical attachment. The carbon nanotube chemistry involves three main approaches, where reactions target: surface groups generated through acid-induced oxidation of the carbon nanotube surface; direct addition to the carbon nanotube sidewalls; groups attached to polycyclic aromatic hydrocarbons that are immobilised to the carbon nanotube surface through Van der Waals forces. There are several methods of the chemical treatment such as acid-treatment, plasma treatment and etc.

2.2 Copper [3, 6]

Copper (Cu) is Atomic Number 29, that is, an atom of copper has 29 protons. The Atomic Weight is 63.54. The Atomic Symbol is Cu. Cu is in column IB of the

Periodic Table of the Elements, above Silver (Ag) and Gold (Au). Elements in the same column have some similar properties. Like Ag and Au, Cu is soft (with a Moh's hardness of 3, that is, harder than a fingernail, but softer than a steel pocketknife). The surface has a metallic luster. When Cu combines with other elements, it has a charge of either +1 (called "cuprous") or +2 (called "cupric").

Figure 2.2 Native copper
(en.wikipedia.org/wiki/Copper)

Properties of Cu. The melting point of Cu is 1083.4 °C. Liquid Cu boils at 2567 °C. Like Ag and Au, Cu is **malleable**; that is, it can be bent and shaped without cracking, when either hot or cold. It can be rolled into sheets as thin as 1/500 of an inch. Cu is also **ductile**; that is, it can be drawn out into thin wire. A Cu bar with 4 inches in thickness can be heated, rolled, and drawn into a round wire so thin that it is thinner than a human hair. Industry values Cu for these properties. Cu is second only to Ag in its ability to conduct electricity, but Ag is too expensive for this sort of use. Cu is also an excellent conductor of heat, making it an important metal in cookware, refrigerators, and radiators. Besides, Cu is resistant to corrosion; that is, it will not rust. If the air around it often is damp, it will change from its usual reddish orange color to reddish-brown. Eventually, it is coated with a green film called a "patina" that stops all further corrosion. Cu is an industrially important material that is widely used in fields such as magnetic storage media, solar energy transformation, electronics, sensors, catalysis, batteries and etc. The properties of copper are shown in Table 2.1.

Table 2.1 Properties of copper

Physical properties	
Phase	solid
Density (near r.t.)	8.94 g·cm^{-3}
Liquid density atm.p.	8.02 g·cm^{-3}
Heat of fusion	13.26 kJ·mol^{-1}
Heat of vaporization	300.4 kJ·mol^{-1}
Molar heat capacity	24.440 J·mol^{-1}·K^{-1}
Atomic properties	
Oxidation states	+1, **+2**, +3, +4 (mildly basic oxide)
Electronegativity	1.90 (Pauling scale)
Atomic radius	128 pm
Covalent radius	132±4 pm
Van der Waals radius	140 pm
Miscellanea	
Crystal structure	face-centered cubic
Magnetic ordering	diamagnetic
Electrical resistivity	(20 °C) 16.78 nΩ·m
Thermal conductivity	401 W·m^{-1}·K^{-1}
Young's modulus	110–128 GPa
Shear modulus	48 GPa
Bulk modulus	140 GPa
Poisson ratio	0.34
Mohs hardness	3.0

2.3 Microwave-Polyol Process [3, 6]

The polyol process has been used in preparing colloidal metal particles. Polyol stands for polyalcohols with a high boiling temperature, which are able to dissolve inorganic salts. In the preparation of colloidal metal particles, the polyol method is applied because of its moderate reducing properties and also for its chelating effect, which avoids the agglomeration of particles during the synthesis. The physical parameters of typical solvents used in microwave heating for synthesis of metal particles are listed in Table 2.2.

Table 2.2 The physical parameters of typical solvents used in microwave heating [7]

	B.P.(^{o}C)	ε′	ε″	tan δ
Water	100	78.3	12.3	0.157
Methanol	65	32.7	20.9	0.639
Ethanol	78	24.3	6.08	0.200
N,N-dimethyl formamide (DMF)	153	36.71	-	-
Ethylene glycol (EG)	198	41.0	41.0	1.00
N-methyl pyrrolidone (NMP)	202	32.0	8.855	0.277

Among various polyol, ethylene glycol is commonly used as polyol as it has a high dielectric constant (ε′) and dielectric loss (ε″), and can be rapidly heated by microwave irradiation. ε′ represents the relative permittivity, which is a measure of the ability of a molecule to be polarized by an electric field and tan $\delta = \varepsilon''/\varepsilon'$ is the energy dissipation factor or loss tangent. ε″ is the most important physical parameter that describes the ability of a material to heat in the microwave field.

Microwave is a portion of the electromagnetic waves with frequencies in the range of 300 MHz to 300 GHz. Electromagnetic waves are waves of electrical and magnetic energy moving together through space. They include gamma rays, x-rays, ultraviolet radiation, visible light, infrared radiation, microwaves and the less energetic radio waves. The corresponding wavelengths of these frequencies are 1 m to 1 mm. The most commonly used frequency is 2.45 GHz. The degree of interaction of microwaves with a dielectric medium is related to the material‟s dielectric constant and dielectric loss. When microwaves penetrate and propagate through a dielectric solution or suspension, the internal electric fields generated within the affected volume induce translation motions of free or bound charges such as electrons or ions and rotate charged complexes such as dipoles. The resistance of these induced motions due to inertial, elastic, and frictional forces, which are frequency dependent, causes losses and attenuates the electric field.

Principles of microwave heating

A microwave oven works by passing non-ionizing microwave radiation, usually at a frequency of 2.45 GHz through the suspension. Substances in the suspensions absorb energy from the microwaves in a process called „dielectric heating‟. Many molecules (such as dielectric materials) are electric dipoles, meaning that they have a partial positive charge at one end and a partial negative charge at the other, and therefore rotate as they try to align themselves with the alternating electric field of the microwaves. Rotating molecules hit other molecules and put them into motion, thus dispersing energy. This energy, when dispersed as molecular vibration in solids and liquids (i.e., as both potential energy and kinetic energy of atoms), is heat. Hence the composition of a suspension will affect how it will be heated up inside the microwave oven. Suspension with higher dielectric loss constant will be heated up faster because of the dipolar interaction. As the concentration of ions (e.g. dissolved salts increase, the rate of heating also increases because of the ionic interaction with microwaves.

.The main advantages of microwave-assisted reactions over conventional methods in particle synthesis are:

(a) the kinetics of the reaction are increased by one to two orders of magnitude

(b) novel phases are formed

(c) the heating is rapid, which can lead to energy saving

(d) selective formation of one phase over another often occurs

(e) superheating of solvents over the boiling point of solvent as a consequence of the microwave dissipation over the whole liquid volume

(f) uniform heating of the solution, so that a more homogeneous nucleation is obtained as well as a shorter crystallization time

(g) generation of localized high temperatures at the reaction sites which results in enhancement of reduction rates of metallic ions

2.4 Literature Reviews

2.4.1 Preparation of Cu-loaded CNTs by Other Techniques

Charinpanitkul et al. [8] synthesized copper (Cu) and carbon nanocomposite by arc discharge in liquid nitrogen. The synthesized carbon nanoparticles (CNPs) consisted of MWCNTs, SWCNHs and multi-shelled carbon nanocapsules (MSCNCs). TEM analysis of the synthesized samples revealed that, with an arc current of 180A, the arc discharge between copper and graphite electrodes in liquid-nitrogen atmosphere could provide MSCNCs with narrow size distribution in a range of 70–150 nm. Meanwhile, MWCNTs with a nominal diameter of 30–50 nm and a length of 250–500 nm as well as SWCNHs with a nominal diameter of 50–80nm could be fabricated by the arc discharge of graphite electrodes with an arc current of 100A. Results from spectroscopic analysis and BET surface measurement confirmed that the synthesized nanocomposites were cuprous oxide (Cu_2O) with a relatively high specific surface area.

Wang et al. [9] prepared MWCNTs with a mean diameter 50–80 nm incorporated with Cu layer by an electroless-deposition process. Results show that the prepared Cu-MWCNTs composite had a fiber-like appearance with a uniform size distribution. The Cu layer had an average thickness of 40 nm, composed of nanocrystalline grains, and thoroughly covered on the MWCNTs surface. The experimental results suggested that this process was an effective means for the fabrication of metal-deposited MWCNTs composites.

Wang et al. [10] prepared Cu nanoparticles deposited on CNTs by solution-infusion method. This method had an advantage in no requirement for purification process or additional reducing agents. In their work, the deoxidization of CuO to Cu was caused by amorphous carbon and carbon nanoparticles contained in the raw CNTs, which acted as reducing agents. Results showed that spherical nanoparticles of Cu with 50–70 nm in diameter were produced and uniformly deposited on the CNTs surface. The % loading of Cu in the prepared sample was approximately about 60 wt.%.

Martis et al. [11] used infrared (IR) irradiation to control decoration copper, cuprous oxide and cupric oxide nanocrystals with homogeneous sizes ranging from 7 to 15 nm on multi-walled carbon nanotubes (MWCNTs). The oxygen functionalities were generated on surface of MWCNTs by treating them with a mixture of concentrated H_2SO_4 and HNO_3 (molar ratio 3:1) followed by impregnation of copper precursor in the presence of IR irradiation. The composite was calcined in hydrogen, nitrogen and air, respectively, at suitable temperatures to achieve the pure phase of copper, cuprous oxide and cupric oxide nanocrystals.

Detail of proposed reviews of the preparation of Cu-loaded CNTs by other techniques is summarized in Table 2.3.

2.4.2 Preparation of Metal nanoparticles and Metal-loaded CNTs by Microwave Irradiation

Yan et al. [12] prepared CNTs/MnO_2 composites by reduction of potassium permanganate under microwave irradiation. Firstly, CNTs were refluxed in 10 wt% nitric acid for 30 min. Then, homogeneous dispersion of MnO_2 layer on CNTs were synthesized under microwave irradiation within 10 min. The CNT/MnO_2 composites prepared by these method show their suitable and promising electrode materials for supercapacitors with high power and energy densities.

Liao et al. [13] studied about preparation of nanocrystalline metal (Cu, Hg, Zn, Bi, Pb) sulfides with different shapes and different particle sizes by microwave irradiation. The metal sulfides were prepared in a microwave refluxing system for 20 min with power 20% (The means of 20% power is that microwave operates in 30 s cycle, on for 6 s, off for 24 s. The total power is 650 W). The products were pure orthorhombic Bi_2S_3 phase, cubic phase HgS, hexagonal phase CuS, cubic phase ZnS, cubic phase PbS, respectively. They found that the size and the shape of CuS, HgS, Bi_2S_3, ZnS, and PbS were different in the same microwave irradiation time. It showed that microwave irradiation could influence selective nucleation and growth rates of different compounds.

Detail of proposed reviews of the preparation of metal nanoparticles and metal-loaded CNTs by microwave irradiation is summarized in Table 2.4.

2.4.3 Preparation of Metal nanoparticles and Metal-loaded CNTs by Polyol Process

Sun et al. [14] prepared ultrafine copper powder by polyol process. Results show that the presence of sodium hydroxide (NaOH) and operating temperature played important roles in the formation of copper powder. It was shown that the reduction of Cu(II) to Cu in ethylene glycol (EG) could be observed by a color-changed process, which the color of the mixture of Cu precursor in the EG solution was changed from Cambridge blue to deep blue, to green, to yellow, to snuff color, to henna. This observation suggested that, in the presence of NaOH, the EG would be partly decomposed to acetaldehyde (CH_3CHO) at the beginning while the $CuSO_4{\cdot}5H_2O$ was subsequently transformed to $Na_2[Cu(OH)_4]$ (which was Cambridge blue) and $Na_2[Cu(OCH_2CH_2O)_2]$ (which was deep blue). The green color of the suspension appeared as the color of which came from the mixture of cuprous oxide (Cu_2O which was yellow) and the deep blue suspension. When the suspension turned yellow and the blue color of the liquid part disappeared and turned colorless, it suggested that the complex compounds in the suspension were reduced to Cu_2O completely. The appearance of henna color at the end of the process was the evidence of the presence of Cu in the suspension, which indicated that the Cu_2O was finally reduced with CH_3CHO to yield Cu and diacetyl ($CH_3COCOCH_3$).

Fievet et al. [15] prepared micrometer-size copper particles by polyol process. Results show that the size of copper particles can be controlled easily by varying the concentration of strong base such as NaOH and the molar ratio of CuO : polyol. They use sorbitol as a protective agent to prevent the particle sintering during the growth step. In their work, they explain the role of NaOH into 2 steps :

(1) Dissolution of the CuO precursor, reduction of Cu(II) species in solution and nucleation and growth of Cu_2 as an intermediate phase.
(2) Redissolution of Cu_2O, the reduction of the Cu(I) species in solution and the nucleation and growth of Cu particles.

Wang et al. [16] also prepared uniform silver (Ag) nanorods in large scale by the polyol process. The average diameter of the nanorods is about 100 nm and aspect ratio is from 15 to 20.

Yu et al. [17] synthesized homogeneous Cu_2O nanoparticles with size of 8–10 nm deposited on MWCNTs by polyol process. Cu_2O nanoparticles on the surface of MWNTs can be leafage-like or big spherical particle coated on the surface of MWNTs due to the change of the reaction conditions. They show the 4 procedures for the deposition of Cu_2O on the surface of MWNTs as follows :

(1) Diffusion of precursor to the surface of MWNTs and then serves as nucleation precursor
(2) Dissolution of the metal salts in solution
(3) Precipitation of an intermediate solid phase that acts as a reservoir phase and controls the supersaturation concentration of the metal ions in solution
(4) Nucleation and growth of the metal oxide particles from the solution at a temperature close to the boiling point of the polyol

Detail of proposed reviews of the preparation of metal nanoparticles and metal-loaded CNTs by polyol process is summarized in Table 2.5.

