THE INFLUENCE OF DIFFERENT REDUCING AGENTS ON THE POLYOL SYNTHESIS OF COPPER NANOPARTICLES

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Abstract

This paper focused on the preparation of copper (Cu) nanoparticles from copper nitrate as metal precursor by Polyol reduction. Ethylene glycol, Glycerol and Glycerine were used as a reducing agent and stabilizer. The copper particles formed were identified by EDXRF, XRD and SEM. The effect of solvent showed that small spherical copper nanoparticles and the good dispersion of nanoparticles are found by using solvent either glycerol or glycerine. EDXRF spectrum also informed that there was no other metal impurity in the formation of Cu NPs. From XRD pattern, the average crystallize size of Cu NPs was found to be 38 nm as each particle observed from SEM is not a single crystallite of Cu but the agglomerates of many single crystallites. The aggregation of nanoparticles caused the inhomogeneous size distribution.

Keywords: Copper nanoparticles, spherical shaped nanoparticles, inhomogeneous size distribution

Introduction

Metals and their compounds such as Copper (Cu), Gold (Au), Silver (Ag), Palladium (Pd) and Platinum (Pt) are widely used these days (Bell *et al,* 2001) (Hutter et al, 2001). Nanoparticles of these metals and metal compounds have been interested extensively in recent years because of their unexpected physical and chemical properties shown at nanoscale (Ozin, 1992). Among various nanoparticles, the copper nanoparticles can be utilized in several applications. Owing to extremely small size, copper nanoparticles exhibit enhanced properties when compared with the bulk material including

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large surface area relative to their volume, ability to easily interact with other particles and increased antibacterial efficiency (Carrol et al, 2011). Because of its excellent electrical conductivity, catalytic behaviour, good compatibility and surface enhanced Raman scattering activity, Cu nanoparticles have drawn the attention of scientists to be used as essential component in the future nano-devices (Wu et al., 2006). The general problems like aggregation and oxidation of copper nanoparticles limit their usage. However, the usage of suitable separate stabilizing agent in the preparation rectifies this problem easily. Copper nanoparticles have been synthesized by different methods. To date, thermal reduction, thermal decomposition, direct electrochemical reduction from CuO nanoparticles, mechano-chemical process, polyol process, chemical reduction, *in-situ* synthesis in polymers, electro-exploding wire (EEW) and ion beam radiation have all been developed to prepare nanostructured copper (Dang et al, 2011).

In this paper, a polyol reduction method to synthesize copper colloids in different solvent without protective gas is presented. Ethylene glycol, glycerin and glycerol mixed with and without water were used as solvents. Their influence on the different reducing agent affects the nanoparticle solutions will be discussed.

2. Experimental

2.1 Materials

Analytical grade (BDH, England) Copper Nitrate $Cu(NO_3)_2$, Sodium Hydroxide (NaOH) and different solvent such as Ethylene Glycol $(CH_2OH)_2$, Glycerol ($C_3H_8O_3$) and Glycerin($C_3H_8O_3$) were used as starting precursor. All chemicals were used as purchased without further purification.

2.2 Synthesis of copper nanoparticles

The copper nanoparticle was prepared by polyol reduction of copper nitrate with sodium hydroxide solution. Copper nitrate was used as starting material and glycerol was used as solvent, reducing agent and a stabilizer. Sodium Hydroxide is used for faster the chemical reaction. Cu $(NO_3)_2$ (0.5 M) was dissolved in 2 ml double distilled water. To this solution, 10 ml of

ethylene glycol was added. NaOH (2.5 M) was dissolved in 2 ml double distilled water. Ethylene glycol 10 ml was added to Sodium Hydroxide and water solution. Then mixture of NaOH and $Cu(NO_3)_2$solution was heated on a hot plate stirrer at temperatures of 135ºC for half an hour. The change in colour of test solution from dark blue to reddish brown colour was observed visually. The reddish brown coloured solution was removed from the heating magnetic stirrer and cooled down. Then, the colloidal solution was separately centrifuged for 15 mins at 6000 rpm, washed three times with double distilled water (DDW) and ethanol. The wet precipitates were dried at 70 ºC overnight to obtain the Cu nanoparticles. Cu NPs have been prepared by polyol reduction of copper nitrate as precursor using water and ethylene glycol, water and glycerine, water and glycerol as reducing agent until the dark blue coloured solution turns to reddish brown colour. Another experiment was carried out by using the same precursor and solvents without water. The obtained colloid solution is shown in figure 2(a, b and c) with a deeper red colour.

