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Synthesis and Characterization of Copper Nanoparticles for Conductive Ink Applications

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                      NANOPARTICLES FOR CONDUCTIVE INK

                      APPLICATIONS

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โรจน์รุ่ง ศิริมาสกุล : การสังเคราะห์ และวิเคราะห์อนุภาคนาโนทองแดงสำหรับประยุกต์ใช้เป็นหมึกนำไฟฟ้า(SYNTHESIS AND CHARACTERIZATION OF COPPER NANOPARTICLES FOR CONDUCTIVE INK APPLICATIONS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก:ผศ. ดร. สุรเทพ เขียวหอม, 47 หน้า.

ในงานวิจัยนี้ได้ทำการศึกษาการสังเคราะห์อนุภาคนาโนทองแดงโดยวิธีอาร์คดิสชาร์ต (Arc discharge) ในของเหลวที่เป็นฉนวนไฟฟ้า (dielectric liquid) คือ ethylene glycol และ diethylene glycol ที่สภาวะความดันบรรยากาศปกติ โดยใช้ XRD SEM และ TEM ในการวิเคราะห์เพื่ออธิบายลักษณะโครงสร้างของผลึก รูปร่างและขนาดของอนุภาคตามลำดับ อนุภาคนาโนที่สังเคราะห์พบว่าประกอบไปด้วยทองแดง และออกไซด์ของทองแดง โดยออกไซด์ของทองแดงเกิดจากการทำปฏิกิริยากับอนุมูลอิสระของออกซิเจนที่เกิดขึ้นในระหว่างการสลายตัวของสารที่เป็นฉนวนไฟฟ้า อนุภาคนาโนที่สังเคราะห์ได้มีลักษณะเป็นทรงกลมโดยมีขนาดอยู่ที่ 10-20 nm ในงานวิจัยนี้ได้ทำการศึกษาผลของการเติมสารรีดิวซ์ คือ โซเดียมโบโรไฮไดรด์ โซเดียมไฮโปฟอสไฟท์ และกรดแอลแอสคอร์บิคที่ความเข้มข้น 0.1~1 M จากผลการทดลองพบว่ากรดแอลแอสคอร์บิคและโซเดียมโบโรไฮไดรด์สามารถที่จะรีดิวซ์อนุภาคให้เกิดเป็นทองแดงได้ที่อุณหภูมิต่ำ และได้ทำการศึกษาผลของการเติม PVP 0.05~0.5 M โดยพบว่า PVP สามารถที่จะป้องกันการเกิดการรวมตัวกันของอนุภาคทองแดงและสามารถป้องกันการเกิดออกไซด์ของทองแดงได้ โดยได้ทำการยืนยันการเกิดอนุภาคนาโนทองแดงกับPVP โดยใช้FTIR ในการวิเคราะห์ จากการศึกษาพบว่าการเติมPVP 0.1M และ 0.5M ลงในอนุภาคที่สังเคราะห์ได้ในEG และDEG ตามลำดับ จะทำให้อนุภาคนาโนทองแดงที่สังเคราะห์ได้สามารถเก็บไว้ที่สภาวะบรรยากาศปกติเป็นเวลา 30 วัน โดยไม่เกิดออกไซด์ของทองแดง

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The synthesis of copper nanoparticles by arc discharge submerged in dielectric liquid (ethylene glycol and diethylene glycol) at ambient atmosphere was studied in this work. The XRD, SEM, and TEM were used for depiction crystalline structure, morphology, and size of copper nanoparticles, respectively. The nanoparticles synthesized contained of both copper and copper oxide. The copper oxide was formed by oxygen free radicals during decomposition of the dielectric liquid. The copper nanoparticles synthesized were spherical morphologies with 10-20 nm. We studied the effect of sodium borohydride sodium hypophosphite and L-ascorbic acid with concentration of 0.1~1 M used as reducing agent. L-ascorbic acid and sodium borohydride could reduce particles synthesized to pure copper at low temperature. The effect of PVP (0.05~0.5M) was then studied. PVP could prevent agglomeration of copper nanoparticles and provide protection for copper oxide formation. We confirmed the formation of copper nanoparticles with in PVP matrix by using FTIR. By adding 0.1 M and 0.5 M PVP in copper nanoparticles synthesized in EG and DEG respectively, the produced copper nanoparticles could maintain for 30 days without oxide formation

Department : __Chemical Engineering__   Student's Signature :_____

Field of Study : __Chemical Engineering__   Advisor's Signature :_____

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Chapter 1
Introduction

1.1 Background and motivation

In production of electronic devices, the method to fabricate conductive patterns is needed to improve because the traditional process requires many production steps (etching, electroplating and etc.). So that it is time consuming and height cost. Recently, inkjet printing is an interesting alternative way to fabricate conductive lines because it is convenience to produce and less cost than traditional process. There are several kinds of conductive ink which were studied such as molten metal [1-3], conductive polymers [4,5], organo-metallic compounds [6,7],metal precursors [8], and metallic nanoparticles suspensions, but metal nanoparticles suspensions is interesting because it has high metal concentration and can be made conductive film at low temperature.

Silver ink is one of conductive ink which is widely used in ink jet printing because of high conductivity. Moreover silver nanoparticles can sinter at low temperature and their oxide can conduct however silver is costly. So copper is one alternate metal that can displace silver because of high conductivity and cheap. However copper is easy to form oxide and obstruct to conductivity. There are many researches which used polyvinyl pyrrolidone (PVP) [9-11] as capping agent to prevent copper from oxidation of oxygen and agglomeration. For synthesis copper nanopaticles there are many routes such as wet chemical reduction, electro reduction, micro emulsion, microwave irradiation, and arc discharge [12-14] etc.

While wet chemical reduction method is widely used, as it is required a long time of synthesis and high temperature of reaction for some reducing agents. There are many research involving types of solvent, encapsulating agent, concentration of metal precursor and reducing agent, and temperature. The polyol process is often used because liquid polyol can act as both solvent and reducing agent [15]. Electro reduction of copper is widely used in industry for application of coating of metal and it can deposit nanoparticles on the surface. The electro reduction can also used to

synthesis copper nanoparticles too. This method is convenient to prepare and environment friendly because it is used aqueous solvent however copper particles are agglomerated together. Now a day, there are many new applications of microwave irradiation because it can supply energy and heating to high temperature in a short period time. So, we can synthesis copper nanoparticles at high temperature reaction in rapid time and this will induce to small particles sizes and narrow particles size distribution, however amount of copper nanoparticles are too small for used in the large scale. The new way to synthesized copper nanoparticles is arc discharge which method is convenient to prepare and can produce copper particles more enough for use in the industrial.

In this study, we investigated arc discharge submerge in ethylene glycol and diethylene glycol for the synthesis of stable copper nanoparticles for conductive ink in printed electronics applications.

1.2 Objective of the research

The objects of this research are to investigate the synthesis copper nanoparticles by DC arc discharge copper wires submerged in dielectric liquid, and study the effects of current apply, dielectric liquid, capping agent, and reducing agent on the size, shapes, and stable of synthesized copper particles.

1.3 Scope of the research

1.3.1 The DC power supply (DC Inverter Arc welder, Iweld) with current 10-140A., voltages 25.6 volts, and frequency 50/60 Hz is used.

1.3.2 Copper nanoparticles are synthesized by arc discharge submerged in ethylene glycol and diethylene glycol which applied current 10~50 A. 25.6 volts at atmospheric condition and cooling system by using dry ice.

1.3.3 A gap between cathode and anode electrodes is set as 1 mm by varying feed speed of copper wire.

1.3.4 Reducing agents (sodium hypophosphite, sodium borohydride ($NaHB_4$), and L-ascorbic acid (0.1~ 1M.) are used in this study.

1.3.5 PVP (0.05~0.5 M.) as a capping agent.

1.3.6 To investigate the stability of copper particles synthesized, the particles will collect in dielectric liquid and exposure to atmosphere condition for 1month and then characterization particles by UV-vis and XRD.

1.3.7 The copper particles are characterized by Scanning electron microscope (SEM), Transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR), UV-vis spectroscopy, and x-ray diffractrometer (XRD).

1.4 Expected benefits

1.4.1　To obtain convenient and suitable routes to synthesized copper particle in industrials.

1.4.2　To determine the suitable condition for synthesized ultrafine particle size of copper nanoparticles for used in printing process

Chapter 2

Literature review

Copper particles are needed to use in electronic applications for electronic industrial because high electrical conductivity and low cost. So the copper nanoparticle is interesting to replace expensive silver nanoparticles for conductive printing in a large scale production. The major problem of copper nanoparticles is easily to form oxide in ambient condition. In the past, Copper particles have been synthesized for a long time with varies routes which demonstrate that copper nanoparticles can resist to oxidation of oxygen by used of protecting agents to coat surface of copper particles. The coated layer may consist of an organic polymer, alkene chains, amorphous carbon or graphenes, or inorganic materials such as silica, or an inert metal [11].

The traditional synthesis and widely used is wet chemical reduction Bong Kyun Park et al.[12], synthesized copper nanoparticles by wet chemical reduction, while used poly vinyl pyrrolidone (PVP) as capping molecule, sodium phosphinate monohydrate ($NaH_2PO_4.H_2O$) as a reducing agent, copper(II)sulfate as precursor and (DEG) as solvent. The size of synthesized copper particles is about 45±8 nm, spherical in shape, and can exposure to atmospheric condition for a month without oxide. SunhoJeong et al[16]. were studied synthesized aqueous based copper nanoparticles ink on PI film. Copper nanoparticles were synthesized by wet chemical reduction in toluene and with under inert atmosphere, and oleic acid, hydrazine and copper acetate were used as surface capping agent, reducing agent and metal precursor respectively. Then modified the surfaces of synthesized copper nanoparticles by methanol based solution with carboxyl terminated anionic polyelectrolyte and polyoxylethyleneoleylamine ether and oxalic acid. The results show that copper nanopatricles were synthesized in this studied

are about 40 nm, spherical in shape and found only phase pure copper from XRD. Xiao-Feng Tang et al. [17] prepared copper nanoparticles by used hexadecyltrimethylammonium bromide (CTAB) and PVP as co-capping agent and hydrazine as reducing agent. The copper nanoparticles had a diameter between 10-80 nm by varying amount of CTAB, PVP, reducing agent and reaction temperature separately. Then copper were purified by electrolysis in order to avoid oxidation, agglomeration and re-dispersion of particles from centrifugation. The synthesized copper nanoparticles were determined to be phase pure copper without any oxide. Szu-Han et al [18] studied preparation of copper nanoparticles at high concentration of copper chloride (0.2M) with hydrazine in the aqueous CTAB solution. The adding ammonia solution to adjust pH of solution to 10 and using of hydrazine as a reducing agent are important to synthesis copper nanoparticles without used of inert gas because ammonia and hydrazine can act as a complex agent to prevent formation of oxide. The diameter of copper nanoparticles are about 5-15 nm with phase pure copper and from result of TGA, it show that copper nanoparticles were coated with bi-layer assembly of CTAB on the surface.

However, wet chemical reduction process can produce a little amount of copper, used of reducing agent and have many parameters to be controlled. Then there is convenient process, less used of chemical and possible to produce in a large scale which is electro reduction process. Mohan raja et al. [19] prepared copper nanoparticles by electro reduction process using plating bath containing homogenous acidified copper sulphate solution. The results show that copper nanoparticles are formed at electrode as spongy layers of ball structure. The particles size of copper nanoparticles is 45 nm. The UV–vis absorption spectrum of copper nanoparticles show absorption band at 587 nm which is indicated copper metal and no adsorption band of

oxide around 800 nm. The result from XRD shows phase pure copper and calculation particles size from Scherrer's equation are about 40-60 nm.

In a past few years, there are reports about synthesized copper nanoparticles by microwave irradiation in liquid polyol because liquid poyol can be solvent and reducing agent. Hai-tao Zhu et al. [20] investigated copper nanoparticles synthesized by microwave irradiation process with $NaH_2PO_2.H_2O$ as reducing agent. The temperature of solution will rise rapidly and more uniform temperature than heat source from hot plate, so particles were reduced and grow together. Result in size of particles is uniform. The synthesized copper nanoparticles have size about 10.4 nm with pure phase of copper by used molar ratio of NaH_2PO_2 to $CuSO_4$, PVP to $CuSO_4$ and time of microwave irradiation are 2.0, 7.2 and 5 min respectively. The synthesized copper nanoparticles by microwave irradiation has advantage in reduce of heating time and uniform temperature during the synthesis however it still used a little amount of copper concentration to synyhesis because copper particles will growth and agglomerate to large size of particles.