2.4.4 Preparation of Metal nanoparticles by Microwave-Polyol Process

Zhao et al. [6] synthesized different morphologies of copper and copper oxide nanocrystallites, including radially arrayed whiskers, cubic particles and sphere particles by microwave-polyol process. They have proposed a formation process for the Cu nanoparticles as: first, under dielectric heating, copper precursor dissolves completely in EG ($HOCH_2CH_2OH$), and then the intermediate solid is formed; during the second stage of the reaction the re-dissolution of the intermediate solid phase takes place. The reduction action of EG is due to diacetyl ($CH_3COCOCH_3$), which is formed by a duplicative oxidation of acetaldehyde (CH_3CHO) previously produced by dehydration of EG.

Blosi et al. [18] prepared stable Cu nano-suspensions have been obtained by an environment-friendly, microwave-assisted polyol synthesis. The synthesis was carried out in the presence of additives such as ascorbic acid (reducing agent) and PVP (chelating polymer) to improve the reduction kinetics and sols stability. They show that a dynamic equilibrium between reduction, nucleation, and growth impact to the size of particle directly. If the reduction rate is too slow, only a few nuclei are generated and the growth step is enhanced, and the particle size increase. Likewise, particles also increase if the reduction rate is too fast because numerous nuclei are formed and nucleation occurs in both multiple step dissolution and crystallization phenomena.

Detail of proposed reviews of the preparation of metal by microwave-polyol process is summarized in Table 2.6.

2.4.5 Preparation of Metal-loaded CNTs by Microwave-Polyol Process

Chen et al. [19] employed a microwave-polyol process to prepare platinum (Pt) nanoparticles supported on HNO_3-treated CNTs for electro-oxidation of methanol. It was shown that the synthesized Pt nanoparticles had a very uniform particle size with an average diameter of about 3.0 nm, and well dispersed on the CNTs surface.

Kim et al. [20] also reported on microwave-polyol synthesis of ruthenium oxide (RuO_2) nanoparticles highly dispersed on MWCNTs, which was applicable for use in electrochemical capacitors. It was shown that crystalline and partially hydrous $RuO_2 \cdot 0.64H_2O$ nanoparticles with about 2 nm in diameter were uniformly deposited on the MWCNTs surface and the loading amount of RuO_2 was approximately about 70 wt.%.

Raghuveer et al. [21] also employed microwave radiation with polyol reduction of a metal salt to decorated CNTs with Au nanoparticles. They used the microwave functional technique to prepare functional groups on the CNT surface. The functional groups serve as preferred nucleation points for reducing metal ions from solution by a microwave-assisted reduction reaction, yielding CNTs that are uniformly decorated with size range between 3 and 10 nm of gold nanoparticles.

Detail of proposed reviews of the preparation of metal-loaded CNTs by microwave-polyol process is summarized in Table 2.7.

Though there would be some reports related to the preparation of Cu/MWCNTs composite, clear understanding on the effect of microwave irradiation on the formation of Cu/MWCNTs composite is still insufficient. Some preparation parameters, which are irradiation power, irradiation time and initial feed compositions, would be experimentally investigated and discussed.

Table 2.3 Literature reviews of the preparation of Cu-loaded CNTs by other techniques

Researcher	Method	CNTs		Experimental results
		Dia. (nm)	**Pretreatment method**	
Charinpanitkul et al. (2009)	Arc discharge in liquid nitrogen	30-50	-	CNPs (include MWCNTs, SWCNHs and MSCNCs) containing Cu clusters inside
Wang et al. (2004)	Electroless deposition process	50-80	12.8 M conc. HNO_3 for 12h	Cu layers with average thickness of 40 nm deposited on CNTs
Wang et al. (2007)	solution infusion method	70-90	-	Uniform, sphere Cu particles with dia. 50-70 nm. loaded on CNTs
Martis et al. (2011)	IR irradiation	10	mixture of conc. H_2SO_4 and HNO_3 (molar ratio 3:1)	Uniform Cu, Cu_2O and CuO decorated on CNTs with sizes ranging from 7 to 15 nm

Table 2.4 Literature reviews of the preparation of metal nanoparticles and metal-loaded CNTs by microwave irradiation

Researcher	Metal	Microwave			CNTs		Experimental results
		Type	Power (Watts)	Time	Dia. (nm)	Pretreatment method	
Yan et al. (2009)	MnO_2 5 nm in thickness	Household microwave oven (Haier MA-2270, 2450 MHz)	700	10 min	20	refluxing in 10 wt% HNO_3 for 30 min	Homogeneous dispersion of MnO_2 layer on CNTs
Liao et al. (2001)	CuS HgS Bi_2S_3 ZnS PbS	Household microwave oven (Sanle general electric corp. Nanjing)	650	20 min with on/off heating	-	-	Nanocrystalline of orthorhombic Bi_2S_3 phase, cubic phase HgS, hexagonal phase CuS, cubic phase ZnS, cubic phase PbS,

Table 2.5 Literature reviews of the preparation of metal nanoparticles and metal-loaded CNTs by polyol process

Researcher	**Metal**	**Polyol**	**CNTs**		**Experimental results**
			Dia. (nm)	**Pretreatment method**	
Sun et al. (2005)	Cu	EG	-	-	Ultrafine Cu powder
Fievet et al. (1993)	Cu	EG	-	-	Fine, equiaxed with micrometre range Cu particles
Wang et al. (2010)	Ag 100 nm	EG	-	-	Uniform Ag nanorods
Yu et al. (2005)	Cu_2O	DEG	-	refluxing in conc. HNO_3 for 4 h at 413 K	Cu_2O with different morphologies (monodisperse nanoparticles, leafage-like particles to larger sphere) on CNTs

Table 2.6 Literature reviews of the preparation of metal nanoparticles by microwave-polyol process

Researcher	**Metal**	**Polyol**	**Microwave**			**Experimental Results**
			Type	**Power (Watts)**	**Time**	
Zhao et al. (2004)	Cu Cu_2O CuO	EG	Household microwave oven (NN-S570MFS)	365	15 min	different morphology and particle size
Blosi et al. (2010)	Cu 45-130 nm	DEG	Milestone MicroSYNTHplus	2x800 W magnetrons	10 min 50 min	Stable Cu nanosuspensions with a high solid concentration

Table 2.7 Literature reviews of the preparation of metal-loaded CNTs by microwave-polyol process

Researcher	Metal	Polyol	Microwave			CNTs		Experimental results
			Type	Power (Watts)	Time	Dia. (nm)	Pretreatment method	
Chen et al. (2005)	Pt dia. 3 nm	EG	Household microwave oven (National NN-S327WF, 2450MHz)	700	50 s	30-50	refluxing in conc. HNO_3 at 413K for 4h.	Uniform Pt nanoparticles and good dispersion on CNTs
Kim et al. (2010)	RuO_2 dia. 2 nm	DEG	Microwave digestion system MARS-5 (CFM Corporation)	1600	< 2 min	10-20	conc. HNO_3 at 80°c for 4h	Uniform and highly dispersed RuO_2 on CNTs
Raghuveer et al. (2006)	Au 3-10 nm	EG	Household microwave oven (General Electric model JES738WJ)	700	4500 s with on/off heating	30-40	microwave functional technique	Equiaxed and uniform Au on CNTs

CHAPTER III

EXPERIMANTAL

3.1 Pristine MWCNTs

MWCNTs, which are used as raw materials in this work, was bought from Bayer MaterialScience. The purity of MWCNTs are 95+%. From TEM images, MWCNTs have regular morphology with a diameter of about 15-20 nm and the wall surface is smooth as shown in Fig. 3.1.

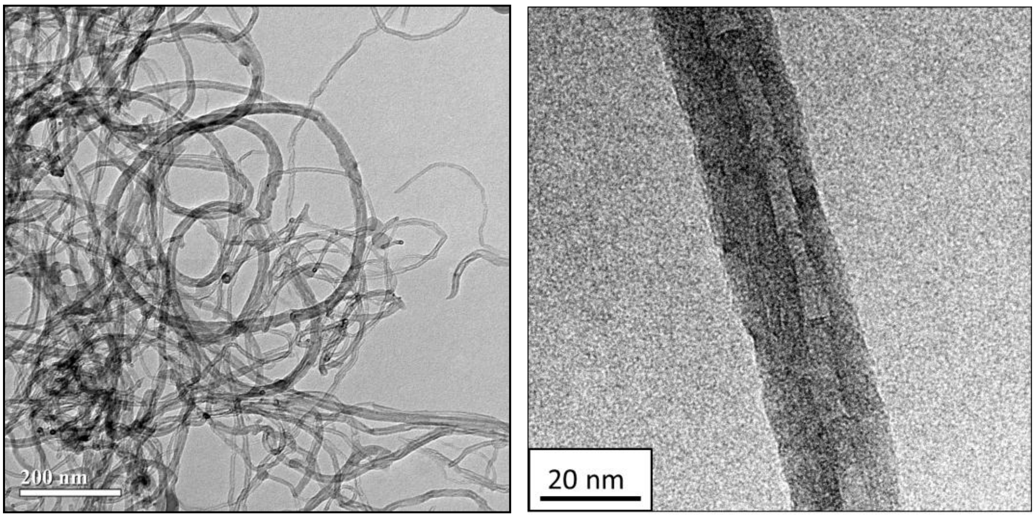


Figure 3.1 TEM images of pristine MWCNTs

3.2 Chemical agents

The list of chemical agents used in this research are shown in Table 3.1.

Table 3.1 List of chemical agents used in the research.

Chemical agents	Manufacturer/Grade
1. MWCNTs	Bayer Materials Science purity > 95 %
2. Copper(II) sulphate ($CuSO_4 \cdot 5H_2O$)	Asia Pacific Specialty Chemicals / grade AR
3. Ethylene glycol ($HOCH_2CH_2OH$)	QRëc / grade AR 99.5 %
4. Sodium hydroxide ($NaOH$)	Ajax Finechem
5. Nitric acid (HNO_3)	J.T. Baker 69-70 %
6. Sulfuric acid (H_2SO_4)	QRëc / grade AR 95-97 %

3.3 Microwave oven

The household microwave oven used in this work is LG MS-2127CW, whose equip with a 800 W magnetron operating at 2450 MHz.

Figure 3.2 Microwave oven

3.4 Experiment procedures

The experiment procedures of this work were separated into 3 parts as follow :

3.4.1 Preparation of Cu Particles by Microwave-Polyol Process

In a typical procedure, $CuSO_4 \cdot 5H_2O$ precursor was added into the mixed solution of EG and NaOH in a glass beaker by stirrer for 20 min at room temperature. Then the 100 ml mixture was placed at the middle of a household microwave oven (LG MS-2127CW, 2450 MHz , 800 W) and heated at a given microwave irradiation power for a given time. The mixture was then removed from the oven and allowed to cool down to room temperature. Finally, the mixture was filtered, washed with de-ionized water for several times and was dried in an oven overnight.

To study the effects of different conditions on the final particles, different experiment parameters were investigated, while keeping all other experimental conditions as in the typical run, as follows: (a) time of microwave irradiation: 1, 3, 5, 7 and 9 min, (b) microwave-irradiation power : 360, 600 and 800 Watts

3.4.2 Acid Pretreatment of MWCNTs Process

The commercial MWCNTs used in this work were produced by chemical vapor decomposition method as reported by supplier. 1 g of the commercial MWCNTs were sonicated in 200 ml of a mixture of concentrated sulfuric acid (H_2SO_4) and nitric acid (HNO_3) with a volumetric ratio of 3 to 1 at room temperature for 3 h. The MWCNTs dispersed in the acid mixture were then filtered, washed with de-ionized water for several times until the pH value reached neutral, and were dried in an oven overnight. Such acid treatment could lead to modification of the MWCNTs surface and enhancement of the interfacial adhesion between the MWCNTs and metal ions [22].

3.4.3 Preparation of Cu/MWCNT Composite by Microwave-Polyol Process

In a typical procedure, $CuSO_4{\cdot}5H_2O$ precursor was added into the mixed solution of EG and NaOH in a glass beaker by stirrer for 20 min at room temperature. Then the acid-treated MWCNTs was added to the 100 ml mixture and then sonicated at room temperature for 20 min. The MWCNTs dispersion was later placed at the middle of a household microwave oven (LG MS-2127CW, 2450 MHz , 800 W) and heated at a given microwave irradiation power for a given time. The MWCNTs dispersion was then removed from the oven and allowed to cool down to room temperature. Finally, the dispersion was filtered, washed with de-ionized water for several times and was dried in an oven overnight.

3.5 Analytical instruments

The instruments used to characterize the synthesized Cu nanoparticles and Cu-loaded MWCNTs composite are SEM (JSM-6400), XRD (Bruker AXS model D8 discover), TEM (JEOL JEM-2100), FT-IR (Model Spectrum One (Perkin Elmer)) and zetasizer (Malvern Nano – ZS).

3.5.1 Scanning Electron Microscopy (SEM)

Morphology of the obtained products was studied using scanning electron microscope (SEM) model JSM-6400 equipped with energy dispersive X-ray spectroscopy (EDS) at Scientific and Technological Research Equipment Centre Foundation, Chulalongkorn University. A photo of the Scanning Electron Microscopy (SEM) machine is shown in Fig. 3.3.