Figure. 1. Color changes (blue , green, red to dark brown) of solution after mixing NaOH 2.5 M $CuNO_3$ of 0.5 M

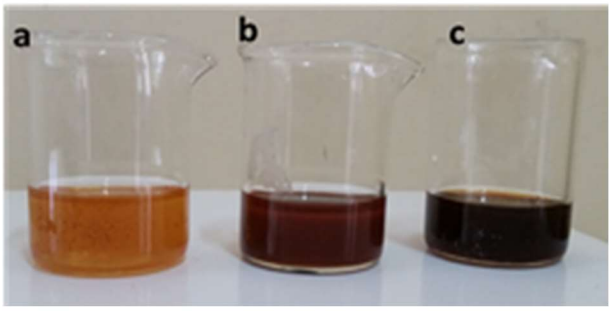


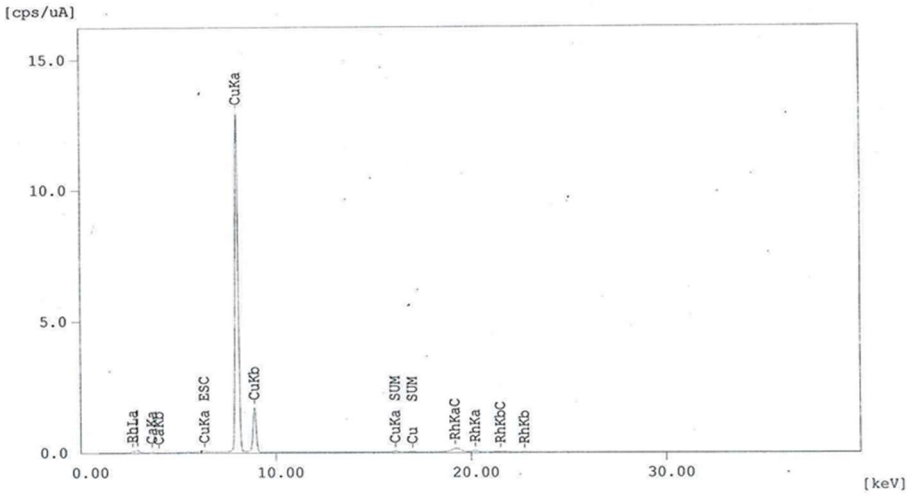
Figure 2. Fresh Colloid solutions of Cu nanoparticles in (a) glycerol (b) glycerin and (c) ethylene glycol

2.3 Characterization

Centrifuge machine (Kokusan H-200 series) was used to separate the colloid from the solutions. The influence of solvent on formation of Cu NPs was confirmed EDXRF Energy Dispersive X-rays Spectrometer (EDX 720), X-ray powder diffractometer (Type: RIGAKU–RINT 2000), and SEM (Type: JEOL 15 kV).

3. Results and Discussions

3.1 EDXRF and XRD analysis of Cu NPs



Quantitative Result

Analyte	Result	[3-sigma]	Proc.-Calc. Line		Int.(cps/uA)
	12.745 mg/cm2	[------]	Total	--------	--------
Cu	17141.54 mg/l	[42.337]	Quan-FP	CuKa	116.3318
Ca	150.424 mg/l	[6.078]	Quan-FP	CaKa	0.2983
C 6H10 O5	12.500 mg/cm2	[------]	Fix	--------	--------

Figure 3. EDXRF Cu nanoparticles by using ethylene solvent, after centrifugation an drying Cu nanoparticles obtained from different solvent shows same EDXRF spectrum.

EDXRF of all samples show similar spectrum. EDXRF analysis shows a very rich copper composition for metal. No other chemical impurities is detected. The weak calcium (Ca) signals may be due to some impurities that surrounds the Cu particles.