In recent years, the synthesized nanoparticles by Arc discharge process is interested because of low cost to produce, convenient process and suitable for production in large scale. Moreover there are reports which were successful to prepare uniform novel nanoparticles such as Ag, Ni, and TiO_2 [21-23]. Chih-Hung Lo et al. [12].preparenanofluid in H_2O by using submerged arc nanoparticles synthesis system using copper electrode. Copper oxide nanofluid is produced at 8.5-10A, voltage of 220 V, and dielectric temperature of 2°C. The arc was done under vacuum condition at 30 Torr and the system which is called vacuum submerged arc nanoparticles synthesis system (vacuum-SANSS) was show in figure 1. The system consists of the heating

source, vacuum chamber, pressure control, isothermal system and servo control. The obtained copper oxide particle is 49.1 nm, spherical in shape and narrow size distribution.
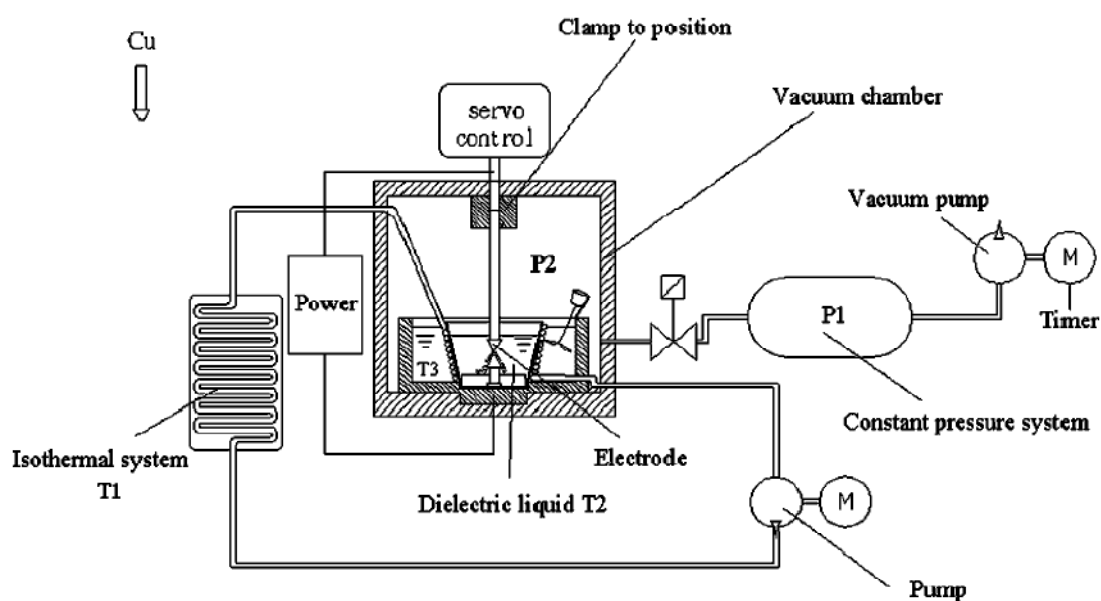
Figure 2.1 Schematic diagram of SANSS.

After a year [13] they were studied by changed dielectric liquid from H_2O to mix with ethylene glycol and pure ethylene glycol. The results show that obtained phase pure copper particles and spherical in shape were found when used ethylene glycol as dielectric liquid and size of particle is less than 10 nm. While the dielectric solutions which are pure DI warter and mixed DI water with ethylene glycol were used, the copper oxide was found and morphology of particles are changed depend to ratios of pure DI water to ethylene glycol such as needle-like, polygon, polygon with square, and square which are obtained from pure DI water and ratios DI water to ethylene glycol 70:30, 50:50 and 30:70, respectively. The different morphologies are mainly influenced and

determined by various thermal conductivity properties of the dielectric liquids. It seem like that high nucleation rate can be obtained when the metal is vaporized at high temperature and condensed rapidly at low temperature and the uniform particles cannot be obtained when the saturation rate is insufficient. M.Z. Kassaee et al. [15] prepared copper nanoparticles in H_2O by adding PVP aqueous medium as capping agent to protect copper particles from oxide. The apply current to arc system at 50 A and voltage 25V at approximately 1 mm of gap between cathode and electrode gives best results with copper nanoparticles spherical morphologies and 20 nm in size indicated by TEM.

Figure 2.2 TEM images of (a.) needle-like CuO (b.) polygon and square-shaped Cu$_2$O (c.) polygon-shaped Cu$_2$O (d.) square-shaped Cu$_2$O and (e.) circular-shaped Cu were synthesis by vacuum SANSS in pure DI water and dielectric liquid with ratios DI water to ethylene glycol are 70:30, 50:50 and 30:70, respectively.

The aim of applications of copper nanoparticles is to replace the expensive silver nanoparticles in printing conductive pattern when production in large scale. The synthesis copper conductive ink for i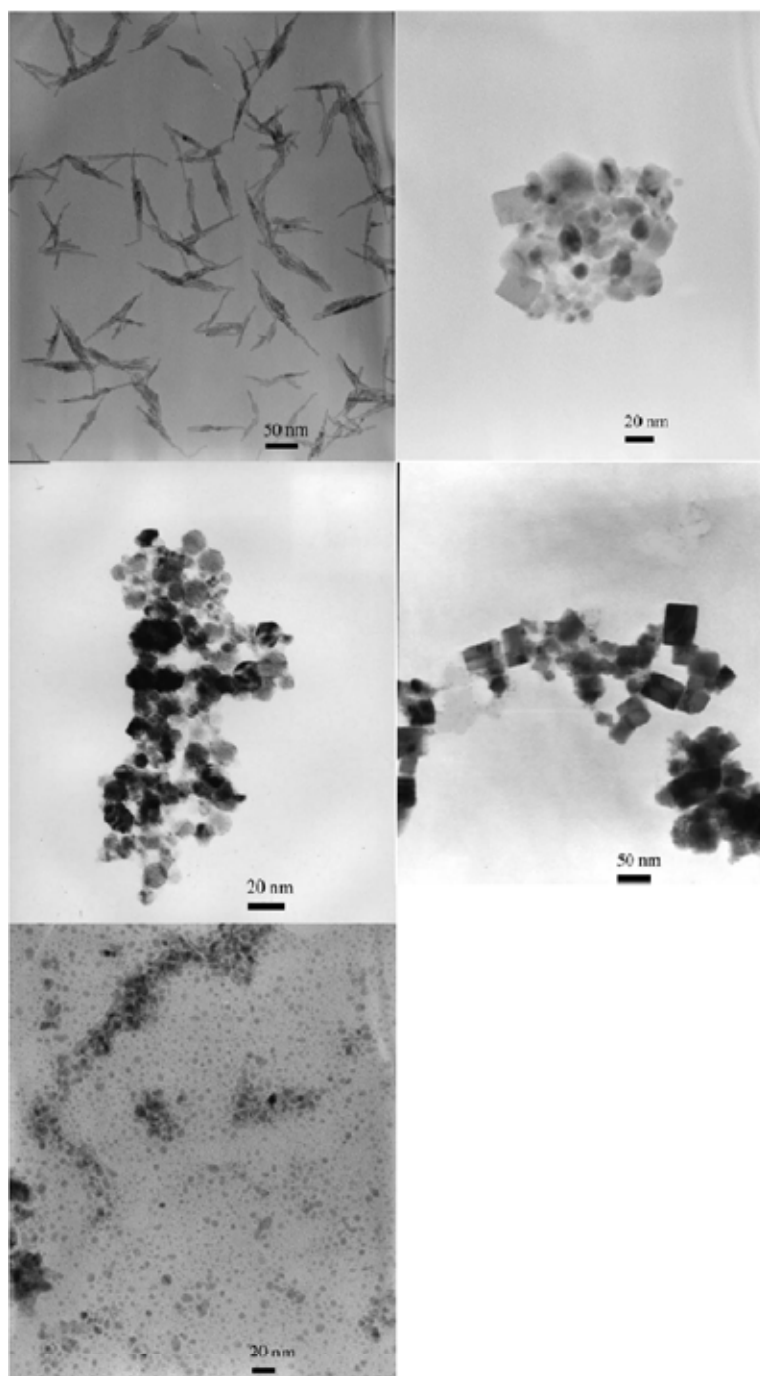nkjet printing has been reported. Bong Kyun Park et al. [12] used their synthesized copper nanoparticles with size 40-50 nm to prepare copper conductive ink. The synthesized copper conductive ink was consisted of copper nanoparticles with 20% solid loading and mixed solvent of ethylene glycol and 2-methoxyethanol. The synthesized ink can be successful to print on glass substrate, then annealed at various temperature between 200°c and 300°c in vacuum atmosphere. The annealing temperature at 325°c for 1 hour in vacuum oven gives the best resistivity 17.2 μΩcm which was about ten time higher resitivity than of bulk copper's resistivity. The morphology of printed pattern from confocal microscopy image shows that the particles are accumulated at the edge and depleted at the center which is called "coffee ring effect". While SunhoJeong et al [16] presented method to improve the coffee ring effect by used of mixed solvent of different boiling point of co-solvent low and high boiling point liquid. The low boiling point solvent will fast evaporate at the edge, higher fraction of the high boiling point solvent than in the center. Which compositional gradient induce Marangoni flow from the regions with low surface tension to high surface tension. So the inward Maragoni flow is opposite to the outward convection flow and the migration of suspending particles toward droplet is suppressed. The printed patterns have resistivity 11 μΩcm after annealed at 250°C.

However, copper nanoparticles are easily to from oxide in ambient condition. To produce stability copper nanoparticles the protecting agents are needed. There are several studies which can achieve to synthesized stable copper nanoparticles by coated layer with protecting agents such as an organic polymer, alkene chains,

amorphous carbon or graphenes, or inorganic materials such as silica, or an inert metal [11].

PVP are widely used as a capping agent to protect copper from oxidation of oxygen and act as surfactant [11]. Wu et al., 2005[9] were studied effect of PVP on copper nanocrystals. The results shown when PVP is added into copper solution, PVP is the key to control the copper nanoclustering and stabilizing. It is belived that PVP can coordinate to the particles surface via O-Cu coordination bond and wrap around the particles with its long and soft polyvinyl chain to stop their growth and aggregation. Furthermore, when they used UV-vis spectroscopy to measure the absorption of surface plasmon resonance of copper nanoparticles in the colloid, it found that the absorption of copper nanoparticles will presence around 587 nm and the plasmon bands show broading and tailing toward longer wavelengths, which indicates the precence of copper oxide while the PVP is added to solution, the surface plasmonresonace absorption of copper nanoparticles is sharp and narrow which is indicated to be pure copper nanoparticles. The ratios of PVP to Cu^{2+} also plays an importants role in the controlling the size, size distribution and morphology of the nanoparticles. When decrease the ratios of PVP to Cu^{2+}, the absorption bands display flat and broader, which is implied that wider size distribution is due to a lower amount of PVP.

Moreover, Wei Yu et al. [24] were synthesized copper particles by used L-ascorbic acid as reducing agent and PVP as protecting agent in aqoues and ethylene glycol. They also report that the size of copper particles depended on the concentration of PVP and the increasing concentration of PVP lead to the smaller size particles. PVP act as both size controller and polymeric capping agents, because it hinders the nuclei from aggregation through the polar group, which strong absorb the copper particles on

the surface with coordination bonds. In addition ascorbic acid plays roles as reduing

agent and antioxidant of colloidal copper, due to its ability to scavenge free radicals and

reactive oxygen molecules.

Chapter 3
Fundamentals

3.1 Nanotechnology

Nanotechnology encompasses the production and application of physical, chemical, and biological systems at scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems. Nanotechnology is likely to have a profound impact on our economy and society in the early 21st century, and it is widely felt that nanotechnology will be the next Industrial Revolution. Nanometer-scale features are mainly built up from their elemental constituents. Examples include chemical synthesis, spontaneous self-assembly of molecular clusters (molecular self-assembly) from simple reagents in solution, biological molecules (e.g., DNA) used as building blocks for production of three-dimensional nanostructures, and quantum dots (nanocrystals) of arbitrary diameter (about 10–105 atoms). The definition of a nanoparticle is an aggregate of atoms bonded together with a radius between 1 and 100 nm. It typically consists of 10–105 atoms.

The discovery of novel materials, processes, and phenomena at the nanoscale and the development of new experimental and theoretical techniques for research provide fresh opportunities for the development of innovative nanosystems and nanostructured materials. The properties of materials at the nanoscale can be very different from those at a larger scale. When the dimension of a material is reduced from a large size, the properties remain the same at first, and then small changes occur, until finally when the size drops below 100 nm, dramatic changes in properties can occur. If only one length of a three-dimensional nanostructure is of nanodimension, the structure is referred to as a quantum well; if two sides are of nanometer length, the structure is referred to as a quantum wire. A quantum dot has all three dimensions in the nano range. The term quantum is associated with these three types of nanostructures

because the changes in properties arise from the quantum-mechanical nature of physics in the domain of the ultrasmall. Materials can be nanostructured for new properties and novel performance. This field is opening new avenues in science and technology.