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Figure 3.3 Scanning Electron Microscope (SEM)

3.5.2 X-Ray Diffraction (XRD)

The X-ray diffraction patterns were done in a Bruker AXS model D8 discover at Scientific and Technological Research Equipment Centre Foundation, Chulalongkorn University using Cu$K\alpha$ radiation, with 40 kV and 40 mA, at 0.02◦ scan rate (in 2θ) with step of 0.3 s per step. Fig. 3.4 shows the XRD analysis system used in this work.

Figure 3.4 X-Ray Diffraction (XRD)

3.5.3 Transmission Electron Microscope (TEM)

The structure of the carbon nanotubes and the composites were observed on a JEOL JEM-2100 Analytical Transmission Electron Microscope (TEM), operated at 80-200 KV at Scientific and Technological Research Equipment Centre Foundation, Chulalongkorn University. The crystallographic information was also obtained from the selected area electron diffraction (SAED) analysis performed in the same instrument. A photo of the Transmission Electron Microscopy (TEM) machine is shown in Fig. 3.5.

Figure 3.5 Transmission Electron Microscope (TEM)

3.5.4 Fourier Transform Infrared Spectroscopy (FT-IR)

Function groups of samples were identified by using Fourier transform infrared spectrophotometer (FT-IR) Model Spectrum One (Perkin Elmer) at Scientific and Technological Research Equipment Centre Foundation, Chulalongkorn University. Infrared spectra were recorded between wavenumber of 400 and 4000 cm^{-1}. A photo of the Fourier transform infrared spectrophotometer (FT-IR) machine is shown in Fig. 3.6.

Figure 3.6 Fourier Transform Infrared Spectroscopy (FT-IR)

3.5.5 Zetasizer

The zeta potential of samples were measured by using zetasizer (Malvern Nano – ZS). A photo of zetasizer machine is shown in Fig. 3.7.

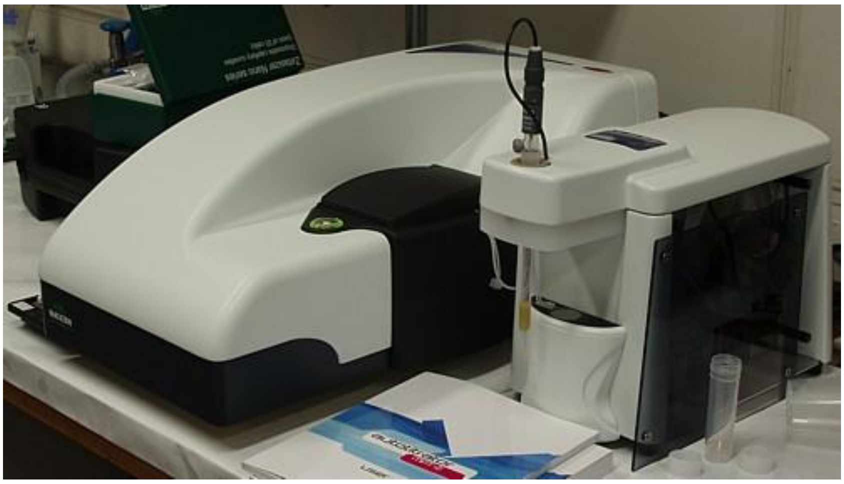


Figure 3.7 Zetasizer

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation of Cu Nanoparticles by Microwave-Polyol Process

To study the effects of different synthesizing conditions on Cu nanoparticles, different experiment parameters were investigated. All experimental conditions investigated in this work are (a) time of microwave irradiation: 1, 3, 5, 7 and 9 min, and (b) microwave irradiation power: 360, 600 and 800 Watts. The experimental conditions for the synthesis of copper nanoparticles are also listed in Table 4.1.

Table 4.1 Experimental conditions for the synthesis of copper nanoparticles

Sample No.	$CuSO_4 \cdot 5H_2O$ (g)	The molar ratio of NaOH to $CuSO_4 \cdot 5H_2O$	Time of microwave irradiation (min)	Microwave irradiation power (Watts)	Figure
Cu-t1	6.26	3	1	360	Fig. 4.2(a)
Cu-t3	6.26	3	3	360	Fig. 4.2(b)
Cu-TC[a]	6.26	3	5	360	Fig. 4.2(c), 4.5(a)
Cu-W600	6.26	3	5	600	Fig. 4.5(b)
Cu-W800	6.26	3	5	800	Fig. 4.5(c)
Cu-t7	6.26	3	7	360	Fig. 4.2(d)
Cu-t9	6.26	3	9	360	Fig. 4.2(e)

[a] Typical conditions.

4.1.1 Effect of irradiation time

It has been reported that formation of copper nanoparticles via polyol reduction process would be dependent upon the reaction time which would be controlled by heating time. In this study, microwave irradiation has been employed for heating a mixture of $CuSO_4{\cdot}5H_2O$ precursor in EG and NaOH. In order to examine the effect of microwave irradiation time, mass of $CuSO_4{\cdot}5H_2O$ precursor in the mixture of EG and NaOH, and microwave-irradiation power were fixed at 6.26 g and 360 Watts, respectively.

In typical experiments, the color of the original precursor solution was blue then the color changed to deep blue, yellow and finally henna when the irradiation time was increased from 1, 3, 5, 7 to 9 min as shown in Fig. 4.1. Sun et al. also investigate the reduction of Cu(II) to Cu in EG, which could be observed by change of solution color [14]. They reported that the color of the mixture of Cu precursor in EG solution changed from cambridge blue to deep blue, green, yellow, snuff, and finally henna. Similarly, these experimental results suggested that with the presence of NaOH, EG and microwave irradiation, Cu(II) ions can reduced to cuprous oxide (Cu_2O) and finally to Cu which could be observed as the appearance of snuff and henna color in these experimental.

Base on the color appearance, it could be concluded that the EG would be partly decomposed to acetaldehyde (CH_3CHO) at the beginning while the $CuSO_4{\cdot}5H_2O$ was subsequently transformed to the intermediate phase (which was deep blue). The intermediate phase formed a slurry suspension, which became diluted with the longer reaction time. The green color of the suspension appeared as the color of which came from the mixture of cuprous oxide (Cu_2O which was yellow) and the deep blue suspension. When the suspension turned yellow and the blue color of the liquid part disappeared and turned colorless, it suggested that the complex compounds in the suspension were reduced to Cu_2O completely. The appearance of henna color at the end of the preparation process was the evidence of the presence of Cu in the suspension, which indicated that the Cu_2O was finally reduced with acetaldehyde (CH_3CHO) to yield Cu and diacetyl ($CH_3COCOCH_3$).Confirmation of each species would be further discussed using XRD analysis. It should be noted that microwave irradiation time of 3 and 5 minutes would be sufficient for changing Cu(II) to Cu(I) then Cu would be obtained with the irradiation time was longer than 7 minutes.

Figure 4.1 Color changes of prepared suspension with different microwave irradiation time

Fig. 4.2 shows the SEM images of the synthesized products with different irradiation time. When the suspension is deep blue with 1 min of irradiation time, SEM image in Fig. 4.2(a) shows the amorphous particles which could be confirmed by XRD pattern. As shown in Fig. 4.3(a), crystalline copper was not identified. It indicated that $CuSO_4 \cdot 5H_2O$ dissolved in EG to form an intermediate phase which is deep blue. After 3 min of irradiation time the SEM image and XRD pattern as shown in Figs. 4.2(b) and 4.3(b) show some Cu_2O sedimented at the phase of yellow color. The diameter of Cu_2O is about 170 nm and no Cu nanoparticles occur. In our experimental, no peak in the XRD pattern can be indexed to CuO. It might be caused of Cu_2O is more thermodynamically stable than CuO. When the irradiation time is increased from 5 to 9 min, the product is the mixture of Cu and Cu_2O as shown in Figs. 4.2(c-e) and 4.3(c-e). It was obvioused that a diffraction peak at $2\theta = 36.4°$ and other two peaks at $2\theta = 42.3°$ and 61° were attributed to Cu_2O [6, 8, 11]. Meanwhile, peak at $2\theta = 43.3°$and $2\theta = 50.5°$ represented Cu [6, 8, 9, 11, 18, 23]. With the irradiation time of 5 min and microwave-irradiation power of 360 W, Cu nanoparticles can be synthesized with some derivatives.

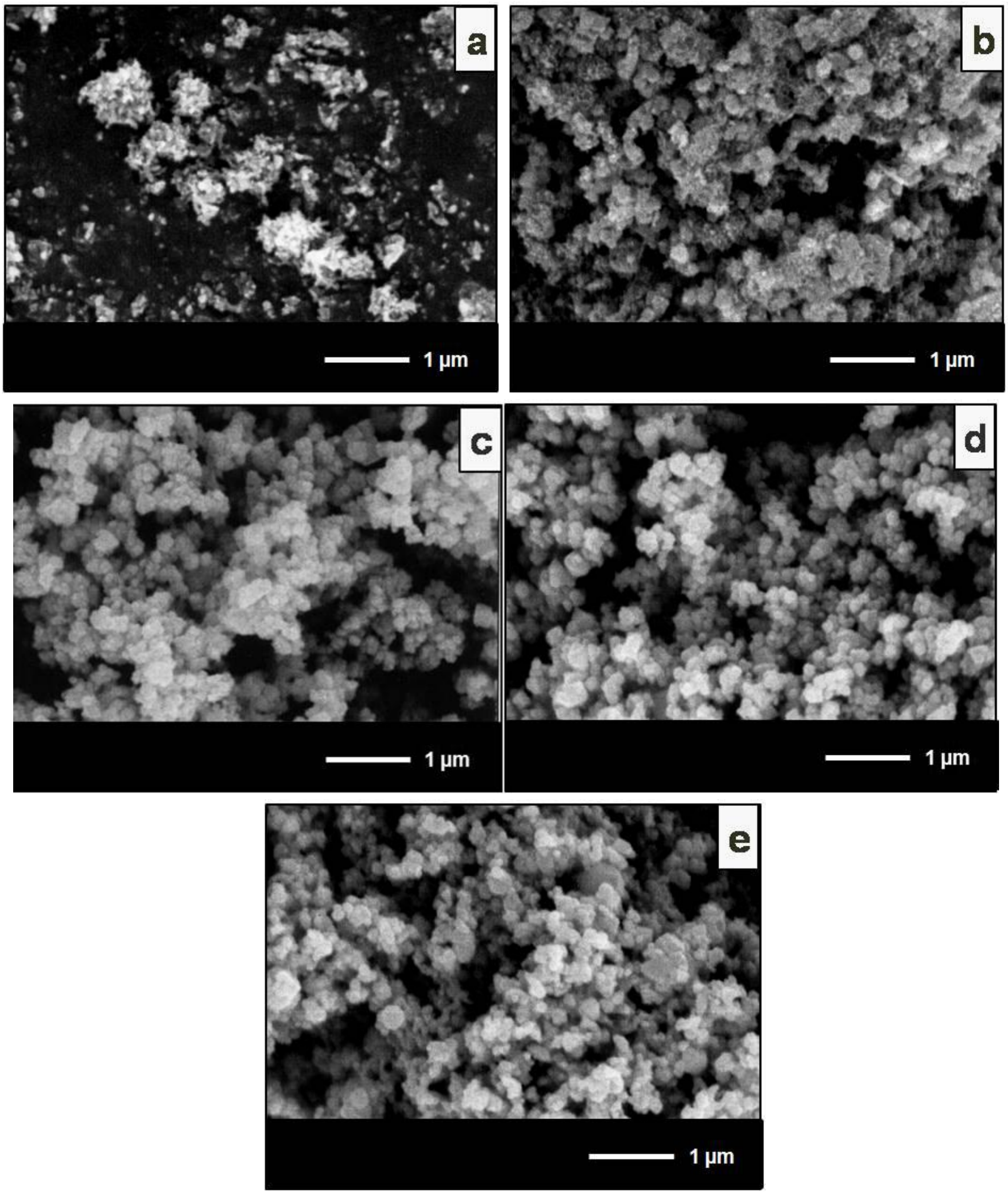


Figure 4.2 SEM images of the synthesized products with different irradiation time : (a) 1 min, (b) 3 min, (c) 5 min, (d) 7 min and (e) 9 min

Figs. 4.2(c-e) show some agglomerate with broad range of particles size. Fievet et al. [15] suggested that due to high reaction temperature, the Brownian motion of particle and atomic mobility are high enough to enhance the probability of particle collision and then of particle adhesion and agglomeration [15]. Otherwise the reduction rate in our experimental is slower than adding strong reducing agent in system. Blosi et al. [18] also show that if the reduction rate is too slow, only a few nuclei are generated and the growth step is enhanced, and the particle size would increase. So if we have a dynamic equilibrium between reduction, nucleation, and growth, the synthesized particle will become small in size.