To confirm the crystalline structure of the copper (Cu) nanoparticles was analyzed on X-ray diffractometer (Model RIGAKU–RINT 2000). The polycrystalline properties for drop coated glass thin film of Cu powder were analyzed by using Cu / K-α_1 radiation (40 kV, 40 mA) in 2θ range from 10° to 70° on a Rigaku powder X-ray diffractometer equipped with a diffracted-beam graphite monochromator. The crystallite domain diameters *D* were obtained from XRD peaks according to the Scherrer equation: $D = \frac{0.89\lambda}{\Delta W \cos\theta}$, where λ is the wavelength of the incident X-ray beam (1.5405 Å for Cu / K-α_1), λ is the Bragg's reflection angle, ΔW is the width of X- ray pattern line at peak half peak height in radians. The Miller indices in XRD pattern of Cu NPs (upper spectrum) and standard Cu particles (lower) were shown in Figure 4 and 5.

XRD graph of Cu powder synthesized from Copper nitrate precursor and different solvent such as ethylene glycol, glycerin, glycerol mixed with water has been shown in Figure 4. The pattern in Figure 4 shows that three XRD peaks appeared at 38.8°, 43.163° due to strong Bragg reflections from (111), (200) and (222) planes of Copper (I) Oxide and Copper (II) Oxide respectively. All reflections are agreed with standard library file (ICDD-PDF#99-041) of with Copper (I) Oxide and (ICDD-PDF#78-0428) of Copper (II) Oxide. Based on Scherer equation, the average crystallite size of Cu NPs was found to be 38 nm.

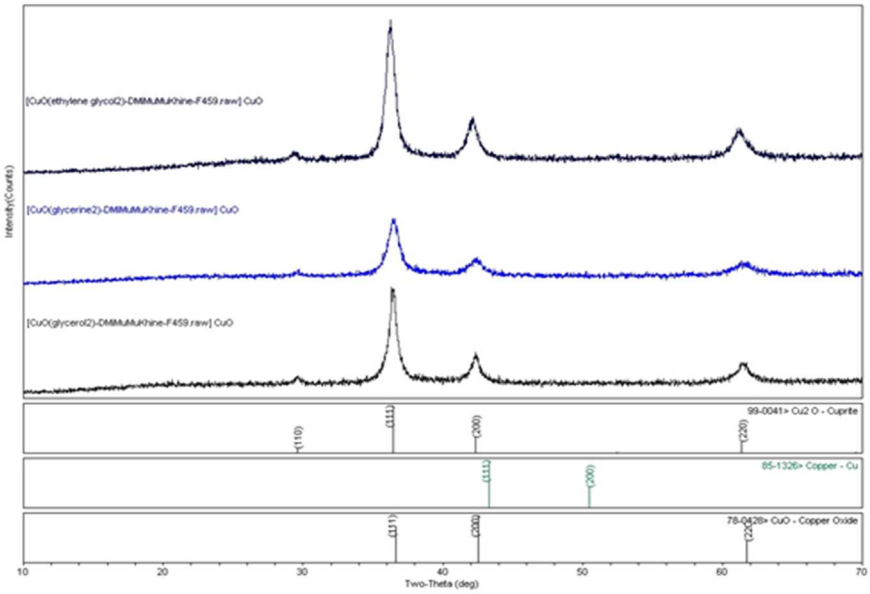


Figure 4. XRD Cu nanoparticles synthesized by using different solvents such as ethylene glycol, glycerin and glycerol. In this reaction all solvents and precursor mixed with water.

XRD graph of Cu powder synthesized from same precursor with different solvent such as ethylene glycol, glycerin and glycerol which are not mixed with water is shown in Figure 5. The XRD patterns of sample synthesized with glycerol and glycerin appeared at 43.5°, 50.163°, due to strong Bragg reflections from (111) and (200) planes of copper respectively. All reflections are agreed with standard library file (ICDD-PDF#04-0836) of pure copper metal with fcc (face centred cubic) symmetry. The XRD patterns of sample synthesized with Ethylene glycol give the Cu_2O peaks. Based on Scherrer equation, the average crystallite size of Cu NPs was found to be around 35- 38 nm.

