Article

Preparation of Ultrafine Copper Powders with Controllable Size via Polyol Process with Sodium Hydroxide Addition

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Abstract. A facile polyol process for producing copper powders with controllable size is described here. The copper powders have been readily synthesized by the reduction of copper (II) nitrate trihydrate with the solution of glycerol and sodium hydroxide. The X-ray diffraction, SEM and FESEM were used to characterize the obtained copper powders. The effect of the concentration of NaOH and the reaction temperature were investigated. The sizes and the complete reaction time of the copper powders were decreased at the condition of increasing the concentration of NaOH and the reaction temperature. For example, at the constant reaction temperature of 140 °C, the sizes of the obtained powders of the molar ratio of NaOH:$Cu(NO_3)_2$ range from 2:1 to 5:1 were decreased from 1.40 to 0.10 μm as well as the complete reaction times which were reduced from 240 to 17 minutes, respectively. By controlling the process parameters the uniform nano-sized copper powders could be achieved at the optimal condition.

Keywords: Copper powder, ultrafine, polyol.

1. Introduction

Recently, copper powders have been used in wide variety of fields, for examples, paints to make a non-metal materials with metallic-like surface, coatings preventing wear and corrosion, catalysts as well as conductive materials in electronic appliances, especially in form of paste for using in the main component of printed circuit board, multi-layer ceramic capacitors and hybrid integrated circuits [1-3]. Nowadays, copper powders are increasingly brought in those mentioned works instead of noble metal such as Ag, Au and Pt due to rapid price increase of precious metals. Consequently, several researches have been substantially focused on improvement of controlling size and shape as well as oxidation resistance.

Many methods have been used for synthesizing metal powder such as electrolysis [4], atomization [5], pyrolysis [6], chemical reduction methods [7, 8]. Among chemical reduction processes, the reduction of copper salts by polyol process possesses the major advantage in controlling of powder morphology with uniform size and narrow size distribution and acquiring high-purity phase [9]. This process concerns with the reduction of metal salts by polyol liquid, such as ethylene glycol and glycerol, which act as .both reducing agent and solvent. For examples, Obraztsova *et al.* [10] produced the fine particles of ultra-dispersed copper powders in the range of 10-400 nm via a reduction of various copper salts by glycerol in the presence of PVP stabilizer. Blosi *et al.* [11] synthesized copper nanoparticles with a mean diameter of 46 nm using DEG as reducing agent and PVP as stabilizer.

In this research, fine copper powders with uniform distribution and controllable size ranging from nanometer to micrometer produced by polyol process have been achieved. The reaction was carried out in the mixture of alkaline (NaOH) and glycerol without using any stabilizer and dispersing agent additions. The experiments were examined under various NaOH concentration and reaction temperature. The advantages of this process are that it can be successfully operated by simple apparatus, low-cost production method and no need for any stabilizer. Moreover, it can be counted as the green technology due to the usage of non-toxic reducing agent [12]. The effects of concentration of NaOH, reaction temperature and reaction time on size and shape of obtained copper powders were also discussed.

2. Experimental Procedure

All chemical substances were AR grade and used without further purification. In a typical synthesis, copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, Carlo Erba) was dissolved in the solution of sodium hydroxide (NaOH, Mallinckrodt) and glycerol ($C_3H_8O_3$, Carlo Erba) with varying the molar ratio of NaOH:$Cu(NO_3)_2 \cdot 3H_2O$ in the range of 0:1 to 5:1 while giving the constant molar ratio of $Cu(NO_3)_2 \cdot 3H_2O$:glycerol at 0.02:1. This mixture was then heated up to reaction temperature in the range of 120 - 160 °C with constantly stirring at 1,000 rpm until the reduction reaction became completed. The copper particles were then separated by filtration and washed with absolute ethanol for several times.

The identification of copper powders was determined by X-ray diffraction (XRD, Rigaku SA-HFM3) by using CuKα radiation at the scan rate of 0.2°/min. The powder morphology was characterized by using scanning electron microscope (SEM, JEOL JSM-6400) and field emission scanning electron microscope (FESEM, JEOL JSM-7001F). The average particle size and size distribution were analyzed from SEM micrographs by image analysis method.