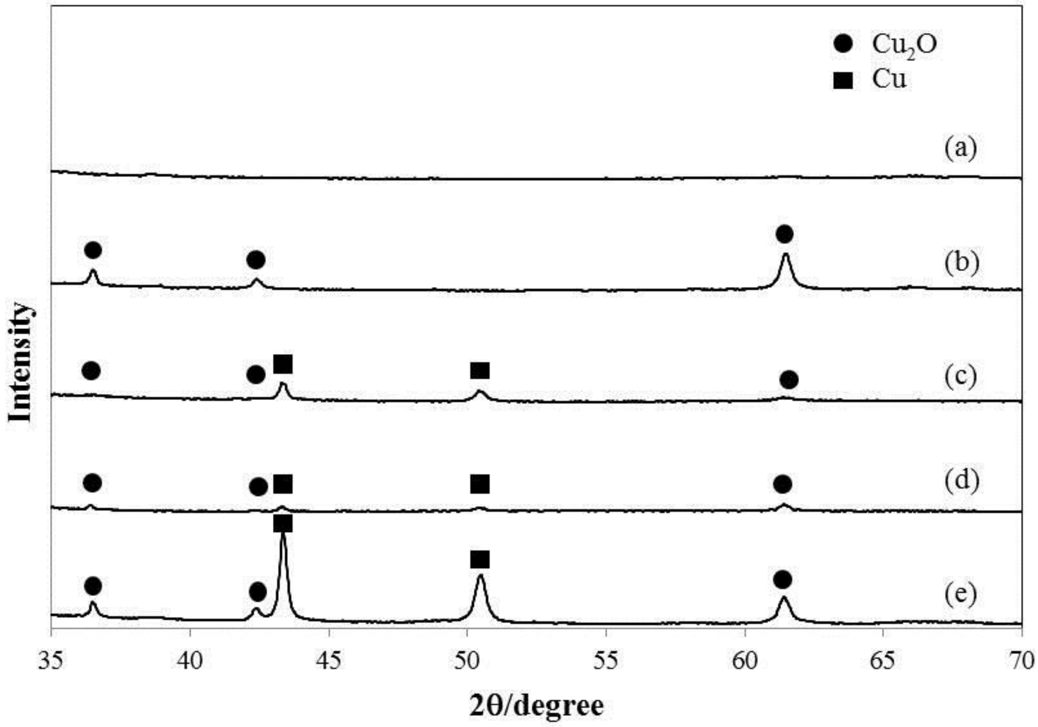


Figure 4.3 XRD patterns of the synthesized products with different irradiation time : (a) 1 min, (b) 3 min, (c) 5 min, (d) 7 min and (e) 9 min

Regarding to these microscopic analysis and the experimental observation in our study, Cu and Cu_2O nanoparticle formation step is proposed as shown in Fig. 4.4. It would take at least 5-9 min for the formation of Cu nanoparticles after the microwave irradiation. It suggests that microwave irradiation time had an important role in the preparation of copper nanoparticles.

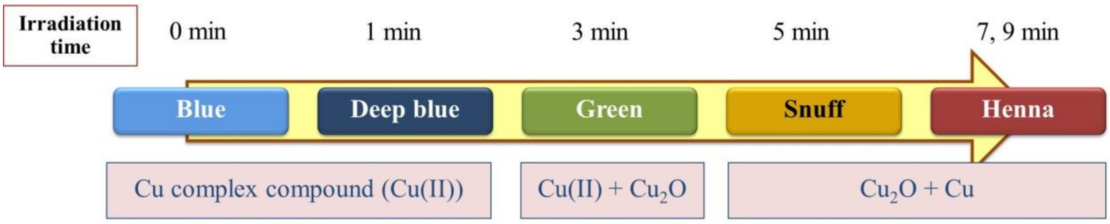


Figure 4.4 Formation scheme of synthesized products with different irradiation time

4.1.2 Effect of microwave-irradiation power

Based on other previously reported literatures, several nanoparticles of metal could be prepared by a microwave-polyol process using a microwave irradiation power from 365 to 1600 Watts [6, 7, 12, 18-20]. Therefore, the microwave-irradiation power might play a role in this reaction. In our investigations, the microwave irradiation powers of 360, 600 and 800 W were used. From the previous result of the irradiation time effect, 5 min of microwave irradiation time can provide Cu nanoparticles. For further investigation on effect of microwave-irradiation power, mass of $CuSO_4 \cdot 5H_2O$ precursor in the mixture of EG and NaOH, and microwave irradiation time were fixed at 6.26 g and 5 min, respectively.

After heating with microwave-irradiation power of 360 Watts, the color of products was changed to snuff color as shown in previous result. Moreover, it was confirmed by XRD in Fig. 4.6 (a-c) that the mixture of Cu_2O and Cu nanoparticles were prepared. Diffraction peaks at $2\theta = 36.4°$, $42.3°$ and $61°$ were attributed to Cu_2O [6, 8, 11]. Meanwhile, peaks at $2\theta = 43.3°$and $50.5°$ represented Cu [6, 8, 9, 11, 18, 23]. While the color of suspensions were both changed to henna color with microwave power of 600 and 800 Watts. It suggested that Cu nanoparticles occurred in product as shown in Fig.4.5. The particles also agglomerate, leading to a broad range of particles size with higher microwave-irradiation power.

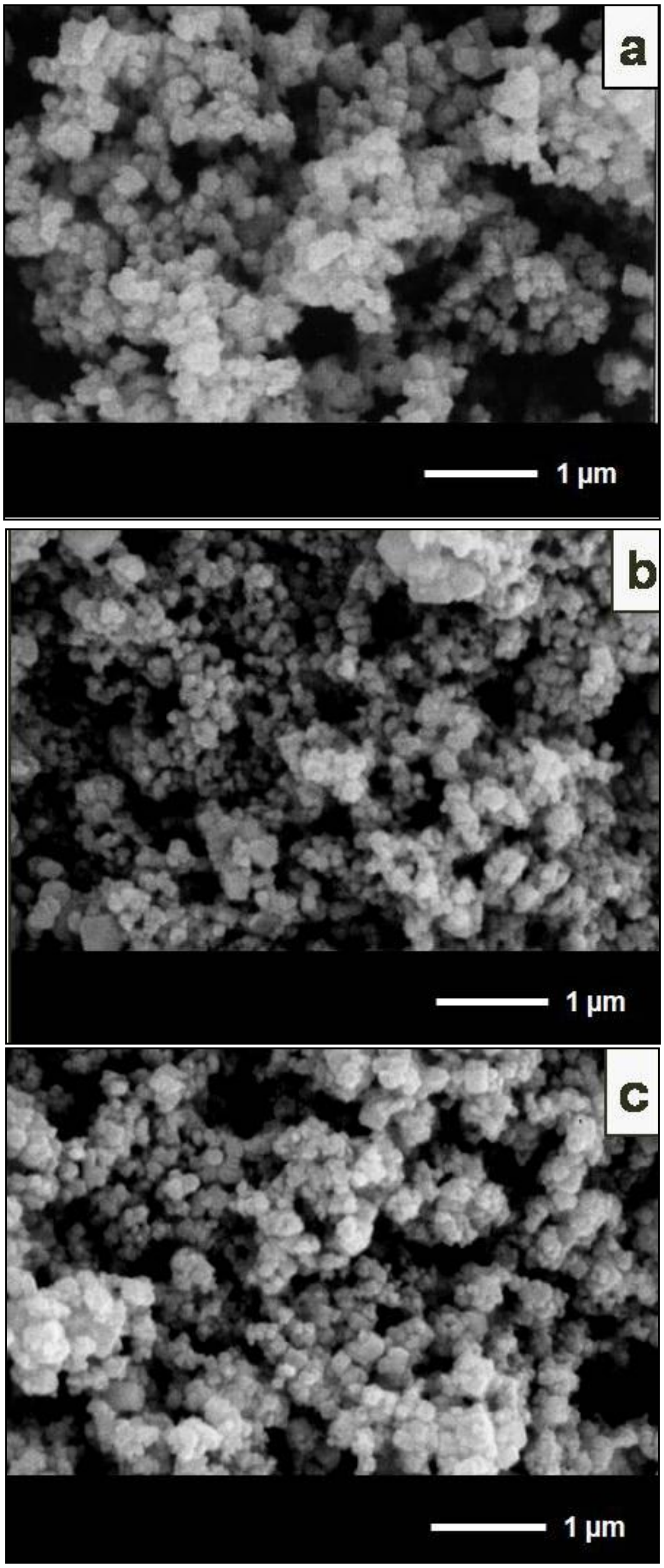


Figure 4.5 SEM images of the synthesized products with different microwave-irradiation power: (a) 360 W, (b) 600 W and (c) 800 W

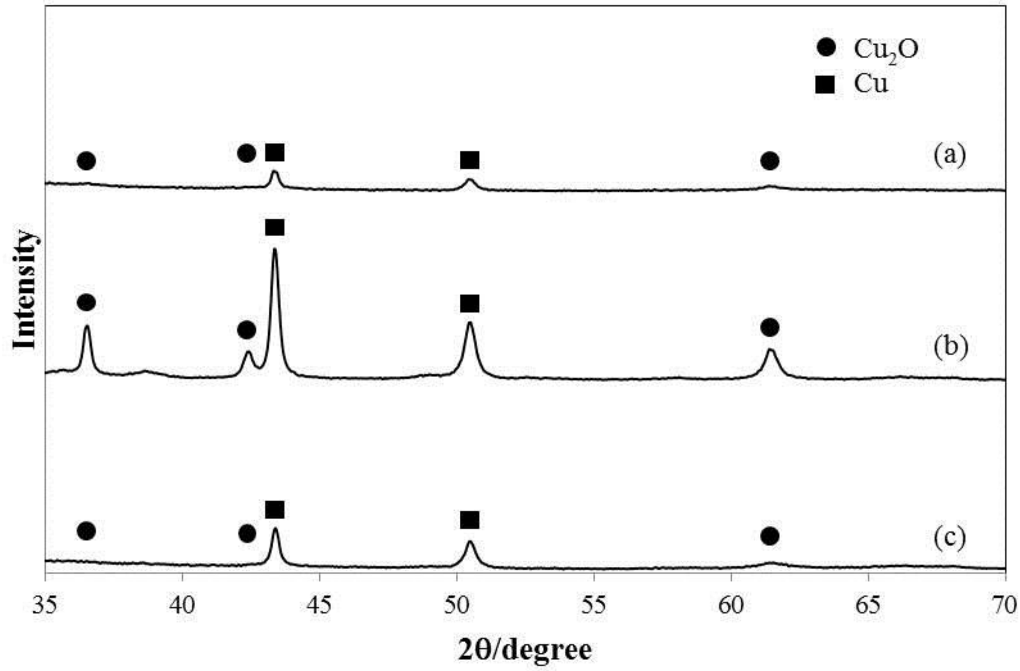


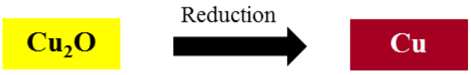
Figure 4.6 XRD patterns of the synthesized products with different microwave-irradiation power: (a) 360 W, (b) 600 W and (c) 800 W

4.1.3 Formation process for the Cu nanoparticles

Cu and Cu_2O nanoparticles can also be prepared by microwave treatment; they follow a reduction mechanism. At 194 °C, the reduction product is Cu. Fievet et al. [15, 24] have proposed that the metal particles were formed by nucleation and growth from the solution. According to this mechanism, we have proposed a formation process for the Cu nanoparticles;

(1) Dissolution of $CuSO_4 \cdot 5H_2O$ precursor in solution (which was cambridge blue), reduction of Cu (II) in solution then nucleation and growth of intermediate phase (which was deep blue)

(2) Redissolution of Cu_2O, reduction of Cu(I) in solution and nucleation and growth of Cu nanoparticles



During the first step EG would be partly decomposed to acetaldehyde (CH_3CHO) to serve as a reducing agent for Cu_2O to yield Cu and diacetyl ($CH_3COCOCH_3$) as shown in equation 4.1 and 4.2.

The reaction can be schematized as follows:

$$HOCH_2CH_2OH \longrightarrow CH_3CHO + H_2O \qquad (4.1)$$

$$Cu_2O + 2\,CH_3CHO \longrightarrow 2\,Cu + CH_3COCOCH_3 + H_2O \qquad (4.2)$$

4.1.4 Effect of reducing agent

To study effect of reducing agent, Ascorbic acid was added into the mixed solution of EG and NaOH. Then, $CuSO_4{\cdot}5H_2O$ precursor was added into the mixed solution in a glass beaker equipped with a stirrer for 20 min at room temperature. Then the acid-treated MWCNTs was added to the mixture and then sonicated at room temperature for 20 min. The MWCNTs dispersion was heated in a 360 W microwave oven with irradiation time of 5 min. The MWCNTs dispersion was then removed from the oven and cooled down to the room temperature. Finally, the dispersion was filtered, washed with de-ionized water for several times and dried in an oven overnight.

From Figs. 4.2 (c) and 4.3 (c), agglomerated Cu_2O and Cu nanoparticles could be observed. It suggested that CH_3CHO, which act as a reducing agent to convert Cu(II) and Cu(I) to Cu, was not strong enough to complete the reduction reaction. CH_3CHO generated from EG could act as a reducing agent and a solvent for solutes during the reduction of $CuSO_4{\cdot}5H_2O$ in the EG.