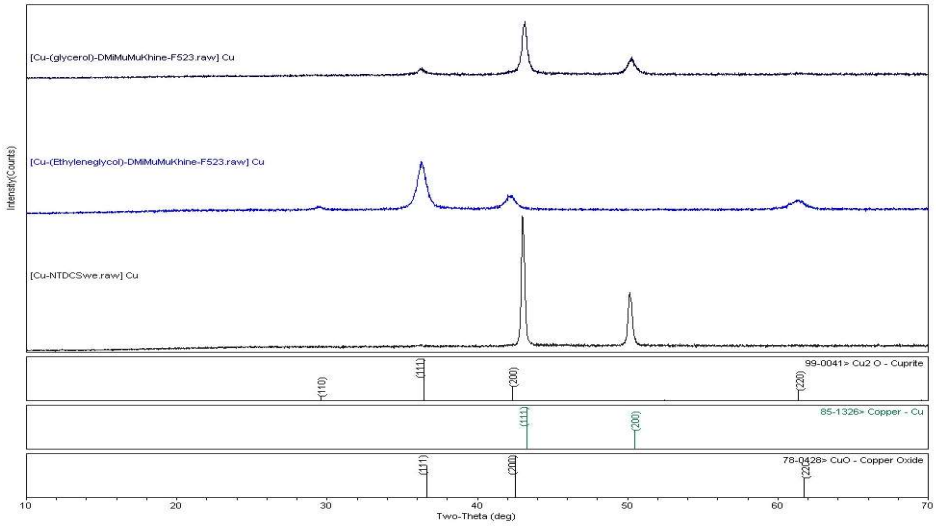


Figure 5. Figure 4. XRD Cu nanoparticles synthesized by using different solvents such as ethylene glycol, glycerin and glycerol. In this reaction, all solvents and precursor do not mixed with water.

From the XRD results, it is obviously appeared that the reaction included water gives the oxide nanoparticles. In this case, copper and copper oxide nanoparticles by the reaction of copper with water can be explained according to the reaction at 135 ºC. As the concentration of Cu^{2+} and OH^- ions exceed a critical value, the precipitation of hydroxide nuclei starts.

$$Cu(OH)_2 \rightarrow 2\ CuO(s) + H_2O$$

The Cu OH can be transformed into the Cu_2O crystals via the sample chemical reaction. The Cu metal on reaction with water slowly gives out hydrogen and the liberated oxygen reacts with metal to give oxides as shown in above reaction. The Cu react with oxygen and forms nuclei, which further serve as seed for CuO and Cu_2O nanoparticles growth. The growth nanoparticles could be occurring at small oxide nuclei that may be present on the metal surface.

SEM analysis

After the preparation of the nanoparticles, SEM analysis was performed on dried nanoparticles to investigate the size and surface morphology of the samples using different solvents such as ethylene glycol, glycerin and glycerol (The samples obtained the reaction without water). Figure 6(a)–(b), 7(a)–(b) and 8(a)–(b) show the top-view SEM images of the prepared Cu samples after centrifugation and drying at 70 ºC. The size of particles observed with SEM is extremely different from the XRD calculated crystallite size (35 nm or 38 nm), as each particle observed from SEM is not a single crystallite of Cu but the agglomerates of many single crystallites. The aggregation of nanoparticles caused the inhomogeneous size distribution.

Figure 6(a)–(b) As-prepared Cu precipitations using ethylene glycol are found to be mixed with big square -like structure particles and sphere form in SEM images. The size of particles are larger than 2 μm. The non-uniform size distribution is found in this sample. Figure 7(a)–(b) and 8 (a)-(b) shows that dried Cu precipitations using either glycerol or glycerin are in good dispersion and found to be small spherical -like structure. In some regions, it is noticed that big nanoparticles (having average diameter of 100nm) which are surrounded by smaller nanoparticles. The surface morphology and size distribution of the samples by using glycerol and glycerin are better in those samples compare with the sample using solvent, ethylene glycol.

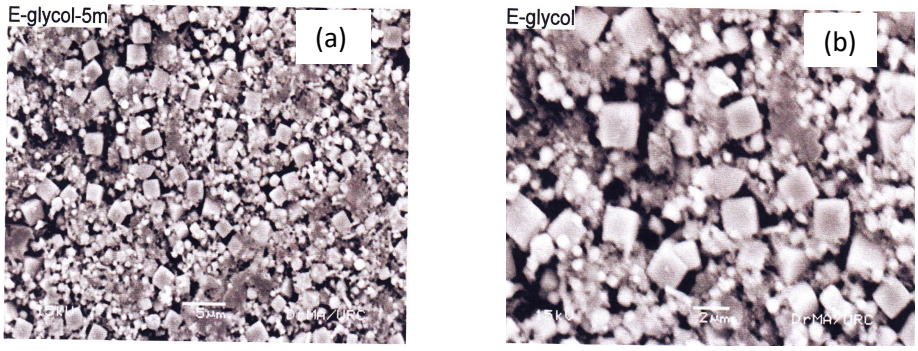


Figure 6. (a) high and (b) high magnification top-view SEM images of as prepared Cu nanoparticles by using ethylene glycol