3.1.1 Properties

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometer (or micron), the percentage of atoms at the surface is insignificant in relation to the number of atoms in the bulk of the material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material.

Nanoparticles often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. For example gold nanoparticles appear deep red to black in solution. Nanoparticles of usually yellow gold and gray silicon are red in color. Gold nanoparticles melt at much lower temperatures (~300 °C for 2.5 nm size) than the gold slabs (1064 °C). And absorption of solar radiation in photovoltaic cells is much higher in materials composed of nanoparticles than it is in thin films of continuous sheets of material, ie. the smaller the particles, the greater the solar absorption.

Other size-dependent property changes include quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and superparamagnetism in magnetic materials. Ironically, the changes in physical properties are not always desirable. Ferromagnetic materials smaller than 10 nm can

switch their magnetisation direction using room temperature thermal energy, thus making them unsuitable for memory storage.

Suspensions of nanoparticles are possible since the interaction of the particle surface with the solvent is strong enough to overcome density differences, which otherwise usually result in a material either sinking or floating in a liquid.

The high surface area to volume ratio of nanoparticles provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. This theoretically does not affect the density of the final product, though flow difficulties and the tendency of nanoparticles to agglomerate complicates matters. Moreover, nanoparticles have been found to impart some extra properties to various day to day products. For example the presence of titanium dioxide nanoparticles imparts what we call the self-cleaning effect, and the size being nano-range, the particles can not be observed. Zinc oxide particles have been found to have superior UV blocking properties compared to its bulk substitute. This is one of the reasons why it is often used in the preparation of sunscreen lotions, and is completely photostable.

Metal, dielectric, and semiconductor nanoparticles have been formed, as well as hybrid structures (e.g., core-shell nanoparticles). Nanoparticles made of semiconducting material may also be labeled quantum dots if they are small enough (typically sub 10 nm) that quantization of electronic energy levels occurs. Such nanoscale particles are used in biomedical applications as drug carriers or imaging agents.

Semi-solid and soft nanoparticles have been manufactured. A prototype nanoparticle of semi-solid nature is the liposome. Various types of liposome nanoparticles are currently used clinically as delivery systems for anticancer drugs and vaccines.Nanoparticles with one half hydrophilic and the other half hydrophobic are

termed Janus particles and are particularly effective for stabilizing emulsions. They can self-assemble at water/oil interfaces and act as solid surfactants.

3.1.2 Morphology

Scientists have taken to naming their particles after the real world shapes that they might represent. Nanospheres, nanoreefs, nanoboxes and more have appeared in the literature. These morphologies sometimes arise spontaneously as an effect of a templating or directing agent present in the synthesis such as miscellar emulsions or anodized alumina pores, or from the innate crystallographic growth patterns of the materials themselves. Some of these morphologies may serve a purpose, such as long carbon nanotubes being used to bridge an electrical junction, or just a scientific curiosity like the stars shown at right. Amorphous particles usually adopt a spherical shape (due to their microstructural isotropy) – whereas the shape of anisotropic microcrystalline whiskers corresponds to their particular crystal habit. At the small end of the size range, nanoparticles are often referred to as clusters. Spheres, rods, fibers, and cups are just a few of the shapes that have been grown. The study of fine particles is called micromeritics.

3.1.3 Synthesis

There are several methods for creating nanoparticles, including both attrition and pyrolysis. In attrition, macro or micro scale particles are ground in a ball mill, a planetary ball mill, or other size reducing mechanism. The resulting particles are air classified to recover nanoparticles. In pyrolysis, a vaporous precursor (liquid or gas) is forced through an orifice at high pressure and burned. The resulting solid (a version of soot) is air classified to recover oxide particles from by-product gases. Pyrolysis often results in aggregates and agglomerates rather than single primary particles.

Thermal plasma can also deliver the energy necessary to cause evaporation of small micrometer size particles. The thermal plasma temperatures are in the order of 10,000 K, so that solid powder easily evaporates. Nanoparticles are formed upon

cooling while exiting the plasma region. The main types of the thermal plasma torches used to produce nanoparticles are dc plasma jet, dc arc plasma and radio frequency (RF) induction plasmas. In the arc plasma reactors, the energy necessary for evaporation and reaction is provided by an electric arc which is formed between the anode and the cathode. For example, silica sand can be vaporized with an arc plasma at atmospheric pressure. The resulting mixture of plasma gas and silica vapour can be rapidly cooled by quenching with oxygen, thus ensuring the quality of the fumed silica produced.

3.2 Electric Arc discharge

The arc discharge can generate from many methods such as arc lamp, welding machine, gas heater, and etc. however the electric arc discharge is one convenient method to generate the arc. The electric arc discharge occurs when current applied to two electrodes which separated with small gap. The current flow through gap which is nonconductive media and leads to a spark jumping between two electrodes. There are three main parts of the arc which are the arc column, the cathode region and the anode region. At the cathode and anode regions, the metal at the end of electrode is turned in to gas phase by high temperature with high electric field these regions are call transition regions and have positive and negative space charges respectively. The arc column has the charge equilibrium, the low electric field and high temperature, so metal gas is heated at this region.

The arc column have voltage drop from the anode electrode and decrease sharply at the cathode electrode of the order of minimum ionizing or minimum exciting potential of the metal vapor as see in Fig3.1.[25]. The stability of arc discharge is depended on current density and distance at electrode region.

During the arc discharge the copper electrodes are heated by hot, bright plasma with high temperature 6,000 to 12,000°c from the applied electric current produces a heating source at arc area. The metals are vaporized and melted from the

electrodes in arc area into metal vapor where liquid media is also vaporized and carry metal vapor out of arc zone and then metal vapor is cooled and condensed in the liquid media to be metal particles dispersed in liquid media through three transformation stages nucleation, growth and condense.
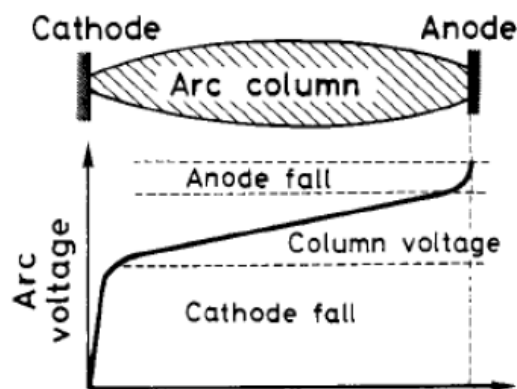

Figure 3.1 Arc voltage distributions

3.3 Applications in printing process

Printed electronic is a method to created conductive line on substrates such as screen printing, flexography, gravure, offset lithography and inkjet printing. In traditional process to made conductive pattern on substrate has many steps, more chemical and time to do and lead to high cost and waste of production, while printed electronics are convenient, low cost to produce and able to create on flexible substrates. The conductive inks are deposited on several substrates which have low cost and flexible properties such as polyimide film, polyethylene (PET) and fabrics.

The high resolution and small structure of conductive line are necessary in electronic printing or printing layer on other layers is required while the traditional process cannot do that. So the printing technology is interested to prepare micro-structure layer of conductive line and low-cost production moreover this method can

create printed pattern on flexible substrate to improve a new devices such as flexible display, smart labels, decorative and animated poster etc.

Inkjets printing are common and convenient method to patterned conductive lines on flexible substrates. The inkjet offer lower throughput of around 100 m2/h and lower resolution 50 μm[26]. This method is suit for low-viscosity conductive inks. The conductive inks for inkjets have many kind such as organo-metallic compounds [10,11],metal precursors [12], and metallic nanoparticles suspensions. The organo-metallic compound ink is left residue and reduce conductivity while metal precursors ink has low content of metal because of limited of solubility of solution. The metallic nanoparticles suspensions contained more metal particles however the nanoparticles can agglomeration and clogging nozzle.

Screen printing is suite for fabricating electronics in large scales because it can paste conductive ink with respective thickness in a short time and resolution is about 100μm[26] as quite equal to inkjet printing.

3.4 Polymeric stabilization

For polymers with molecular weights >10000 D, the chain dimensions are comparable to, or in excess of, the range of the van der WaalsLondon (VDWL) attraction. Hence, as long as they can generate repulsion, these polymer molecules can be used to impart colloid stability. There are two different mechanisms accepted for polymeric stabilization of colloidal dispersion: steric stabilization and depletion stabilization.[28]

Steric stabilization of colloidal particles is achieved by attaching (grafting or chemisorption) macromolecules to the surfaces of the particles. The stabilization due to the adsorbed layers on the dispersed particle is generally called steric stabilization

Depletion stabilization of colloidal particles is involves unanchored (free) polymeric molecules creating repulsive forces between the approaching particles.
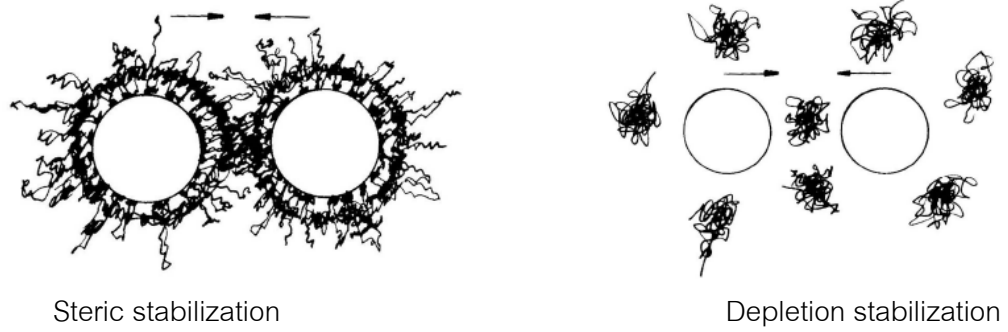
Steric stabilization   Depletion stabilization

Figure 3.2 polymeric stabilization of colloidal dispersion

Chapter 4

Experimental

4.1 Materials

- Copper wires cathode electrode and anode electrode

- Polyvinylpyrrolidone (PVP, K30 avg.Mw 40,000)

- Ethylene glycol (QRëC)

- Diethylene glycol (98% TCI)

- Sodium borohydride ($NaHB_4$)

- Sodium hypophosphite (NaH_2PO_2)

- L-ascorbic acid (UNILAB)

- DC power supply (DC Inverter Arc welder, Iweld)

- Copper wires cathode electrode and anode electrode;

4.2 Methodologies

In this work, copper particles are synthesized by arc discharge copper wires submerged in dielectric liquid at ambient condition. The procedures are shown below.

Synthesis copper particles by arc discharge submerged in polyol liquid.

Copper particles were synthesized by using copper arc discharge submerged in ethylene glycol and diethylene glycol. The schematic diagram of the system was shown in the Fig 4.1. The system consists of the heating source which is DC Inverter Arc welder, the dielectric liquid bath, copper electrodes and controlling feed speed. The apply currents were about 10-50A., apply voltage was at 25.6 V, and the temperature of

dielectric liquid was cooled by used ice and NaCl with ratios 3:1 to maintain temperature of the dielectric liquid not over $5°C$. The rate of feed copper electrode was investigated by vary supply voltage to control speed of motor. The copper colloid was characterization by UV-vis spectroscopy to determine formatiom of copper particles. The copper particles were separated by centrifuge and wash with methanol then dried in oven at $105°C$ for 5 min.

To investigate effect of reducind agents the reducing agents such as sodium hypophosphite, sodium borohydride ($NaHB_4$), and L-ascorbic acid were used with concentration of 0.1~1 M. After arc copper in dielectric liquid then added reducing agent to the colloid solution heated to constant at $45°C$ for 30 min and putted in ultrasonic bath for 30 min. The copper colloid was characterization by UV-vis spectroscopy to determine formation of copper particles.