To avoid the particle growth and agglomeration, ascorbic acid would be added as strong reducing agent. The precursor reduction rate is linked to the following metal nanoparticle nucleation and growth processes. Ascorbic acid was added into the mixed solution to improve the reduction. The introduction of reducing agent increases the reduction rate, by inducing nuclei and leading to small and homogeneous particle size. Equation 4.3 shows the reaction when adding ascorbic acid in the system.

$$Cu_2O + 2\,CH_3CHO + H^+ \longrightarrow 2\,Cu + CH_3COCOCH_3 + H_2O \qquad (4.3)$$

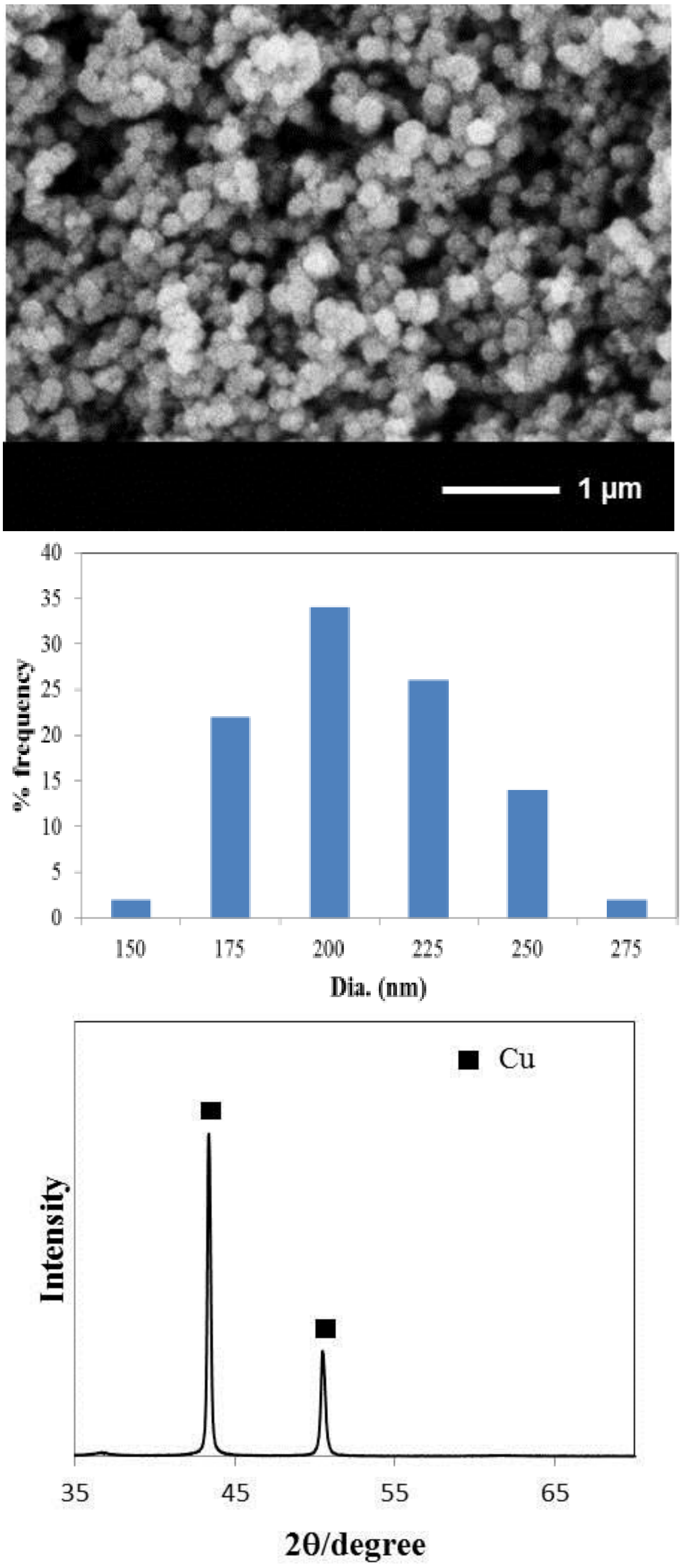


Figure 4.7 SEM image and XRD pattern of the synthesized products with adding ascorbic acid

Fig. 4.7 shows the appearance of small and uniform Cu particles with sub-micron size. The average Cu particles size is 195 nm. From XRD pattern, diffraction peaks at $2\theta = 43.3°$and $50.5°$ confirm that only Cu nanoparticles exist in the sample. Therefore, addition of ascorbic acid can prevent Cu nanoparticles from agglomeration during the growth step and also improve the stability of Cu when contact with oxygen in the air after the microwave irradiation. This is attributed that ascorbic acid with its organic structure and help protecting Cu particles from this reactive surrounding.

4.2 Acid Pretreatment of MWCNTs Process

Due to MWCNTs are a hydrophobic material and it is difficult to adsorb metal on their surfaces. In order to support metals effectively, the surfaces of MWCNTs should have defected to form functional groups, such as carbonyl (>C=O), carboxyl (-COOH) and hydroxyl (–OH). Concentrated acids can be used to introduce functional groups on the surfaces of carbonaceous materials [25] and decreased the hydrophobicity of the carbon nanotubes and made the surface more accessible to the aqueous solution of the metal precursors or deposits.

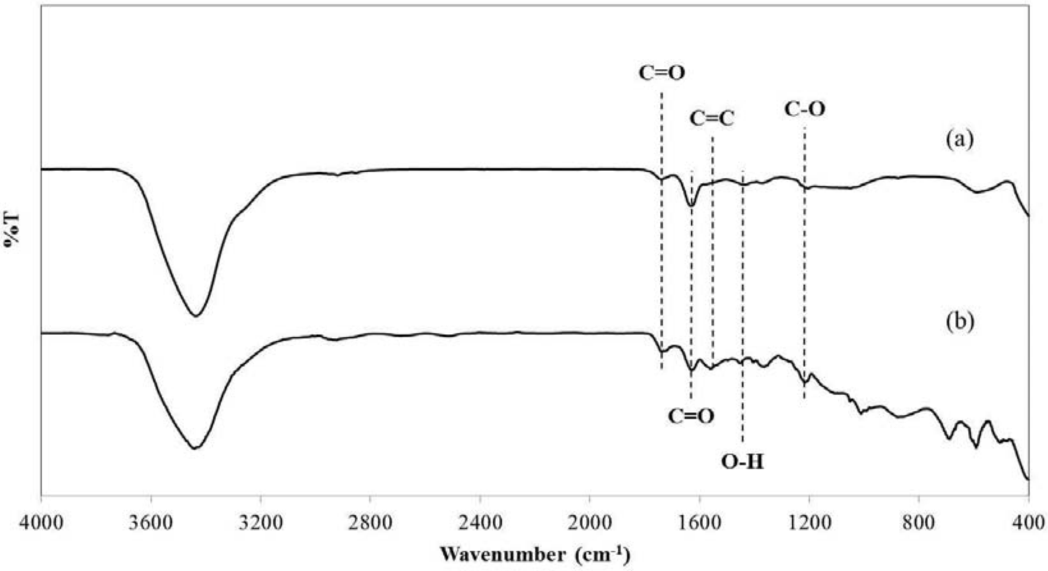


Figure 4.8 FT-IR spectra of (a) pristine MWCNTs and (b) acid-treated MWCNTs

In our experiments evidence of the functionalization by hydrophilic groups (–OH, –COOH, >C=O) of MWCNTs when they were treated with sulfuric/nitric acid mixture comes from the FT-IR spectra and moreover from the observation that such acid-treated MWCNTs give stable dispersions in aqueous solution. Whether MWCNTs was pretreated with acid or not, the peak at 1222, 1435, 1539, 1614 and 1719 cm^{-1} were presented in Fig.4.8. Peak at 1719 cm^{-1} ,which is C=O stretching of carboxylic acids, and another peak at 1222 cm^{-1} which is C–O stretching in the same functionalities are both increased after acid pretreatment. The peak at 1539 cm^{-1} is assigned to C=C stretching, which originates from structure of carbon nanotubes. The peak at 1435 cm^{-1} remained present in the spectra because of a larger amount of O–H bending functional group and peak around 1614 cm^{-1} corresponding to the H-bonded carbonyl groups (C=O) that conjugate with C=C in the graphene wall. Similar results have been reported by several other authors that after acid treatment the functional groups which can be bond with Cu^{2+} ions were increased.

To confirm the functionalities of the acid-treated MWCNTs, zeta potential of the pristine MWCNTs were changed from -9.02 mV to -23.6 mV due to functionalization is observed for the acid-treated MWCNTs. The negative zeta potential of the pristine MWCNTs might be caused by the attachment of hydroxide ions onto the hydrophilic surface or it was due to a slight intentional surface oxidation by the manufacturer. Base on the work by Schierz et al. [26], the zeta potential was decreased by the deprotonation of functional groups. According to our FT-IR measurements, these groups should be carboxylic groups.

4.3 Preparation of Cu/MWCNT Composite by Microwave-Polyol Process

To study the effects of different conditions on the final composite, different experiment parameters were investigated, while keeping all other experimental conditions as in the typical run, as follows: (a) time of microwave irradiation: 1, 3, 5, 7 and 9 min, (b) microwave irradiation power: 360, 600 and 800 Watts and (c) mass of $CuSO_4 \cdot 5H_2O$ precursor: 0.114 and 0.233 g. The experimental conditions for the synthesis of Cu/MWCNT composite were listed in Table 4.2.

Table 4.2 Experimental conditions for the synthesis of Cu/MWCNT composite.

Sample No.	Acid-treated MWCNTs (g)	$CuSO_4$•$5H_2O$ (g)	The molar ratio of NaOH to $CuSO_4$•$5H_2O$	Time of microwave irradiation (min)	Microwave irradiation power (Watts)	Figure
Cu/MWCNTs-t1	0.05	0.114	3	1	360	Fig. 4.10(b)
Cu/MWCNTs-t3	0.05	0.114	3	3	360	Fig. 4.10(c)
Cu/MWCNTs-TC[a]	0.05	0.114	3	5	360	Fig. 4.10(d), 4.12(a), 4.15(a)
Cu/MWCNTs-W600	0.05	0.114	3	5	600	Fig. 4.12(b-c)
Cu/MWCNTs-W800	0.05	0.114	3	5	800	Fig. 4.12(d)
Cu/MWCNTs-t7	0.05	0.114	3	7	360	Fig. 4.10(e)
Cu/MWCNTs-t9	0.05	0.114	3	9	360	Fig. 4.10(f)
Cu/MWCNTs-loading	0.05	0.233	3	5	360	Fig. 4.15(b)

[a] Typical conditions.

4.3.1 Effect of irradiation time

In this study, microwave irradiation has been employed for heating a suspension of acid-treated MWCNTs dispersed in a solution of copper precursor (mixture of $CuSO_4{\cdot}5H_2O$ precursor in EG and NaOH). In order to examine the effect of microwave irradiation time, mass of acid-treated MWCNTs, mass of $CuSO_4{\cdot}5H_2O$ precursor in the mixture of EG and NaOH, and microwave-irradiation power were fixed at 0.05 g, 0.114 g and 360 Watts, respectively. From the results in "effect of irradiation time on preparation of Cu nanoparticles by microwave-polyol process", it shows that microwave irradiation time have an effect on formation of Cu nanoparticles.

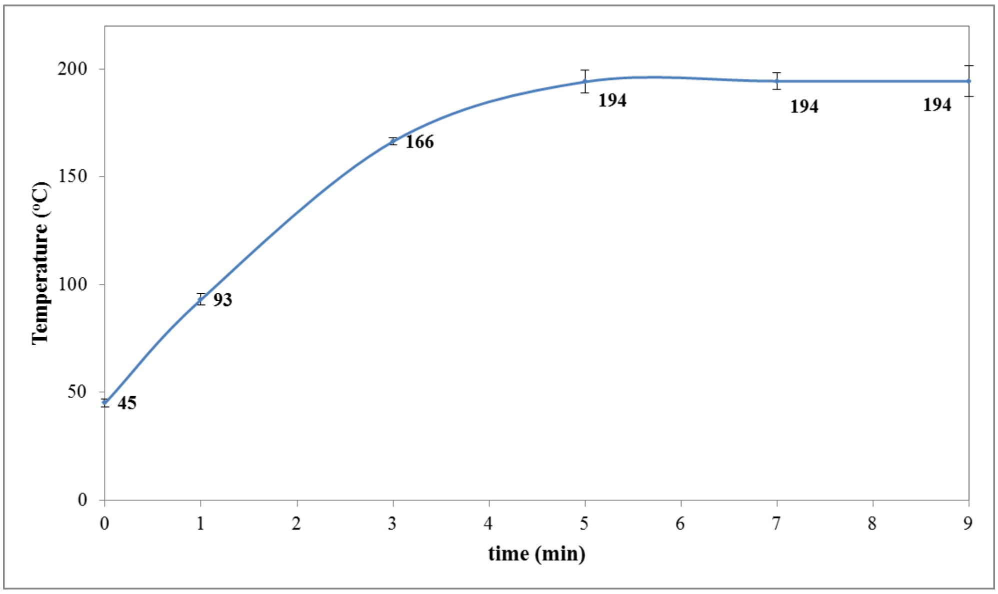


Figure 4.9 Temperature of the suspension after remove from the microwave oven

Experimental measurements in this research indicated that the temperature of a suspension of acid-treated MWCNTs dispersed in a solution of copper precursor increased linearly with a fast heating rate and reached 194 ◦C after 5 min as shown in Fig. 4.9. In order to measure the temperature the suspension of EG solution of copper precursor and acid-treated MWCNTs after microwave treatment, the microwave oven was immediately opened and the temperature of the suspension was quickly measured by a thermocouple. At high temperatures close to the boiling point, EG is decomposed to generate reducing agent, CH_3CHO, for the reduction of the metal ions to metallic particles [14, 19].