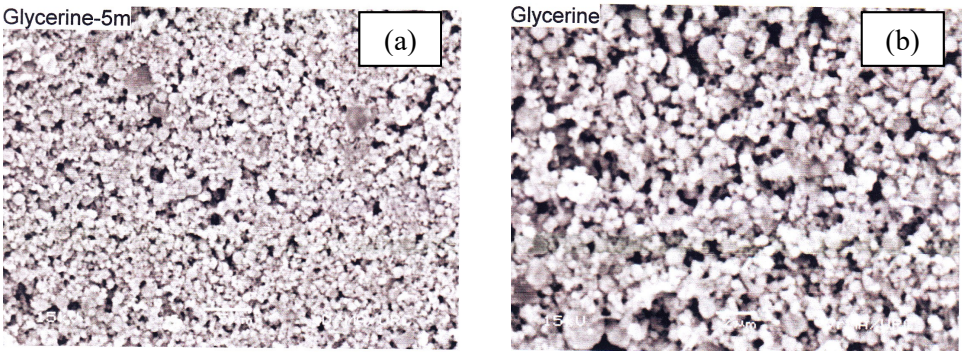


Figure 7. (a) Low and (b) high magnification top-view SEM images of as prepared Cu nanoparticles by using glycerin

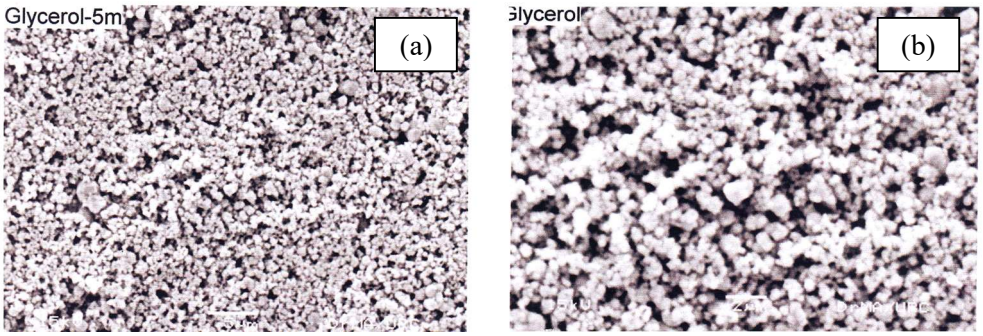


Figure 8. (a) low and (b) high magnification top-view SEM images of as prepared Cu nanoparticles by using glyceol

The following table shows the brief description of all experiments with different solvents.

Table1. List of chemical reaction by using polyol methd

Sr	Solvent/Reducing agent	Cu Precursor	Shape (SEM)	Product (XRD)
1.	Water+ Glycerol	$CuNO_3$	-	Cu+ CuO
2.	Water+ Glycerin	$CuNO_3$	-	Cu+ CuO
3.	Water+ Ethylene Glycol	$CuNO_3$	-	Cu+ Cu2O
4.	Glycerol	$CuNO_3$	Spherical	Cu
5.	Glycerin	$CuNO_3$	Spherical	Cu
6.	Ethylene Glycol	$CuNO_3$	Square	Cu+ CuO

4. Conclusion

In this paper, it was also found that the optimum size and distribution for the formation of Cu NPs was to be using the solvent such as glycerol and glycerin. The effect of solvent showed that small spherical copper nanoparticles and the good dispersion of nanoparticles are found by using solvent either glycerol or glycerin. EDXRF spectrum also informed that there was no other chemical impurities in the formation of Cu NPs. From XRD pattern the average crystallize size of Cu NPs was found to be 38 nm as each particle observed from SEM is not a single crystallite of Cu but the agglomerates of many single crystallites. The aggregation of nanoparticles caused the inhomogeneous size distribution. From the XRD results, it is obviously appeared that the reaction included water gives the oxide nanoparticles.

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