3. Results and Discussion

3.1. Mechanism of Copper Compound Reduction

When the solution of copper (II) nitrate in glycerol was poured into the mixture of NaOH and glycerol in the step of solution preparation prior to heating, color change of the solution can be visibly observed. Moreover, this depends upon the NaOH concentration as shown in Fig. 1. The pale blue color solution was observed in a condition with the absence of NaOH. At the molar ratio of NaOH:$Cu(NO_3)_2$ equal to 1:1, the solution color was changed to clear green color. After further alkali addition to molar ratio of 2:1, the opaque teal

(blueish green) suspension appeared. However, the solution color was then changed to clear navy blue color in which no precipitate was visually observed at the molar ratio of 3:1 to 5:1.
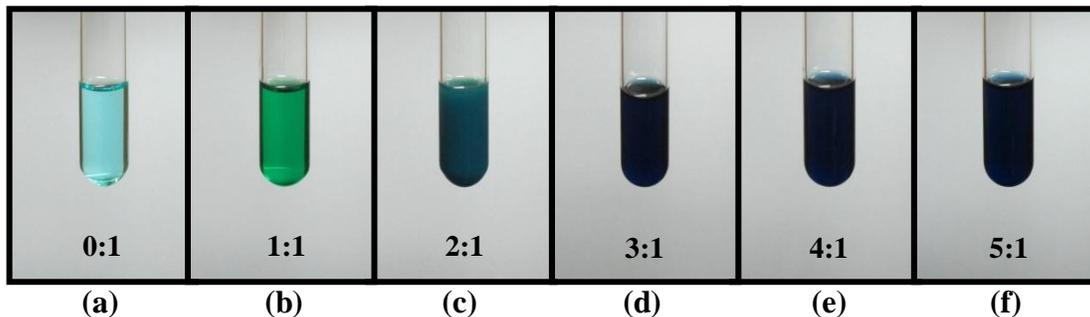

Fig. 1.   Color change of solution after mixing NaOH in various molar ratios of NaOH:Cu(NO$_3$)$_2$: (a) No NaOH addition, (b) 1:1, (c) 2:1, (d) 3:1, (e) 4:1, and (f) 5:1.

During the step of heating the solutions from room temperature to the given reaction temperature (120-160 °C), similar color change from an initial color to green, yellow, orange and henna (dark brown), respectively, occurred for all solutions in Fig. 1, as shown in Fig. 2 (a-d). This phenomenon has been also reported in several research works in which copper metal has been synthesized by means of reducing copper salts with polyol media [9, 13].
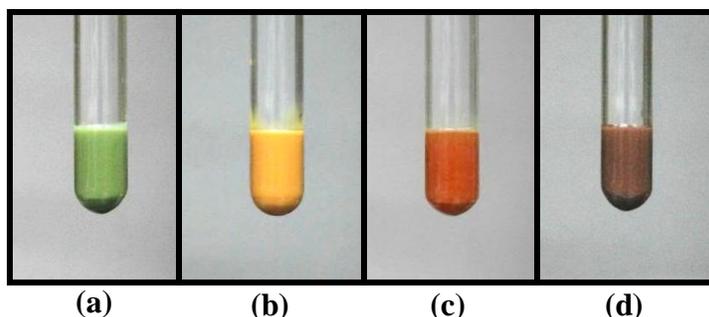

Fig. 2.   The change of suspension color appeared during the reaction between copper salt and polyol at the reaction temperature of 140 °C and molar ratio of NaOH:Cu(NO$_3$)$_2$ = 2:1 at different reaction period (a) 20, (b) 30, (c) 120, and (d) 240 minutes after heating the solution.