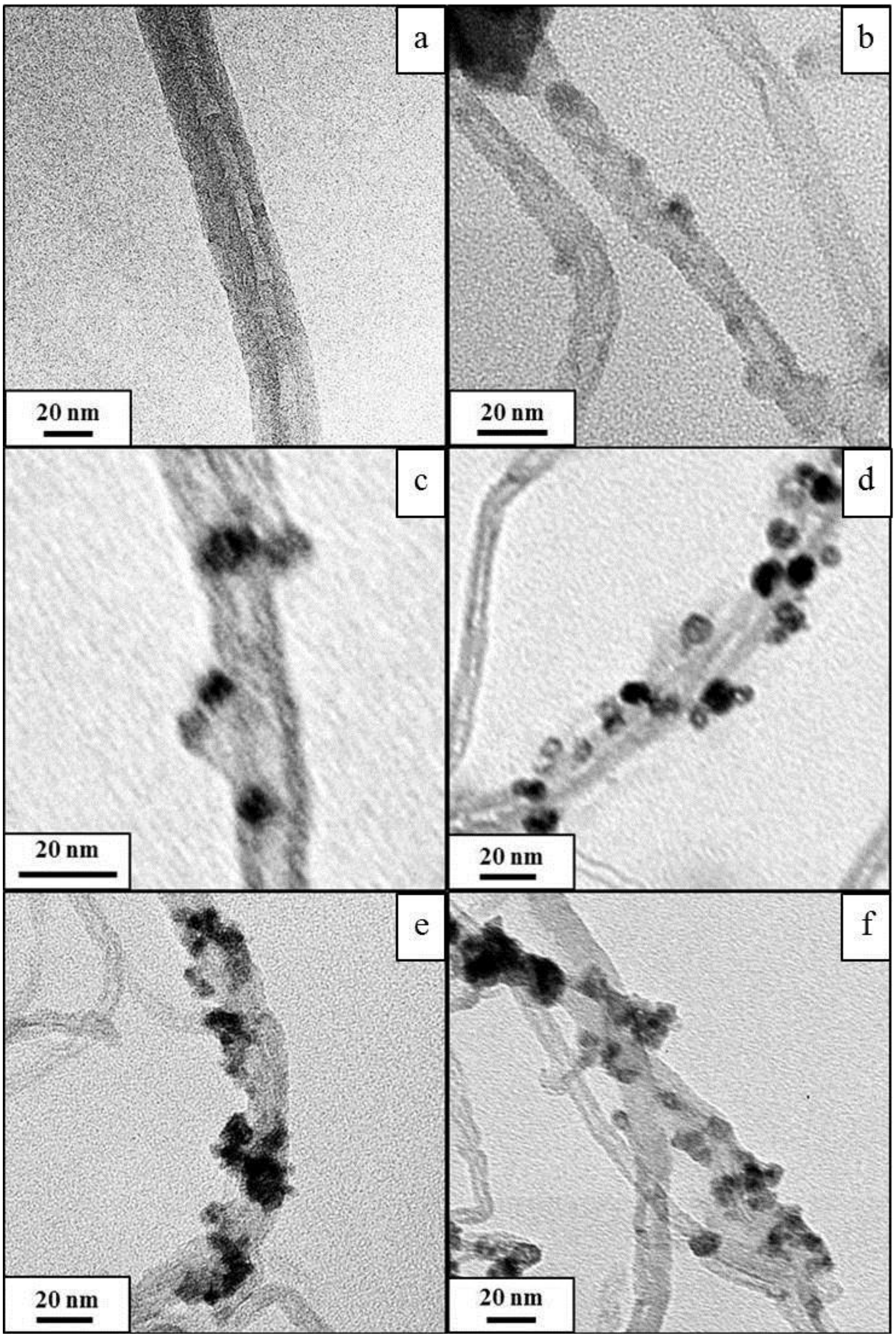


Figure 4.10 TEM images of (a) pristine MWCNTs and composite with different irradiation time : (b) 1 min, (c) 3 min, (d) 5 min, (e) 7 min and (f) 9 min

Fig. 4.10 (a) shows typical TEM image of the pristine MWCNTs. It can be seen that the pristine MWCNTs have regular morphology with a diameter of about 15-20 nm and the wall surface is smooth. The micrographs reveal no particles depositing on the MWCNTs surface. The XRD pattern in Fig. 4.11(a) shows the diffraction peaks at $2\theta = 25.5^{o}$ and 42.5^{o} which represent the MWCNTs and agree well with other reports [8, 9, 11, 27]. After pretreatment with acids and heating in the mixture of $CuSO_4 \cdot 5H_2O$ and EG by microwave irradiation at the specified conditions, it is clearly seen that the morphology of MWCNTs were changed as shown in Fig.4.10 (b-f). The surfaces of the MWCNTs become rougher than before due to the deposition of particles of Cu and Cu_2O on the wall surface. The possible explanation to the deposition of Cu and Cu_2O is that the acid treatment modified the MWCNTs with carbonyl (>C=O), carboxyl (-COOH) and/or hydroxyl (-OH) groups [15], which are more reactive than the graphene surface of the MWCNTs. The functional groups not only enhance the solubility of the MWCNTs, but also gives Cu and/or Cu_2O can be nucleated on the wall of MWCNTs under microwave irradiation. Thus during the reactions, Cu^{2+} ions were diffused to the surface of MWCNTs and reduced to Cu_2O and Cu.

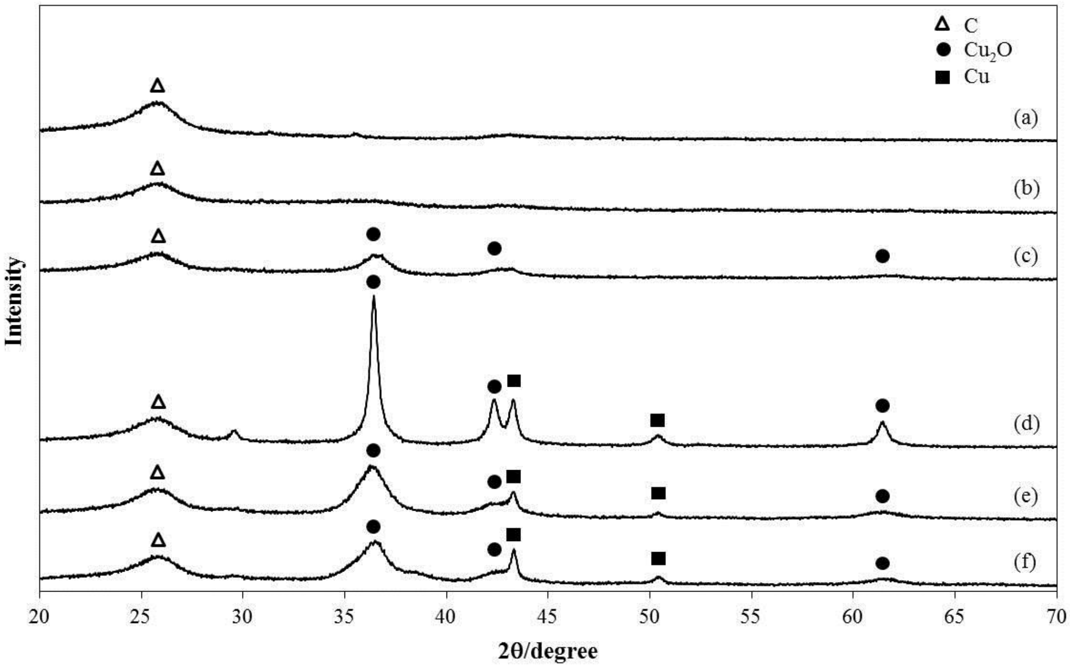


Figure 4.11 XRD patterns of (a) pristine MWCNTs and composite with different irradiation time : (b) 1 min, (c) 3 min, (d) 5 min, (e) 7 min and (f) 9 min

The effect of irradiation time from 1 to 9 min was observed on the TEM images of composites prepared at the microwave-irradiation power of 360 W as shown in Fig. 4.10 (b-f). Their show the different structure of particles deposited on MWCNTs surface. The average diameter size of MWCNTs for the composites are about 12-15 nm.

After 1 min of heating, it has some particle with diameter between 2- 9 nm deposited on MWCNTs surface. However, the XRD pattern in Fig. 4.11 (b) shows that Cu_2O and Cu were not occurred. It suggested that the 1 min of irradiation time which reaction temperature is 93 ^{o}C was not sufficient to allow the reduction of the Cu precursor to yield Cu_2O and Cu. However, we indicate that the particle on MWCNTs surface come from the adsorption of Cu^{2+} ions on the functional groups of the acid-treated MWCNTs surface via electrostatic attraction. Then the Cu^{2+} ions was transformed to intermediate phase as same as previous results. Cu_2O on the MWCNTs surface was first identified when using 3 min of irradiation time. The reaction temperature is 166 ^{o}C in this irradiation time. It suggested that temperature was essential to reduce the Cu(II) to Cu(I). If it was lower than 166 ^{o}C, the reduction could not occur. The diffraction peaks at $2\theta = 36.4°$ and other two peaks at $2\theta = 42.3°$ and 61° were attributed to Cu_2O [6, 8, 11]. After 5-9 min of irradiation time, the particles on MWCNTs surface became increasing in size and were more agglomerated as shown in Fig. 4.10 (d-f). Due to a faster nucleation leads to smaller particles size, while a slower nucleation gives the particles larger and more agglomerated. The agglomeration might be come from the van der Waals attraction of the closer particles. Fig. 4.11 (d-f) confirms that the particles on MWCNTs surface were Cu_2O and Cu by the diffraction peak at $2\theta = 43.3°$and 50.5° which represented Cu [6, 8, 9, 11, 18, 23]. It suggests that the temperature during irradiation time of 5 min was sufficient to allow the reduction of the Cu precursor to yield Cu_2O and Cu. At 194 ^{o}C, the reduction of Cu(I) to Cu was take place.

In our experimental, we cannot synthesize only Cu deposited on MWCNTs surface because of Cu nanoparticles can be easily oxidized to form Cu_2O during synthesis. The remaining of Cu_2O in our samples might be formed by oxidation at the surface of Cu when contact with oxygen in the air after the microwave irradiation [28]
.

4.3.2 Effect of microwave-irradiation power

In this study, microwave irradiation has been employed for heating a suspension of acid-treated MWCNTs dispersed in a solution of copper precursor (mixture of $CuSO_4 \cdot 5H_2O$ precursor in EG and NaOH). In order to examine the effect of microwave irradiation power, mass of acid-treated MWCNTs, mass of $CuSO_4 \cdot 5H_2O$ precursor in the mixture of EG and NaOH, and microwave-irradiation time were fixed at 0.05 g, 0.114 g and 5 min, respectively.

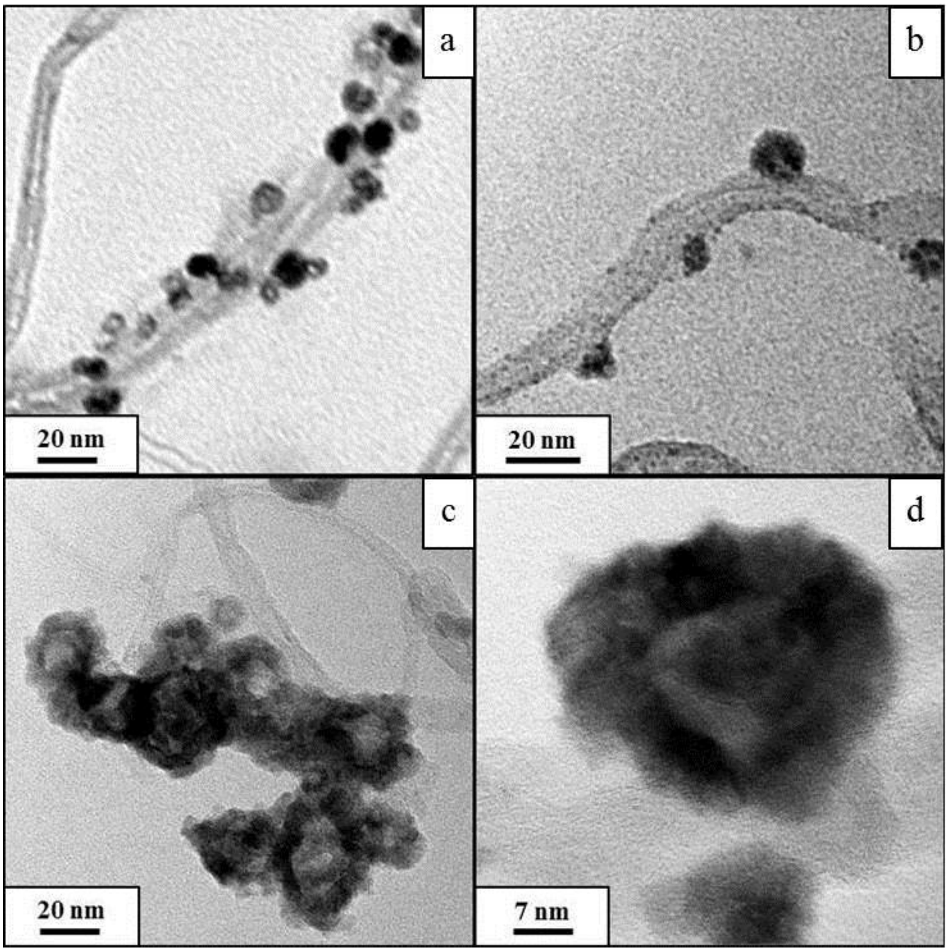


Figure 4.12 TEM images of composite with different microwave power at 5 min of irradiation time : (a) 360 W, (b-c) 600 W and (d) 800 W

The effect of microwave irradiation power was observed on the TEM images of composites prepared at the microwave-irradiation time of 5 min as shown in Figs. 4.12 (a-d). Their show the different structure of particles deposited on MWCNTs surface. The average diameter size of MWCNTs for the composites are about 12-15 nm. Compare with Fig. 4.12 (a), Fig. 4.12 (c-d) show larger particle size and agglomerate particle deposited on MWCNTs surface. Fig. 4.12 (d) shows the interface between Cu nanoparticles and the surface of MWCNTs. It can be inferred that the Cu nanoparticles were nucleated heterogeneously on the external surface of CNTs via microwave treatment. It confirms that the possible formation mechanism of Cu/MWCNT composite is the adsorption positive Cu^{2+} ions on the functional groups of the acid-treated MWCNTs surface via electrostatic attraction.