To investigate amount of PVP protection effects on copper nanoparticles from oxidization. After arc copper wires in dielectric liquid then add the reducing agent to copper colloid solution with different concentration of PVP 0.05, 0.1, 0.3 and 0.5M. The solution was heated to constant at $45°C$ for 30 min and putted in the ultrasonic for 30 min. The copper colloid was characterization by UV-vis spectroscopy to determine formation of copper particles. The copper particles were separated by centrifuge and washed with methanol then dried in oven at $105°C$ for 5 min.
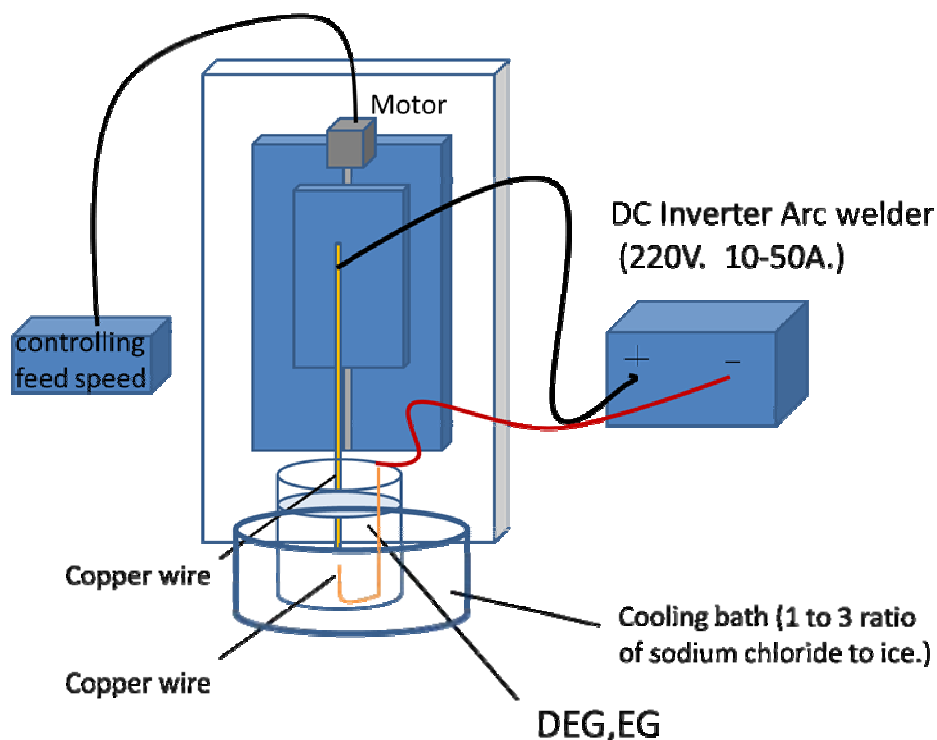
Figure 4.1. The schematic diagram of the Arc system.

4.3 Characterization

The copper particles synthesized were investigated by Scanning electron microscope (SEM) and Transmission electron microscope (TEM) and x-ray diffractrometer (XRD) for depiction morphology, and size of copper nanoparticles, crystalline structure, respectively. UV-vis spectroscopy was used to characterization optical properties of synthesized copper colloid for determine the formation of copper and copper oxide nanoparticles. We confirmed the formation of copper nanoparticles with in PVP matrix by using FTIR. Moreover the stability of synthesized copper nanoparticles store in ambient condition is investigated after about a month by XRD to check formation of copper oxide.

Chapter 5

Results and discussions

The copper nanoparticles suspension was prepared by arc discharge submerged in ethylene glycol and diethylene glycol under ambient condition. The synthesized copper colloid were characterized by UV-vis spectroscopy as show in figure 5.1 and 5.2 of copper nanoparticles synthesized dispersed in dielectric liquid(EG and DEG respectively). The absorption peak of copper nanoparticles was shown broadening around 580 nm and tailing toward longer wavelengths which is mean the absorption of copper nanoparticles with presence of copper oxide [Wu 2005]. The copper oxide (Cu_2O) nanoparticles were present instead of pure copper (Cu) because the copper oxide was formed by oxygen free radicals in ambient condition and during decomposition of the dielectric liquid. However, when we compared with synthesized copper nanoparticles in aqueous dielectric liquid, it found that the ethylene glycol can prevent oxidation under low pressure condition [Lo 2005]. The formations of copper and copper oxide were confirmed by XRD. Figure 5.3 and 5.4 illustrates the XRD results of the prepared particles by used of ethylene glycol and diethylene glycol as dielectric liquid. The results show that copper nanoparticles synthesized are copper (Cu) and copper oxide (Cu_2O) with lattice constants comparable to the reported data of JCPDS 05-0667, and 04-0836 respectively.
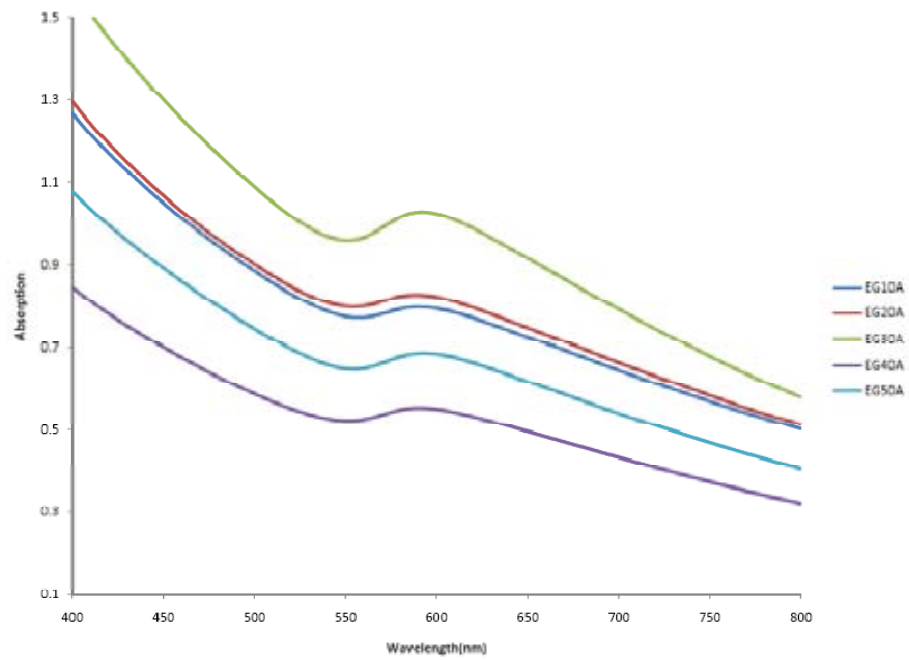
Figure 5.1 the UV-vis of synthesized copper nanoparticles in EG with different of applied currents
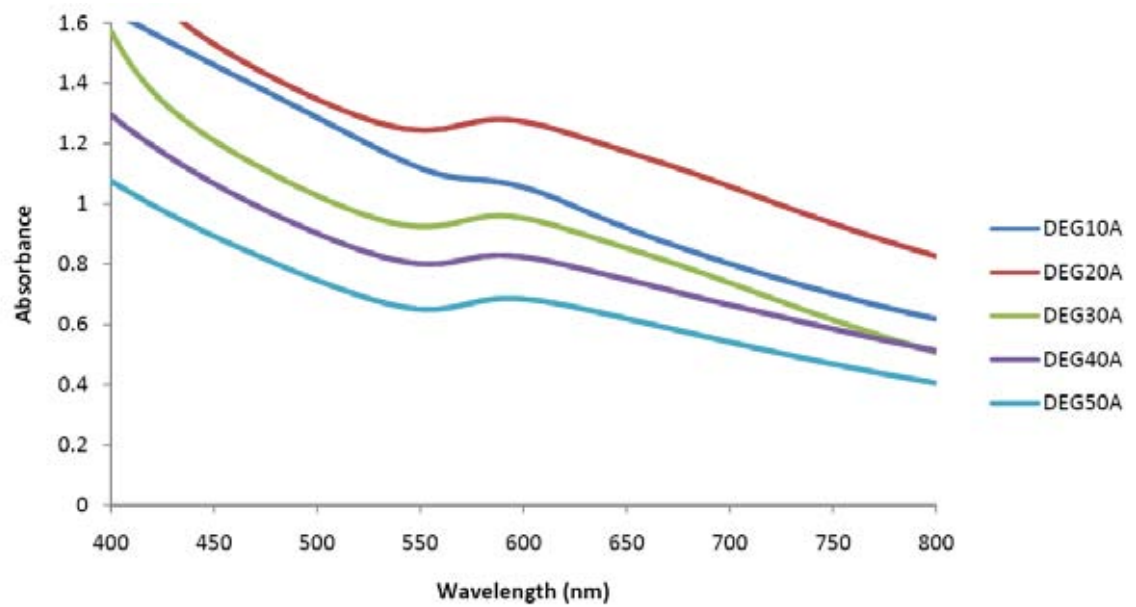

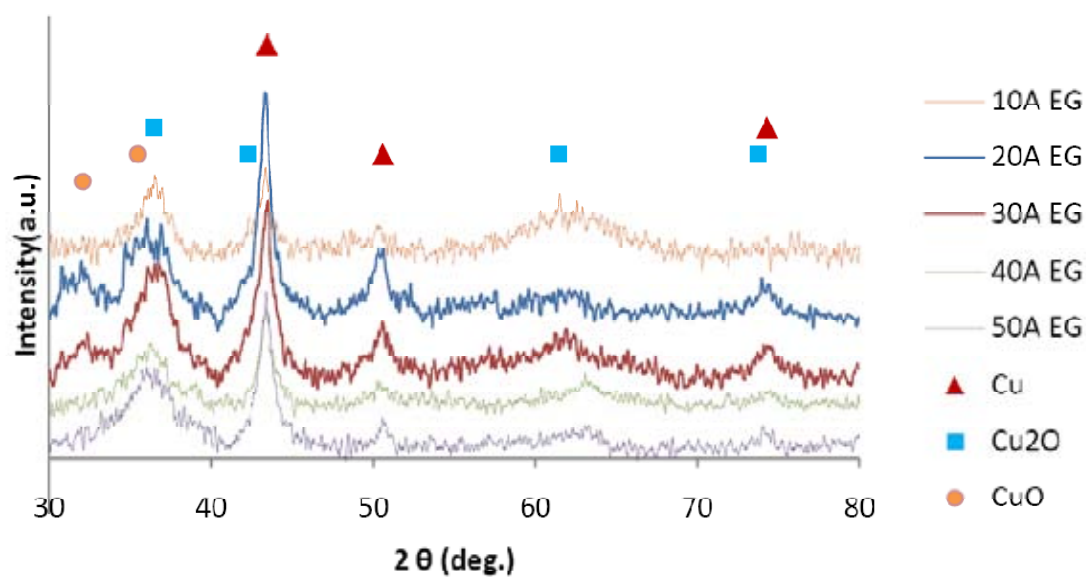Figure 5.2 the UV-vis of synthesized copper nanoparticles in DEG with different of applied currents

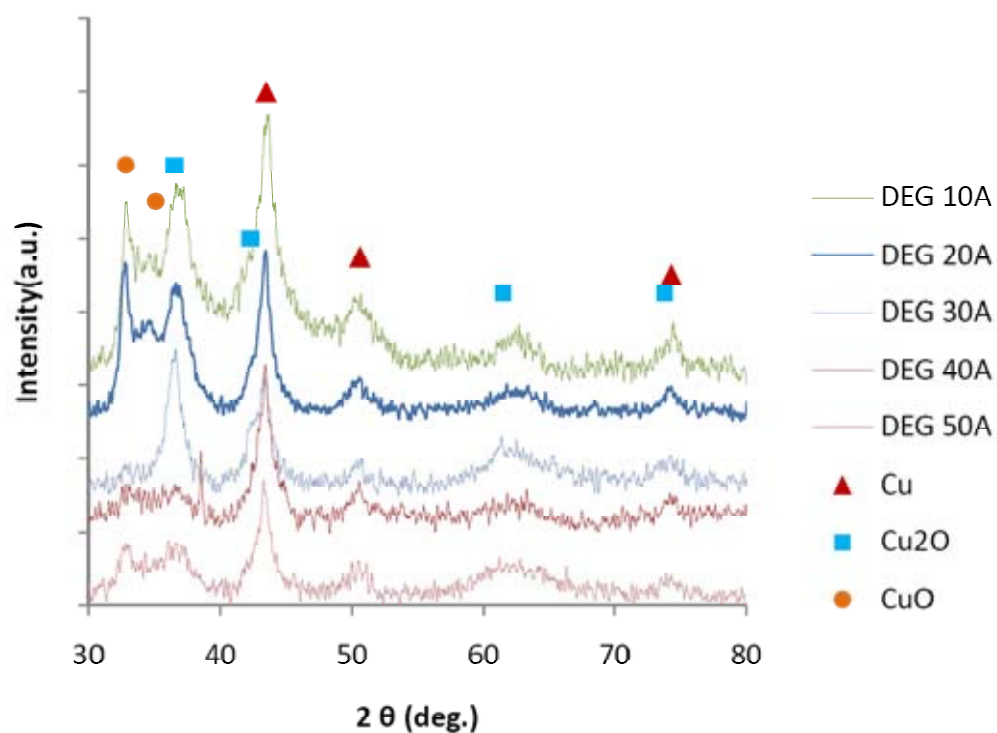Figure 5.3 XRD pattern of synthesized copper nanoparticles in EG with different of applied currents