The XRD patterns in Fig. 3 showed the identification of powders collected from the suspensions at various time, shown in Fig. 2 (a-d). For example, the XRD spectra line (a) in Fig. 3 was characterized from green suspension in Fig. 2(a), and the XRD spectra line (b) in Fig. 3 was characterized from orange suspension in Fig. 2(b). From the XRD patterns (Fig. 3), the diffraction peaks inferred that, during the reaction progress, the cuprous oxide (Cu$_2$O) phase was regularly precipitated as an intermediate product which was evidenced by the XRD spectra in Fig. 3(a-c). This also meant that the copper ions were not completely reduced to copper metal until the color of solution reached henna. The powders collected from the henna color solution was confirmed by XRD patterns to be pure copper metal with face-centered cubic (FCC) structure without any characteristic peak of cuprous oxide as shown in Fig. 3(d). From XRD results, it can be explained that the mechanism of reducing Cu(NO$_3$)$_2$ with the solution of NaOH and glycerol initially

occurred by the reduction of Cu^{2+} ion in the solution to Cu^+ ion which precipitated out of the solution as Cu_2O particles, and then finally the reduction of cuprous oxide to copper metal powders.
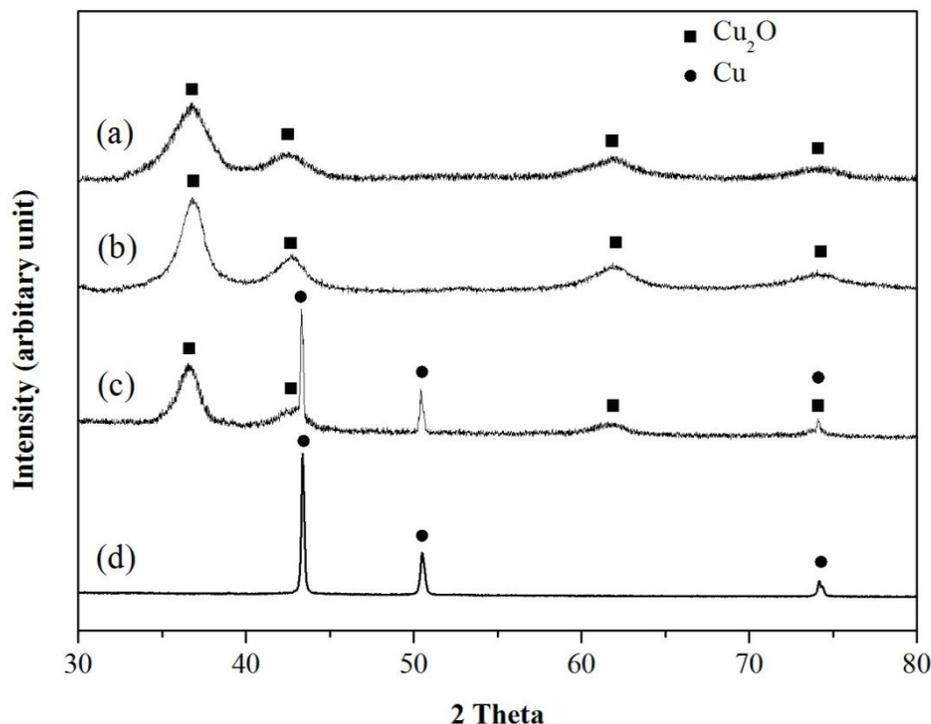

Fig. 3.   XRD spectra of powder samples collected during the reduction interval: (a) green (b) orange, (c) just before henna and (d) henna.

3.2. The Effect of NaOH Concentration

The NaOH concentration greatly influenced the kinetics of the reaction which sequentially affected to the morphology of the copper powders. For example, at reaction temperature of 140 °C, the reaction rate was vastly decreased as the $NaOH:Cu(NO_3)_2$ molar ratio decreased as shown in Table 1. Therefore, it is obvious that the higher the NaOH concentration added, the higher the rate of reaction increased. Several researchers pointed out that raising the pH value resulted in increasing the rate of reaction in polyol process [14, 15].

Table 1.   The effect of NaOH concentration on average particle size and complete reaction time at constant reaction temperature of 140 °C.

$NaOH:Cu(NO_3)_2$	Average particle size (μm)	Standard deviation (μm)	Complete reaction time (minutes)
0 : 1	n/a	n/a	more than 20 hours
1 : 1	n/a	n/a	more than 20 hours
2 : 1	1.30	0.22	240
3 : 1	0.32	0.06	27
4 : 1	0.16	0.03	19
5 : 1	0.10	0.02	17

Remark: n/a shows the results that cannot be analyzed through measuring from SEM photographs because the powders are aggregated and polydispersed.