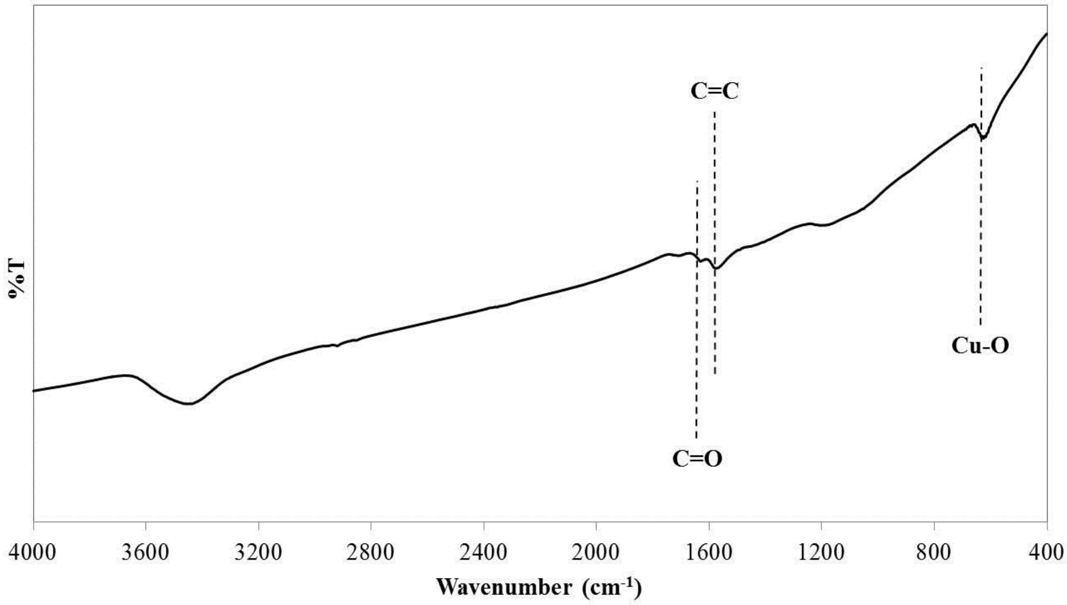


Figure 4.13 FT-IR spectra of Cu/MWCNTs-TC[a]

FT-IR spectra in Fig. 4.13 shows the functional groups in composites which synthesized under 360 W of microwave irradiation power for 5 min. Peak at 1719 cm^{-1} ,which is C=O stretching of carboxylic acids, and another peak at 1222 cm^{-1} which is C–O stretching were disappeared. The peak of C=C stretching, which originates from structure of carbon nanotubes shifts from 1539 to 1548 cm^{-1}. The peak assigned to the H-bonded carbonyl groups (C=O) that conjugate with C=C in the graphene wall shifts from 1614 to 1605 cm^{-1}. Meanwhile, the new peak of Cu-O stretching appears at 609 cm^{-1}[14]. The charge of the composites is -10.8 mV. It increases from -23.6 mV of the acid-treated MWCNTs. Due to the negative charge of the acid-treated MWCNTs surface conjugates with positive charge of copper precursor.

Fig. 4.14 shows that the mixture of Cu_2O and Cu nanoparticles on MWCNTs surface were prepared at microwave-irradiation power of 360 and 600 W, and the Cu/MWCNT composite were prepared when using 800 W of microwave-irradiation time. It also obvious that a diffraction peak at 2θ = 36.4°, 42.3° and 61° were attributed to Cu_2O [6, 8, 11]. Meanwhile, peak at 2θ = 43.3°and 50.5° represented Cu as same as previous result [6, 8, 9, 11, 18, 23]. The particles also agglomerate and broad range of particles size on the MWCNTs surface when using higher microwave-irradiation power.

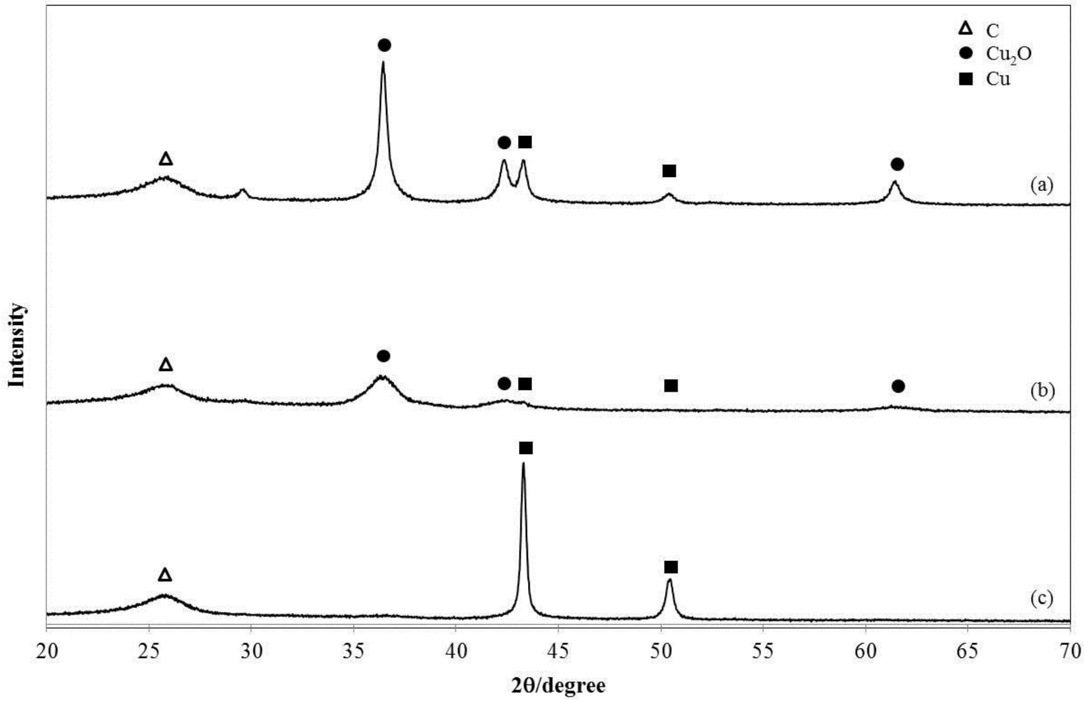


Figure 4.14 XRD patterns of composite with different microwave power at 5 min of irradiation time: (a) 360 W, (b) 600 W and (c) 800 W

4.3.3 Effect of amount of copper precursor

In this study, microwave irradiation has been employed for heating a suspension of acid-treated MWCNTs dispersed in a solution of copper precursor (mixture of $CuSO_4{\cdot}5H_2O$ precursor in EG and NaOH). In order to examine the effect of amount of copper precursor, mass of acid-treated MWCNTs, microwave-irradiation power, and microwave-irradiation time were fixed at 0.05 g, 360 W and 5 min, respectively.

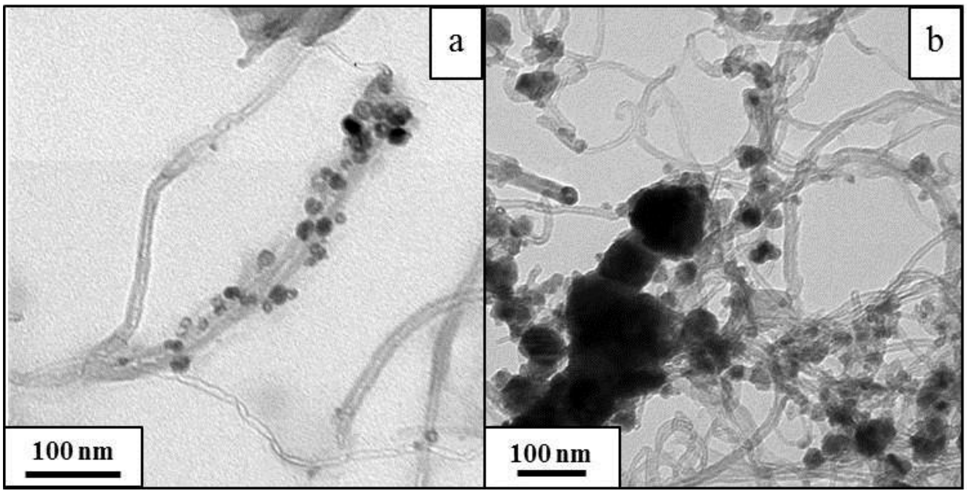


Figure 4.15 TEM images of composite with different amount of copper precursor: (a) 0.114 g and (b) 0.233 g

TEM image in Fig. 4.15 (b) shows the large particles separate with MWCNTs and particles deposited on MWCNTs surface. On the other hand, the composites using 0.114 g of precursor shows only particles deposited on MWCNTs surface. Because of the negative charge of the acid-treated MWCNTs surface are not enough to conjugate with increasing the positive charge of copper precursor. So the particle which not conjugate with the acid-treated MWCNTs would be nucleated homogeneously and then particle adhesion and agglomeration.

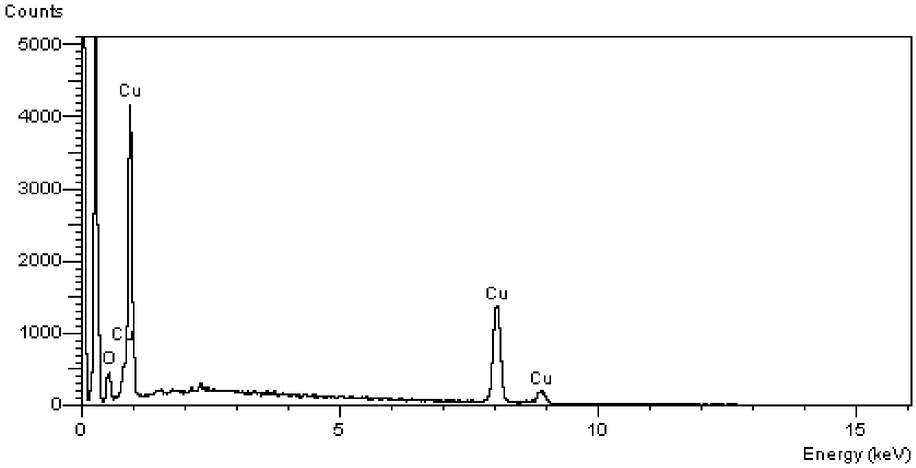


Figure 4.16 EDS spectrum of composite with 0.233 g of copper precursor

The energy dispersive X-ray spectroscopy (EDS) analysis has been performed for elemental analysis as shown in Fig. 4.16. From the result, it is found that the obtained products were composed mainly of Cu and some O . This confirms that Cu and Cu_2O nanoparticles exist in the synthesized products.

4.3.4 Formation process for the Cu/MWCNT composite

Table 4.3 Zeta potential of samples

	Zeta potential (mV)
Acid-treated MWCNTs	-23.6
$CuSO_4{\cdot}5H_2O$ precursor	4.85
Cu/MWCNTs-TC^a	-10.8

The formation of Cu depositing on MWCNTs may involve 3 consecutive steps, namely adsorption, reduction and agglomeration. First, the Cu^{2+} precursor is adsorbed on acid-treated MWCNTs surface; interacts with surface functional group by electrostatic attraction. From the zeta potential measurement summarized in Table 4.3, the charge of acid-treated MWCNTs surface is -23.6 mV. In comparison with 4.85 mV of $CuSO_4{\cdot}5H_2O$ precursor, the different of surface charge between 2 samples shows the presence of attractive electrostatic interactions between ions and sample surface [29]. Then the Cu^{2+} was reduced by EG to form Cu^+ and Cu nuclei on acid-treated MWCNTs surface. The surface charge after microwave-irradiation treatment is -10.8 mV. It suggested that there is interaction between charges which leads to increasing zeta potential. Finally, the suspending Cu^{2+} would further deposit and undergo reduction by EG, resulting in the growth of agglomerating Cu nanoparticles on the surface of MWCNTs. The schematic mechanism of Cu nanoparticle deposition on the MWCNTs surface is shown in Fig. 4.17.