Figure 5.4 XRD pattern of synthesized copper nanoparticles in DEG with different of applied currents

5.1 Effect of applied electric currents on arc discharge submerged in dielectric liquid

In order to investigate the effect of applied electric currents on size of copper nanoparticles synthesized, the parameter such as temperature of dielectric liquid pressure and amount of arc copper were maintained constant. The applied electric current was set at 10, 20, 30, 40, and50 A. The size of copper particles synthesized will increase, when increased applied electric current. Figure 5.5and 5.6 show the TEM image of synthesized copper nanoparticles by arc discharge submerged in EG and DEG. TEM image of nanoparticles synthesized illustrates their spherical morphologies with 10-20 nm. Moreover, the high electric currents lead to yield larger copper nanoparticles than obtained at low electric current condition. The morphology of synthesized copper nanoparticles by used of EG and DEG as dielectric liquid were shown in SEM images of figure 5.7 and 5.8 respectively. The morphology of Copper nanoparticles is spherical with the size of particles was less than 100 nm. Moreover when high electric currents (over 30 A) were applied during the arc, copper wires are easily to melt together after contact between two electrodes. This caused by high temperature occur when high electric currents were used and then lead to melt copper electrodes together.
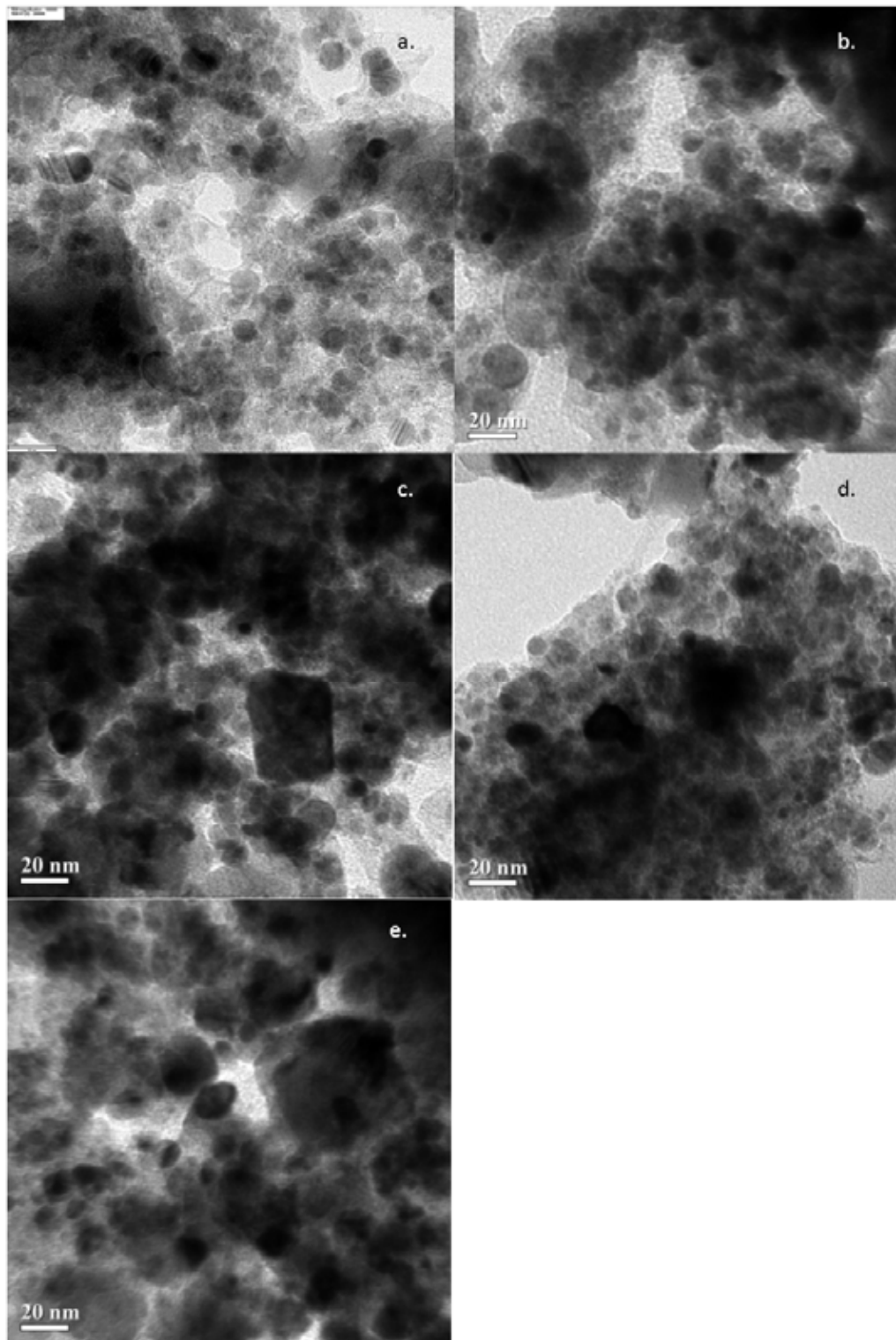
Figure 5.5 TEM image of synthesized copper nanoparticles in EG with different of applied currents: a.10 A, b.20 A, c. 30 A, d. 40 A and e.50 A
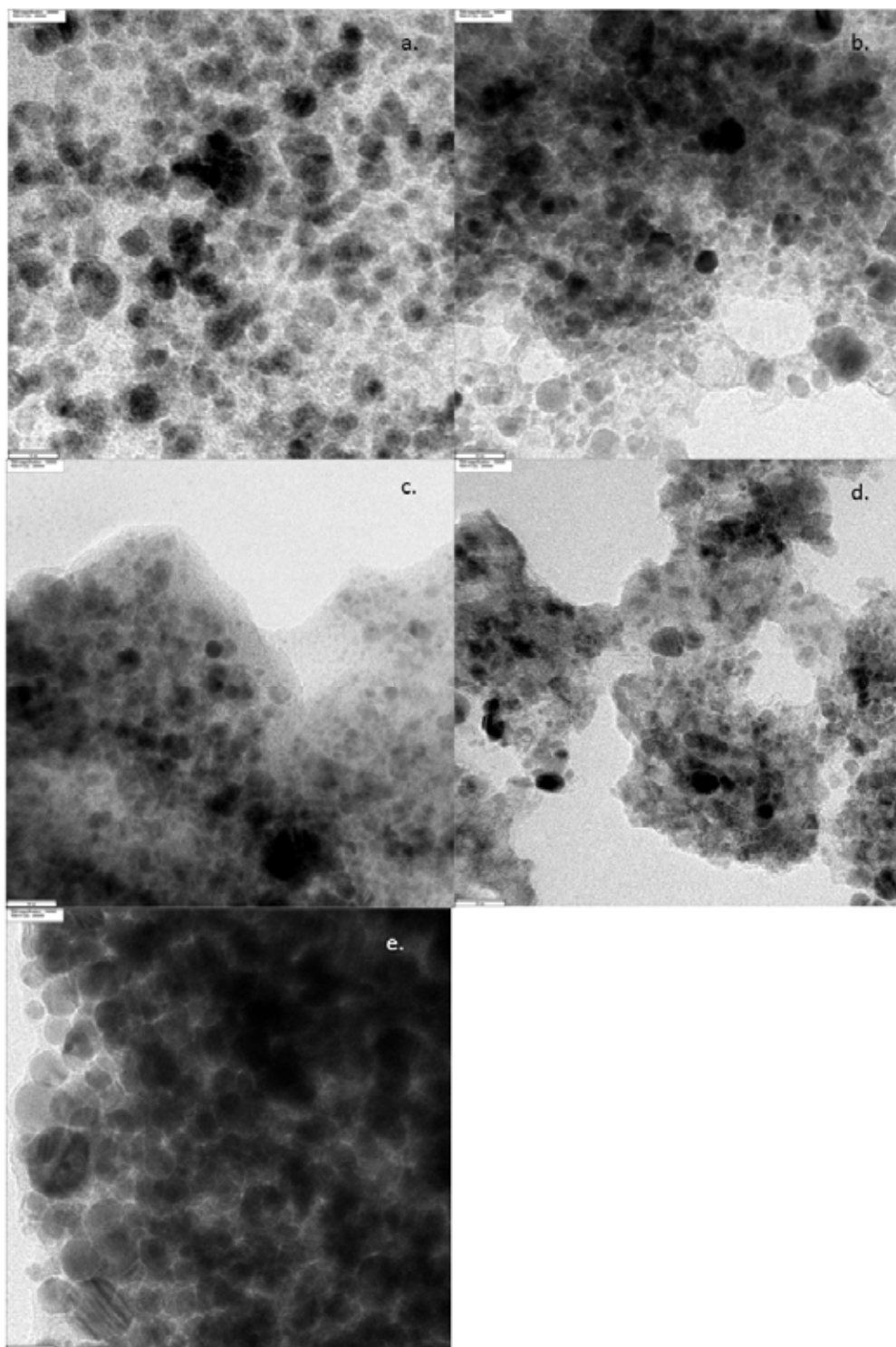
Figure 5.6 TEM image of synthesized copper nanoparticles in DEG with different of applied currents: a. 10 A, b.20 A, c. 30 A, d. 40 A and e.50 A
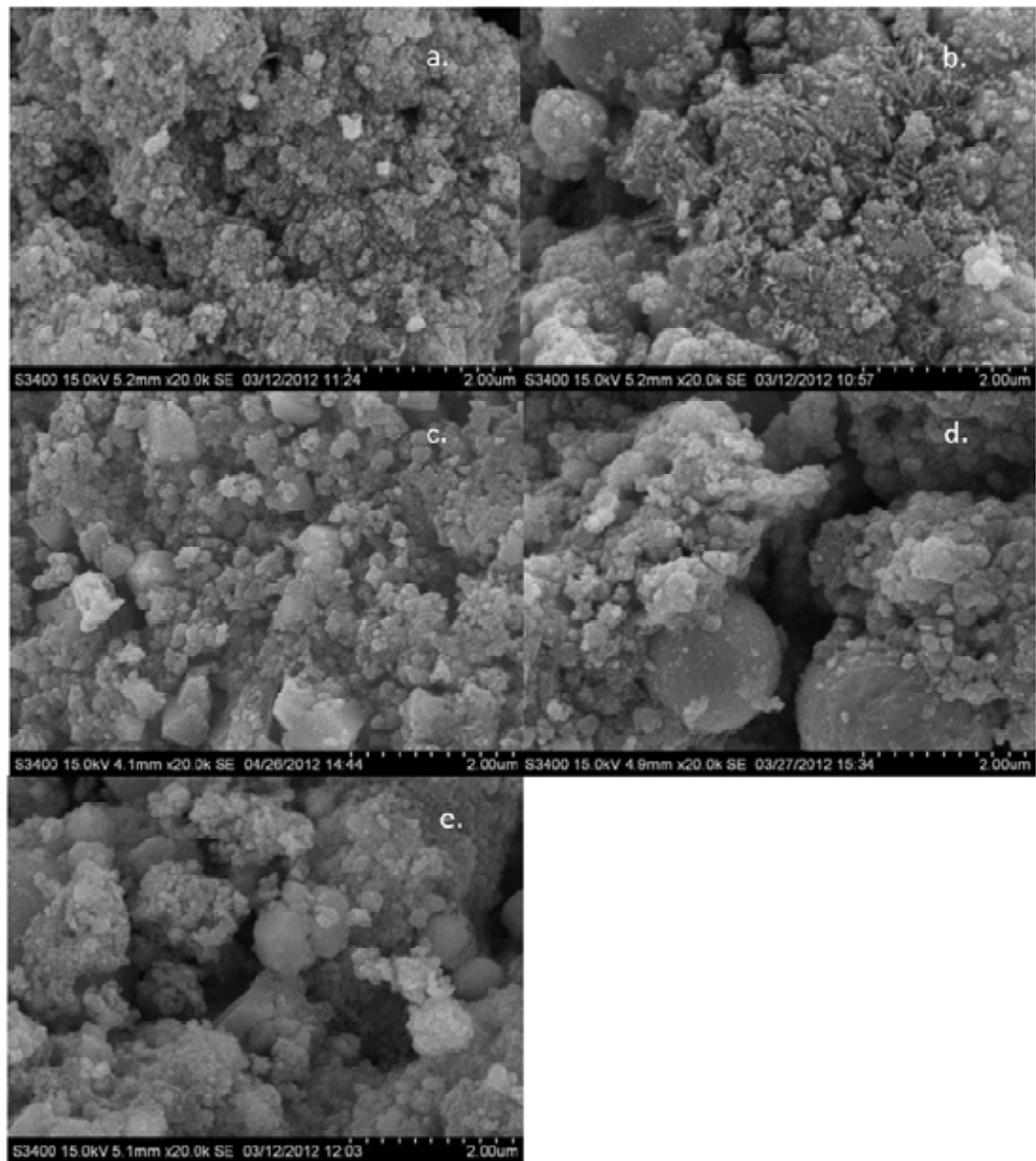
Figure 5.7 SEM image of synthesized copper nanoparticles in EG with different of applied currents: a. 10 A, b.20 A, c. 30 A, d. 40 A and e.50 A
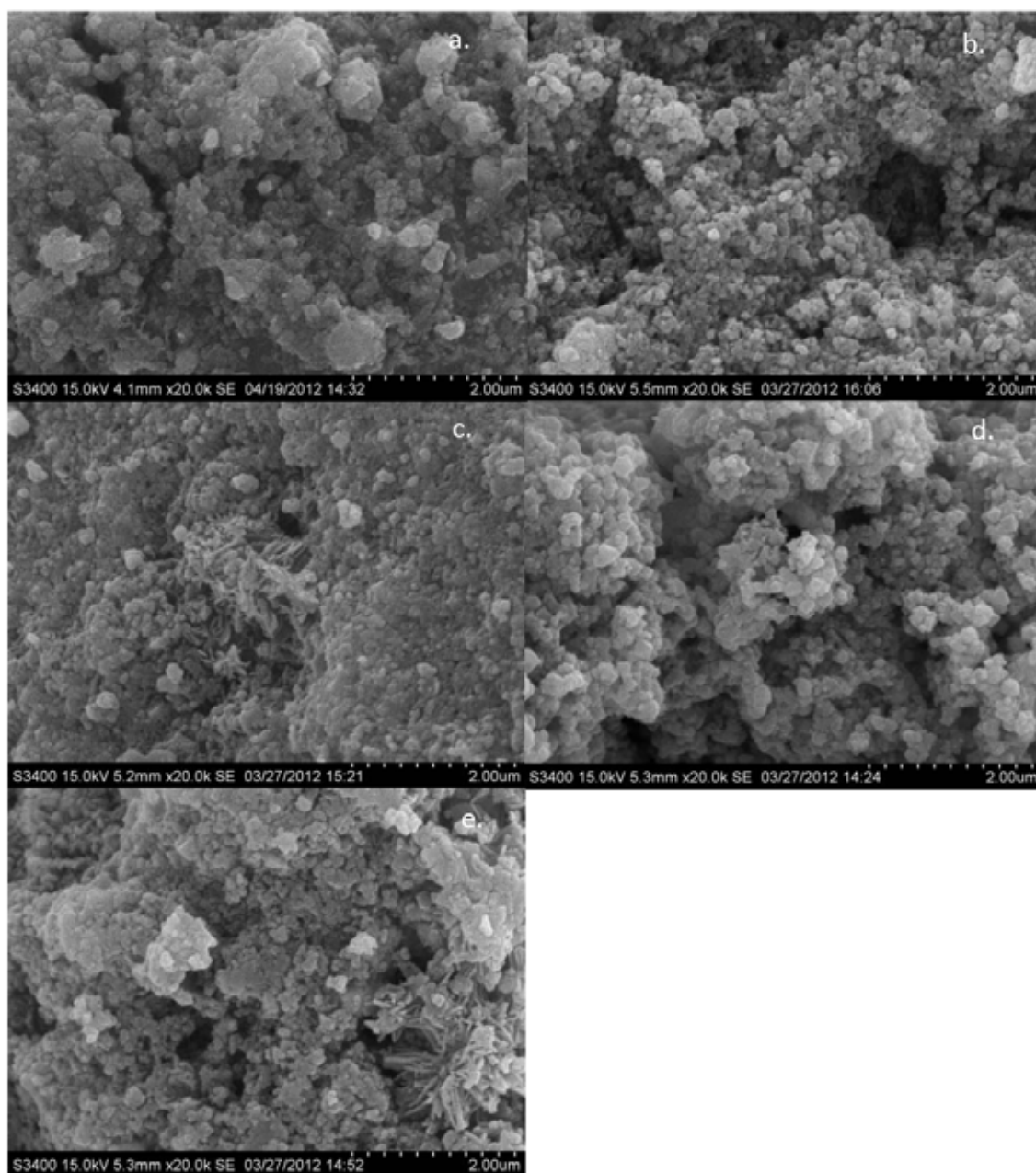
Figure 5.8 SEM image of synthesized copper nanoparticles in DEG with different of applied currents: a.10 A, b.20 A, c. 30 A, d. 40 A and e.50 A

5.2 Effect of reducing agents on copper particles synthesized

The three reducing agents were used in these studies which were L-ascorbic acid, sodium borohydride and sodium hypophosphite. The reducing agents with different concentration of 0.1, 0.3, 0.5 and 1 M. were added into copper colloid synthesized by arc discharge submerged in EG and DEG with applied electric current at 10 A. The results were shown in figure 5.9-5.14. When L-ascorbic acid and sodium brorohydride ($NaBH_4$) were added to the copper colloid synthesized and then heated to 45ºC, the color of solutions was turn from black brown to red brown. It means that copper oxide particles were reduced to copper nanoparticles. The results of adding L-ascorbic acid and sodium borohydride as reducing agents were shown in figure 5.9, 5.12 and 5.10, 5.13. When concentration of reducing agents increases, the absorption of copper colloid also increase around 580 nm because copper oxide particles suspension in dielectric liquid were reduced to be copper particles [Isaeva 2009]. When sodium hypophosphite (NaH_2PO_2) was used, it found that absorption intensity was decreased under pure synthesized copper colloid because it seem like that sodium hypophosphite can react at high temperature rather than low temperature [Park 2007] as see results in figure 5.11 and 14. When we compared results from three reducing agents, it found that L-ascorbic acid (1M) can transform more copper oxide to copper nanoparticles. As present in the absorption peak of copper nanoparticles added with L-ascorbic acid have higher absorbance and shaper than other reducing agents in both of EG and DEG dielectric liquid.
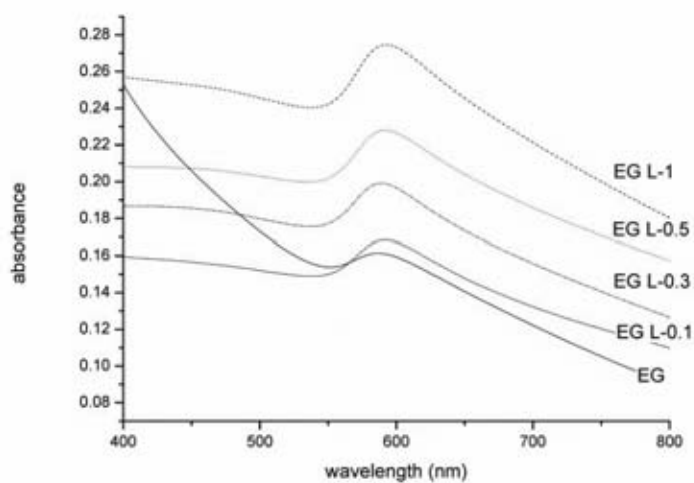
Figure 5.9 the UV-vis spectra of synthesized copper nanoparticles in EG with different concentrations of L-ascorbic acid 1 M, 0.5 M, 0.3 M, 0.1M and synthesized copper nanoparticles in EG without reducing agent.
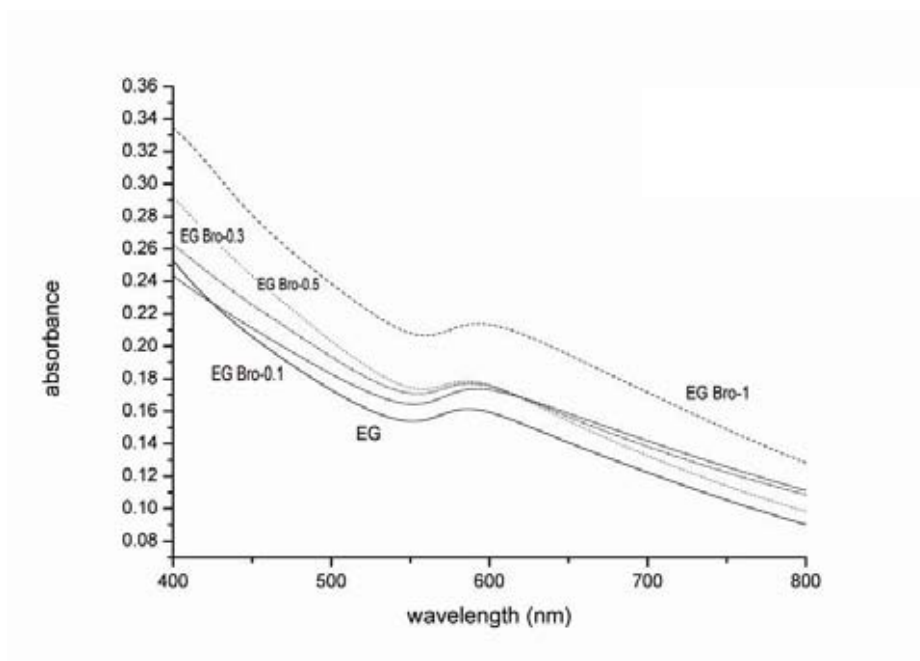

Figure 5.10 the UV-vis spectra of synthesized copper nanoparticles in EG with different concentrations of sodium borohydride ($NaBH_4$) 1 M, 0.5 M, 0.3 M, 0.1M and synthesized copper nanoparticles in EG without reducing agent.
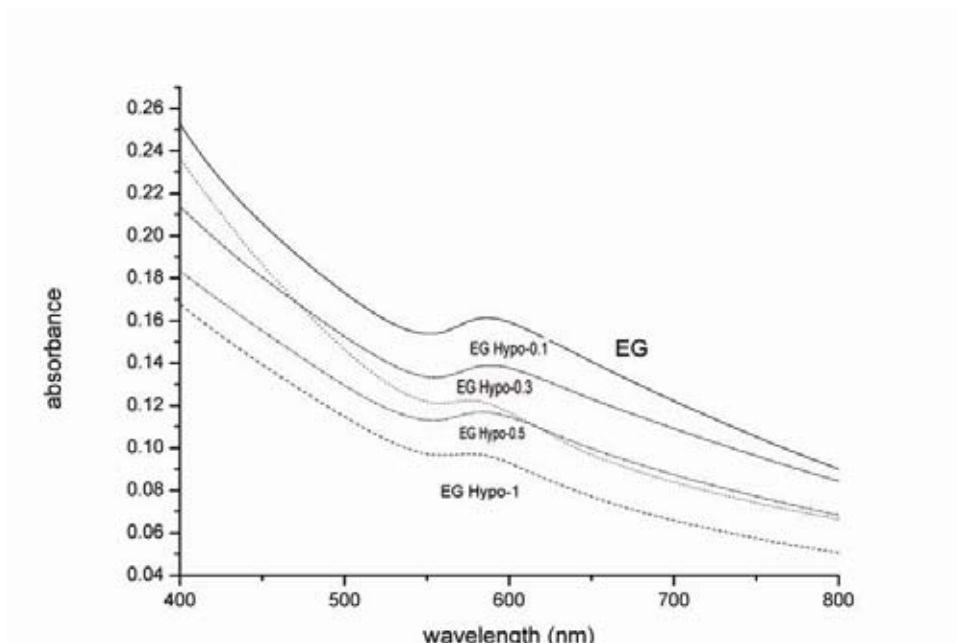
Figure 5.11 the UV-vis spectra of synthesized copper nanoparticles in EG with different concentrations of sodium hypophosphite (NaH$_2$PO$_2$) 1 M, 0.5 M, 0.3 M, 0.1M and synthesized copper nanoparticles in EG without reducing agent.
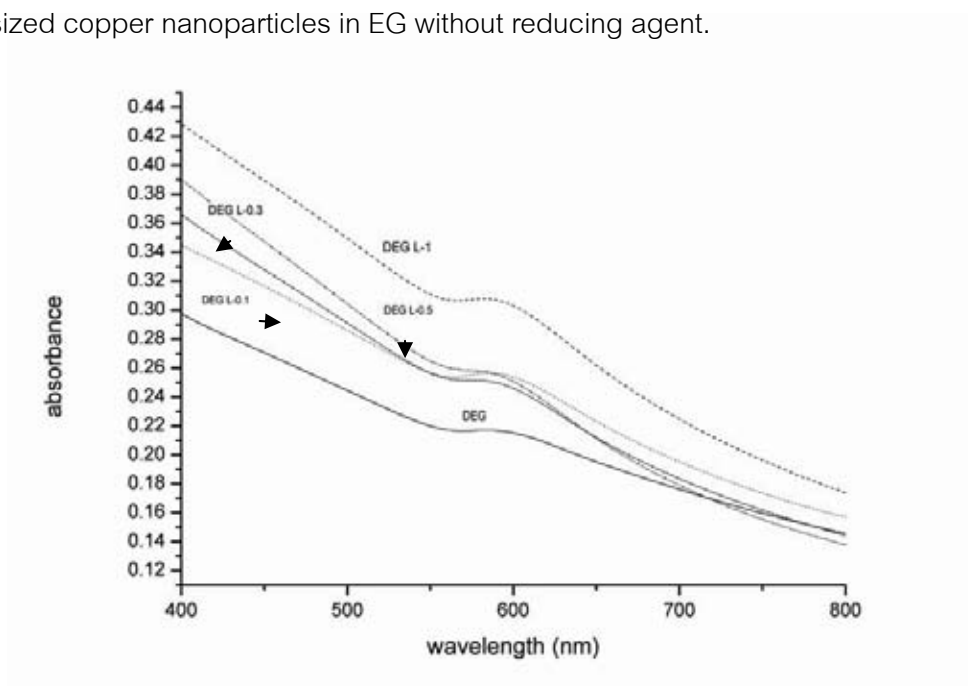