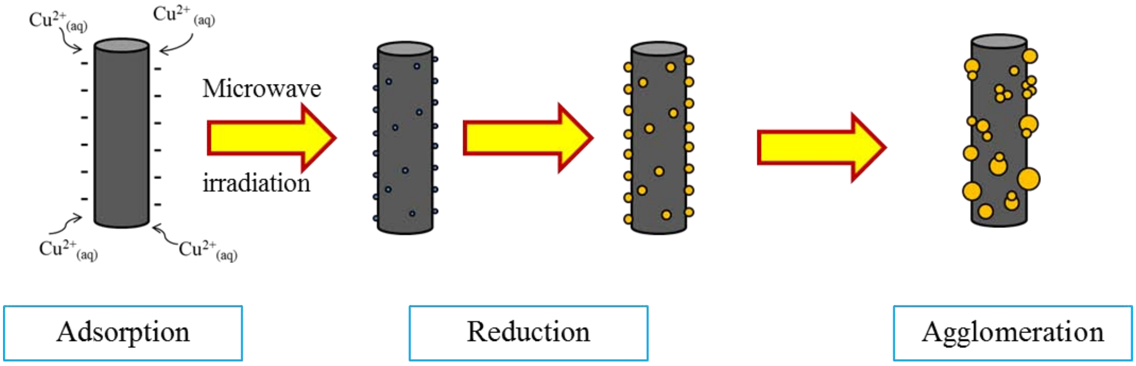


Figure 4.17 Schematic of Cu nucleation and growth on MWCNTs surface

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this work, the preparation of Cu particles and Cu-loaded MWCNT composite via microwave irradiation treatment is conducted. The conclusions of the present research are as follows:

1. CH_3CHO radical generated from EG could act as a reducing agent to convert Cu(II) to Cu nanoparticles, as well as a solvent for solutes, while NaOH enhances the reduction of $CuSO_4 \cdot 5H_2O$ in the EG.
2. Microwave irradiation plays an important role in the formation of the products; temperature was also found to be important in the reaction. At 166 and 194 ^{o}C was suitable for preparing Cu_2O and Cu nanoparticles, respectively.
3. Pretreatment of MWCNTs surface leads to deposition of Cu(II), Cu(I) and Cu particles on their surface.
4. The formation of Cu depositing on MWCNT involve 3 steps, namely adsorption, reduction reaction and agglomeration.
5. The microwave irradiation power and irradiation time affect the morphology of the products.

5.2 Recommendations for Future Work

Regarding to the previous conclusions, the following recommendations for the future studies are proposed.

1. Effect of reducing agent for preparation Cu/MWCNT composite should be investigated.
2. Other conditions of acid-treated MWCNT surface should be investigated for improving the dispersion of uniform Cu on MWCNT.
3. The applications for composites should be also investigated.
4. Effect of reduction condition using stronger alkali species, such as NaOH should be investigated.

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APPENDICES

APPENDIX A

EFFECT OF NaOH ON Cu NANOPARTICLES

Sodium hydroxide (NaOH) enhanced reduction of $CuSO_4 \cdot 5H_2O$ in EG [14]. In order to examine the effect of NaOH, mass of $CuSO_4 \cdot 5H_2O$ precursor in the mixture of EG and NaOH, irradiation time and microwave-irradiation power were fixed at 1.14 g, 5 min and 360 Watts, respectively.

Fig. A.1 show The color of suspension before and after heating in microwave oven with different molar ratio of NaOH : $CuSO_4 \cdot 5H_2O$. When without addition of NaOH, there was less change in color of product. The reduction rate was too slow and copper compound was not prepared. When the molar ratio of NaOH : $CuSO_4 \cdot 5H_2O$ were 1 and 3, the color of the products were changed to snuff color and henna color, respectively. The products were the mixture of Cu and Cu_2O as shown in Figs. A.3 (a-b). When the molar ratio increased to 5 and 7, Cu_2O disappeared in the products as shown in Figs. A.3 (c-d). Fievet et al. [15] found that increase of the NaOH concentration enhanced the solubility of copper precursor in NaOH solutions and they thought that the high concentration of NaOH was favorable to form intermediate phase and favorable for the dehydration of EG to CH_3CHO.

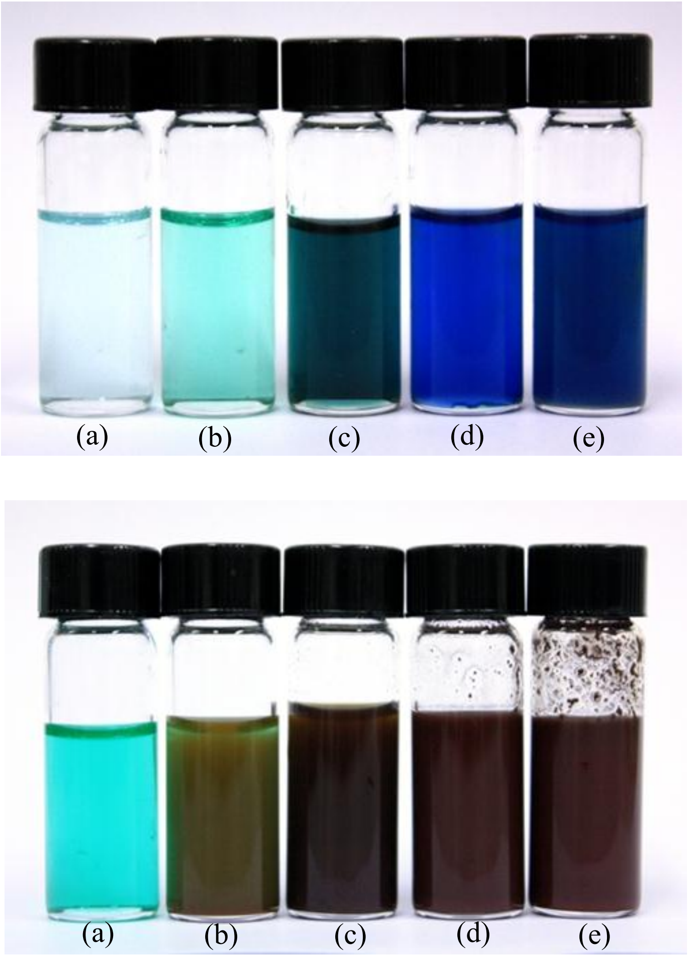

Figure A.1 The color of suspension before and after heating in microwave oven with different molar ratio of NaOH : $CuSO_4{\cdot}5H_2O$;
(b) 0, (b) 1, (c) 3, (d) 5 and (e) 7

SEM images in Figs A.2 show different morphologies of the products. When the molar ratio of NaOH : $CuSO_4{\cdot}5H_2O$ were 1 and 5, the product became agglomerated bulks. The product was subdivided into particles when the molar ratio of NaOH : $CuSO_4{\cdot}5H_2O$ were 3 and 7. It shown that increase of NaOH could be prepared only Cu nanoparticles in the sample.

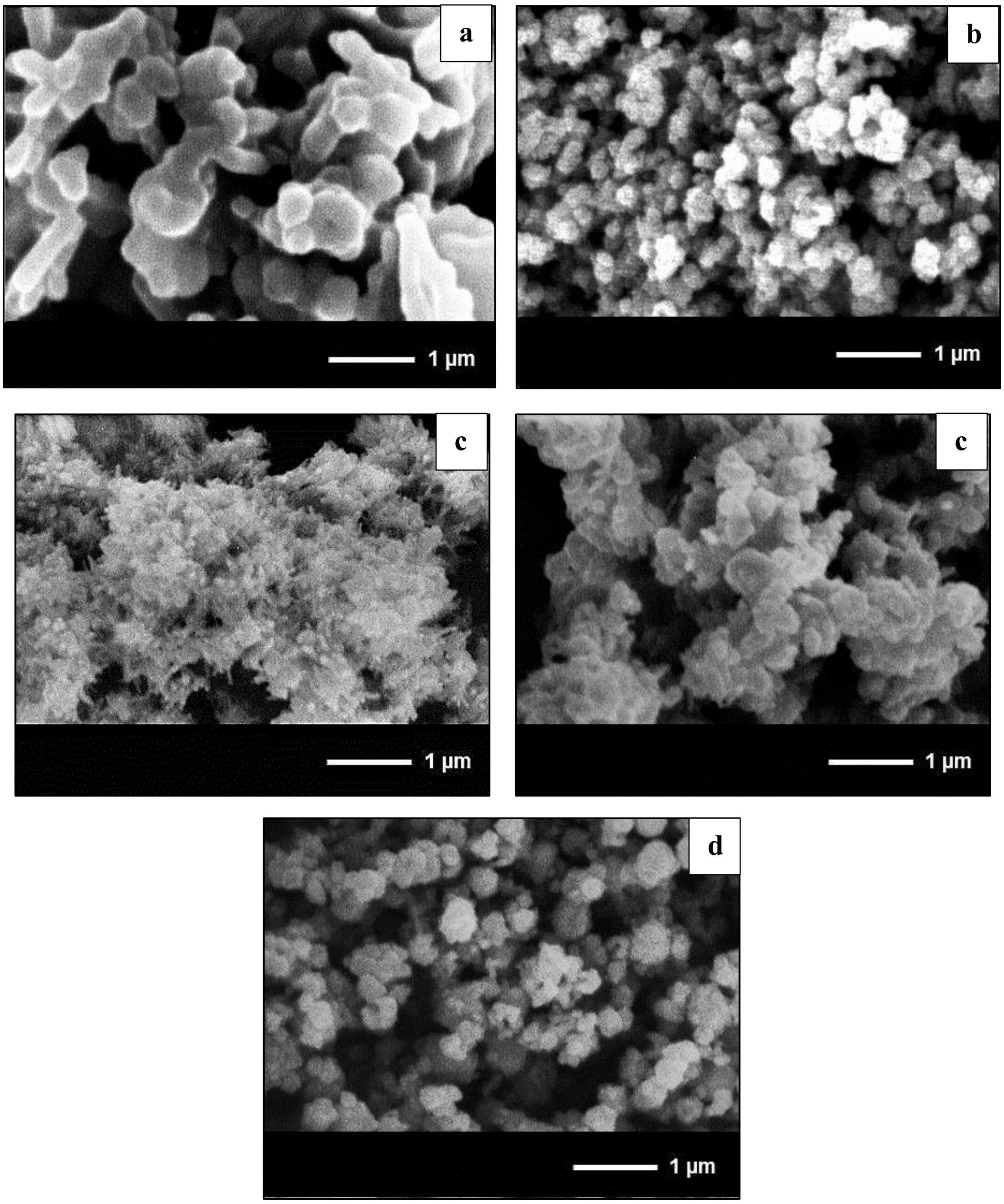

Figure A.2 SEM images of the synthesized products with different molar ratio of NaOH : $CuSO_4{\cdot}5H_2O$; (a) 1, (b) 3, (c) 5 and (d) 7

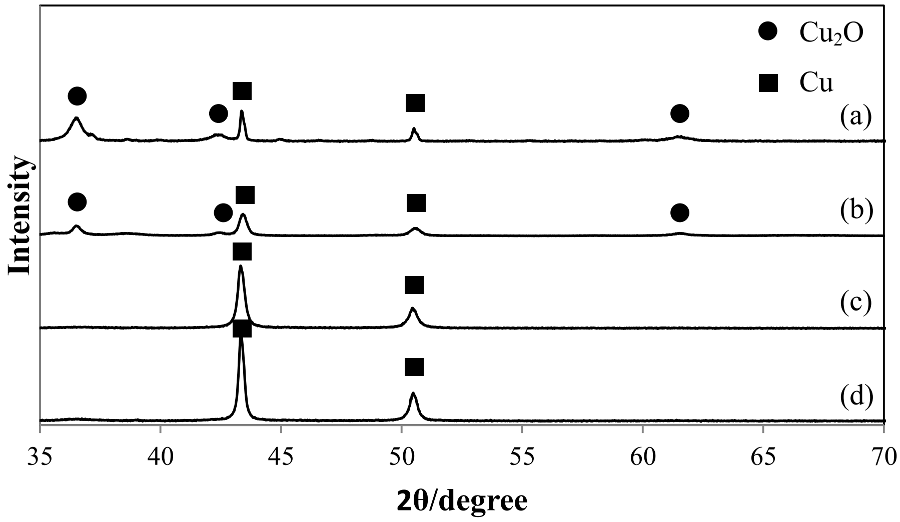

Figure A.3 XRD pattern of the synthesized products with different molar ratio of NaOH : $CuSO_4 \cdot 5H_2O$; (a) 1, (b) 3, (c) 5 and (d) 7

APPENDIX B

DATA OF AVG. PARTICLE SIZE DIAMETER

Table B.1 Data of avg. particle size diameter of the Cu/MWCNT composite with different irradiation time by microwave-polyol process

Irradiation time	MWCNTs		Particle size (nm)			
	Average size (nm)	STDEV	Average size (nm)	STDEV	min	max
1	13	2	5.2	2	2.3	8.9
3	13	3	10.5	3	5.3	17.2
5	12	3	15.1	3	9.4	21.3
7	15	4	36.9	12	11.1	62.7
9	12	4	25.2	15	9.2	65.5

Table B.2 Data of avg. particle size diameter of the Cu/MWCNT composite with different microwave-irradiation power by microwave-polyol process

Microwave-irradiation power	MWCNTs		Particle size (nm)			
	Average size (nm)	STDEV	Average size (nm)	STDEV	min	max
360	12	3	15.1	3	9.4	21.3
600	14	4	13.6	5	4.1	27.7
800	13	2	37	14	14.3	75.6

APPENDIX C
PUBLICATIONS

Journal:

Publications Co-Authored by N. Leelaviwat:

Charinpanitkul, T., Kanjanaprapakul, K., **Leelaviwat, N.**, Kurukitkoson, N., and Kim, K.-S., Effect of arc current on characteristics of nanocarbons prepared by cryogenic arc discharge method. Journal of Industrial and Engineering Chemistry, 2010. 16(6): p. 912-917.

Proceeding:

Leelaviwat, N., Akrapattangkul, N., Monchayapisut, S., Kongsombut, B., Poonjarernsilp, C., Faungnawakij, K., and Charinpanitkul T. Preparation of carbon nanotubes decorated with Cu nanoparticles by microwave thermal treatment. Proceeding of the 17th Regional Symposium on Chemical Engineering, Queen Sirikit National Conventional Center, Bangkok, Thailand, November 22-23, 2010: MSE 493.

VITA

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