Figure 5.12 the UV-vis spectra of synthesized copper nanoparticles in DEG with different concentrations of L-ascorbic acid 1 M, 0.5 M, 0.3 M, 0.1M and synthesized copper nanoparticles in EG without reducing agent.
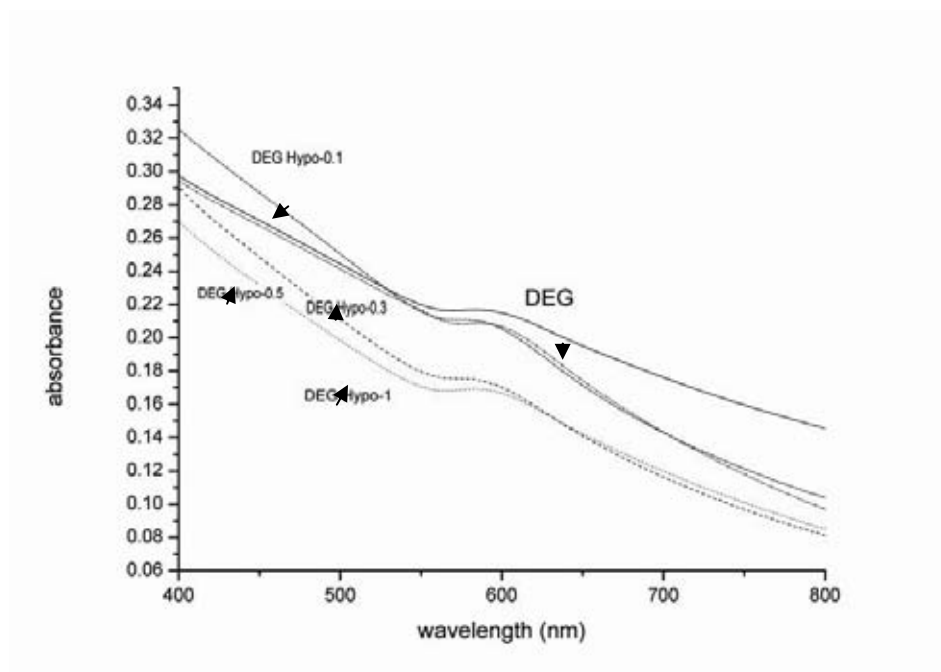
Figure 5.13 the UV-vis spectra of synthesized copper nanoparticles in DEG with different concentrations of sodium borohydride (NaBH$_4$) 1 M, 0.5 M, 0.3 M, 0.1M and synthesized copper nanoparticles in EG without reducing agent.
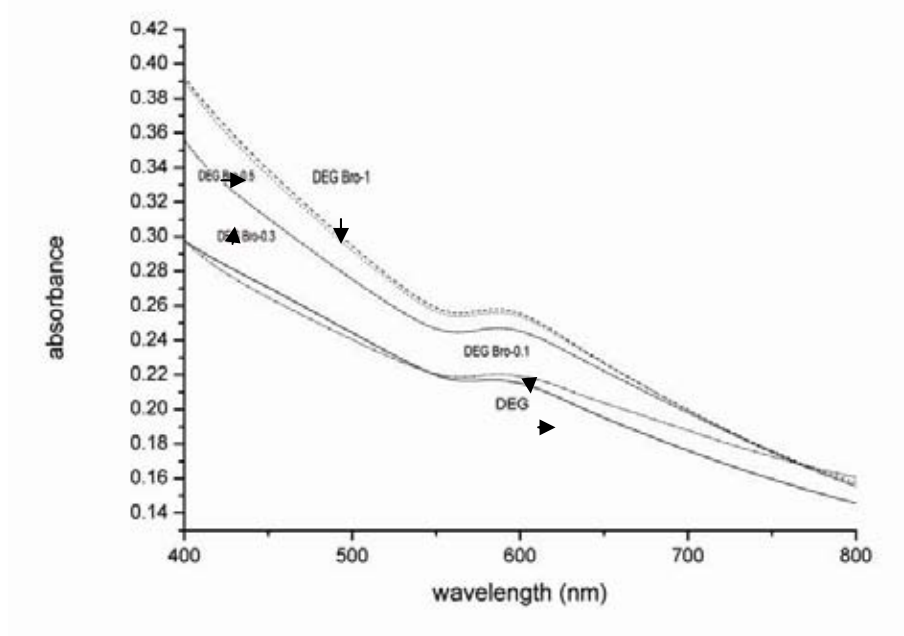

Figure 5.14 the UV-vis spectra of synthesized copper nanoparticles in DEG with different concentrations of sodium hypophosphite (NaH$_2$PO$_2$) 1 M, 0.5 M, 0.3 M, 0.1M and synthesized copper nanoparticles in EG without reducing agent.

5.3 Effect of concentration of PVP

In order to investigate effect of concentration of PVP on copper nanoparticles synthesized in dielectric liquid. The copper colloid synthesized added with L-ascorbic acid 1M was used to study by varied concentration of PVP at 0.05, 0.1, 0.3, and 0.5M. The results from UV-vis spectroscopy of copper nanoparticles synthesized in EG and DEG were shown in figure 5.15 and 5.16. When PVP was added to synthesized copper colloid at any concentration, it found that the absorption of copper colloid is obvious higher and shaper than copper colloid synthesized without PVP. These mean that added PVP can protect copper nanoparticles form oxidation of oxygen in dielectric liquid at ambient atmosphere. The results of adding PVP in copper colloid synthesized in DEG were shown in figure 5.16. When concentration of PVP was increased, the absorption of copper particles around 580 nm was also increased too. The results shown synthesized copper nanoparticles in DEG added with L-ascorbic acid 1 M. and PVP 0.5 M. could give high amount of copper particles as see in high absorbance of copper particles at 580 nm as shown in figure 5.16. For copper nanoparticles synthesized in EG, the optimum added PVP was 0.1 M. with L-ascorbic acid 1M. This condition gave the highest amount of copper particles as show the highest absorbance of copper particles.
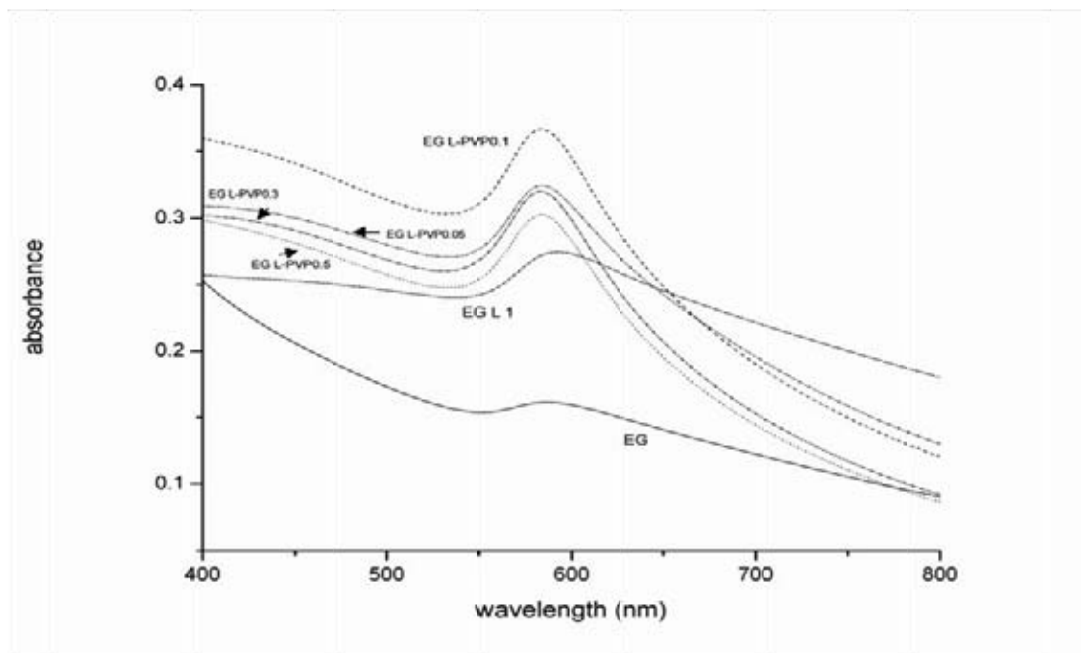
Figure 5.15 the UV-vis spectra of synthesized copper nanoparticles in EG with

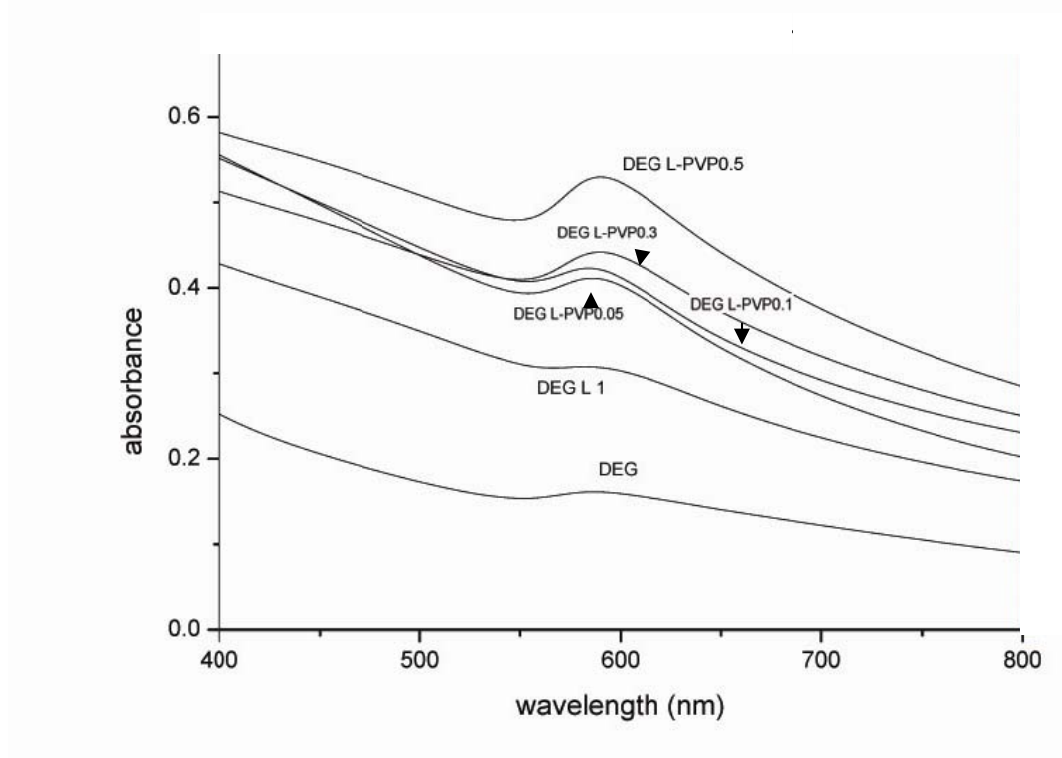L- ascorbic acid 1M and different concentration of PVP

Figure 5.16 the UV-vis spectra of synthesized copper nanoparticles in DEG with

L-ascorbic acid 1M and different concentration of PVP

The copper nanoparticles synthesized added with L-ascorbic acid 1M and PVP 0.1 M and 0.5M (for EG and DEG respectively) were characterized by XRD, FTIR, SEM and TEM. To observe the formation of copper oxide on synthesized copper nanoparticles by XRD. The copper nanoparticles were found to be pure copper from synthesized in DEG and EG as shown in figure 5.17and 5.18. It can infer that PVP can achieve to protect formation of copper oxide at ambient atmosphere. After stored synthesized copper nanoparticles at ambient condition for a month aim to test stability of copper nanoparticles resist to oxidation of oxygen. The results from XRD shown that there was no change and formation of copper oxide after stored at ambient conditions for a month, to confirm formation of oxide on copper nanoparticles without PVP protection, the copper nanoparticles with PVP was washed with methanol for three times and then investigated with XRD. The results shown that the copper nanoparticles synthesized were form oxide when PVP was removed. So this can infer that coating PVP on copper nanoparticles can inhibit oxidation of oxygen in air
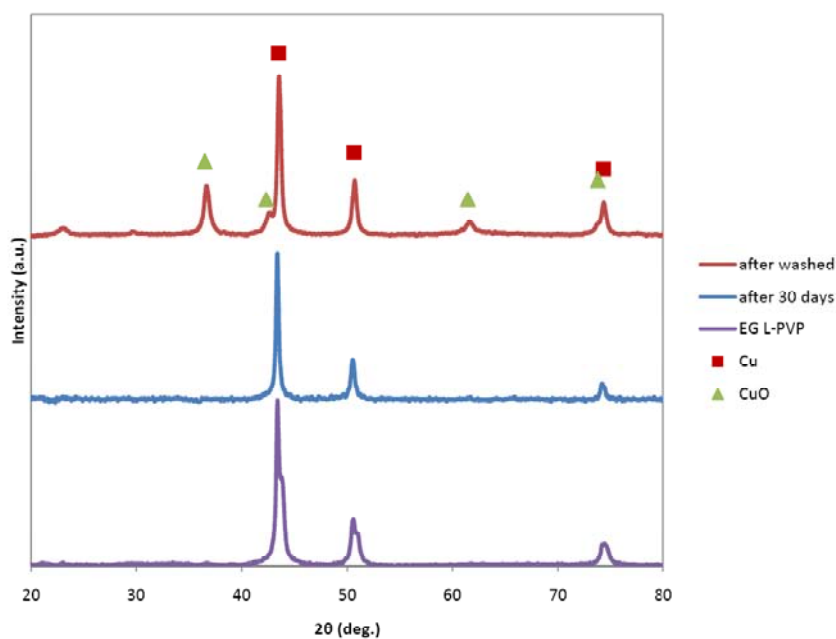

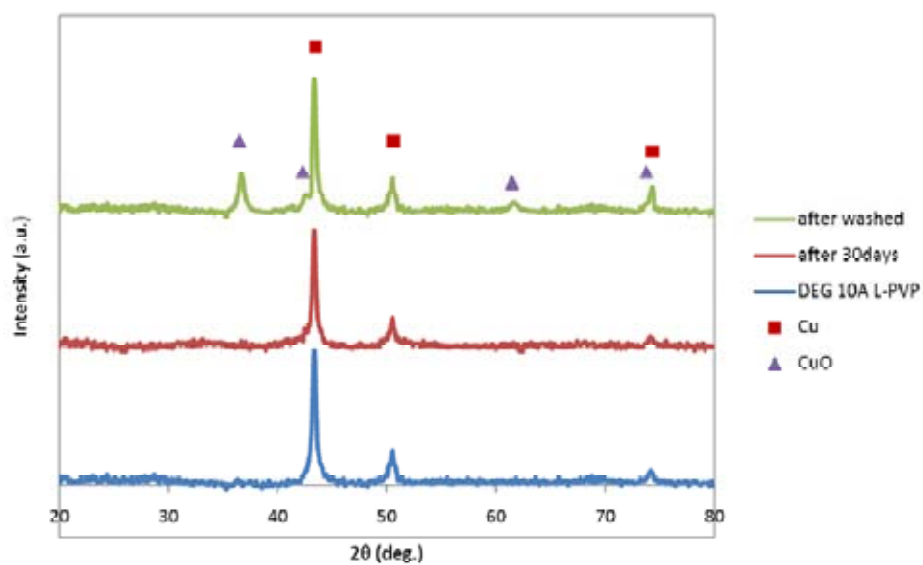Figure 5.17XRD pattern of synthesized copper nanoparticles in EG with L-ascorbic acid 1M and 0.1M of PVP

Figure 5.18XRD pattern of synthesized copper nanoparticles in DEG with L-ascorbic acid 1M and 0.1M of PVP
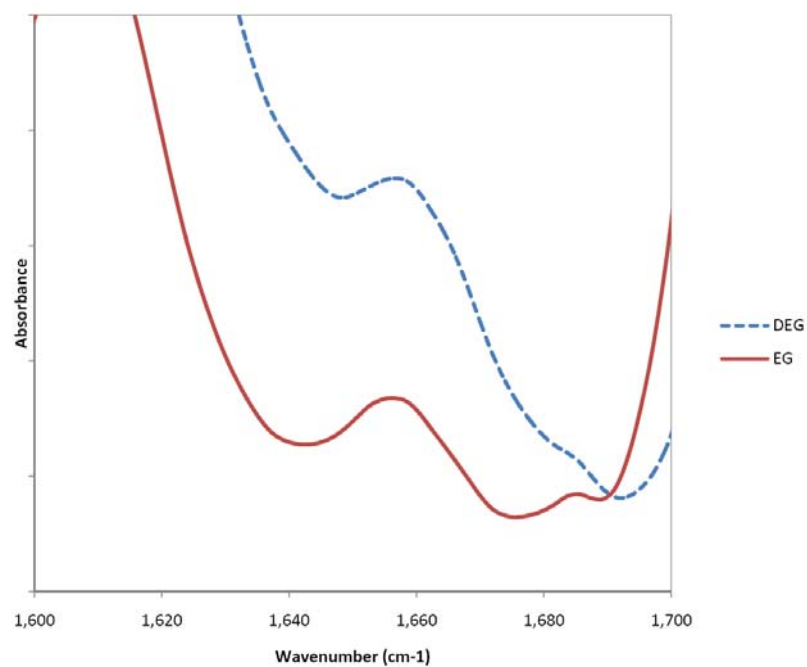

Figure 5.19 FTIR spectra of synthesized copper nanoparticles with added PVP in DEG and EG

We confirmed the formation of copper nanoparticles within PVP matrix by using FTIR. The C=O bond in pure PVP shows at wavenumber around 1660cm-1. As shown in Fig. 5.19, FTIR spectra of copper nanoparticles synthesized with PVP added show the absorbance peak of C=O bond at wavenumber 1656 cm-1 which were display in both synthesized in DEG and EG..The shift in wavenumber of C=O bond occur due to the bond weaking as a result of back bonding via partial donation of lone pair electrons from oxygen in PVP to vacant orbital of metal. This can be inferred that C=O bond in PVP coordinates to the particles surface via O-Cu coordination bond, and PVP wraps around the particles with its long and soft polyvinyl chain [Wu et al. 2005]. SEM image was shown in Fig. 5.20, the copper nanoparticles obtained were spherical, and the size of particles was less than 100 nm. TEM image of copper nanoparticles synthesized by arc discharge submerged in EG with added L-ascorbic acid and PVP is shown in Fig. 10. The copper particles synthesized is spherical with diameter around 10-20 nm.
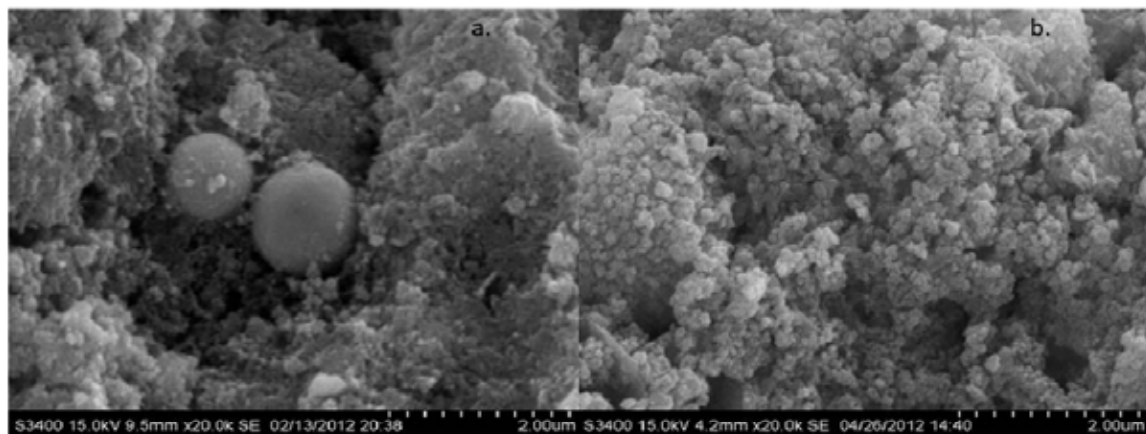

Figure 5.20 SEM images of synthesized copper nanoparticles by in (a.) EG and (b.) DEG with L-ascorbic acid 1M and 0.5 M and 0.1 M of PVP, respectively
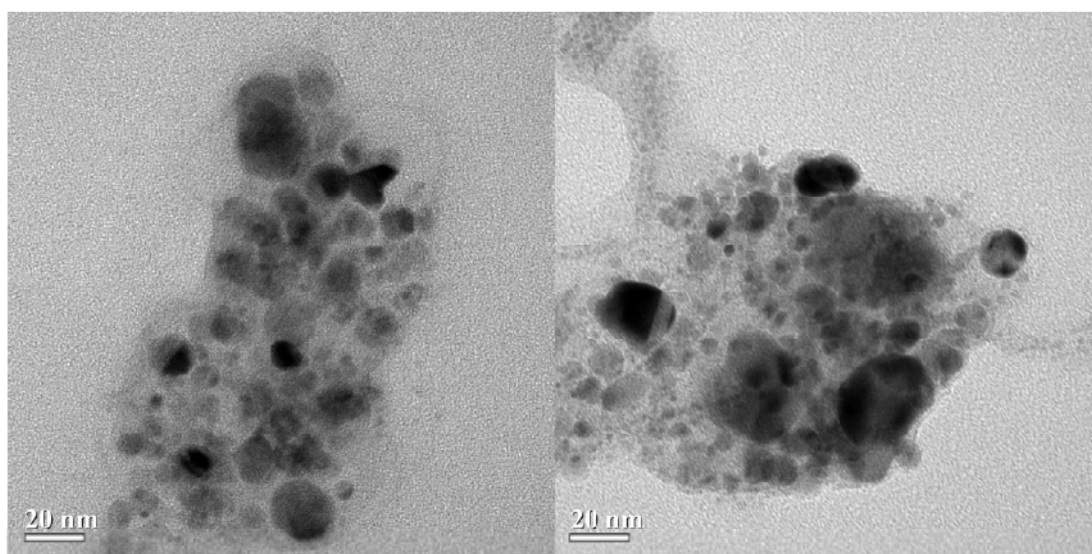
Figure 5.21 TEM images of synthesized copper nanoparticles by in (a.) DEG and (b.)
EG with L-ascorbic acid 1M and 0.5 M and 0.1 M of PVP, respectively

Chapter 6
Conclusions

6.1.   Conclusions

In this study, copper nanoparticles were synthesized by arc discharge submerged in ethylene glycol (EG) and diethylene glycol (DEG) under ambient atmosphere with the applied electric currents 10-50 A. The experimental results indicate that the nanoparticles synthesized contained of both copper and copper oxide. The copper oxide was formed by oxygen free radicals during decomposition of the dielectric liquid. Using the current of 10A obtained 10-20 nm spherical nanoparticles. TEM image of nanoparticles synthesized illustrates their spherical morphologies with 10-20 nm. The size of nanoparticles synthesized increases as the current applied increases. The copper oxide particles can be converted to copper particles by adding reducing agents. L-ascorbic acid and sodium borohydride could reduce copper oxide to pure copper as show the increasing peak high around 580 nm, while sodium hypophosphite need higher temperature to reduce copper. L-ascorbic acid (1M) gave the highest amount of copper particles in both of EG and DEG. To stabilize copper nanoparticles synthesized, PVP was used as capping agent. The effect of PVP (0.05~0.5M) was then studied. PVP could prevent agglomeration of copper nanoparticles and provide protection for copper oxide formation. The addition of PVP 0.1M and 0.5M in copper synthesized in EG and DEG respectively was sufficient. The produced copper nanoparticles could maintain for 30 days without oxide formation and agglomeration when collect at ambient condition.

6.2.   Recommendations

Feed speed is necessary to control because when low electric current was used, too fast of feed speed lead to touch of two electrode and arc does not occur. Inversely, high electric current was used, too fast of speed is lead to touch and melt of two electrode together

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Appendix