Figure 4 showed the secondary electron images in SEM of the copper powders obtained from various NaOH concentrations at the reaction temperature of 140 °C. At low NaOH concentration of 0:1 and 1:1 (Fig. 4(a) and (b)), according to the incomplete reaction even though at the reaction time of 20 hours, copper and cuprous oxide powders were observed as non-uniform aggregated crystalline powders and oval powders, respectively. Due to non-uniform size distribution, the size of crystalline copper powders of molar ratio of 0:1 and 1:1 were difficult to measure but could be roughly estimated as 10 μm. The more uniform and equiaxed crystalline copper powders were obtained by using the higher molar ratio, i.e., the ratio 2:1 with average size of 1.30 μm and the ratio 5:1 with 0.1 μm, as tabulated in Table. 1. Moreover, it can be clearly seen that the average size and distribution of obtained copper powders decreased with increasing the amount of NaOH (Fig. 5).
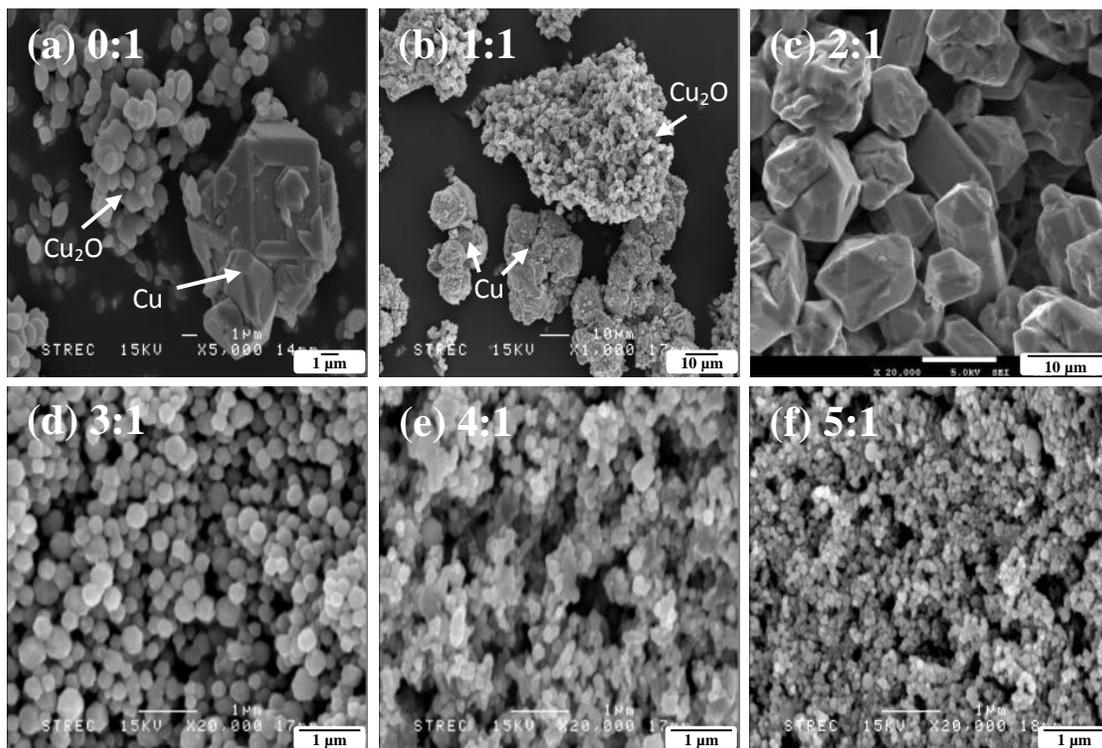

Fig. 4.   The morphology of the powders obtained from different molar ratio of NaOH:Cu(NO₃)₂ at the reaction temperature of 140 °C : (a) 0:1, (b) 1:1, (c) 2:1, (d) 3:1, (e) 4:1 and (f) 5:1.

This relationship between the NaOH concentration and the powders size could be proposed as the so-called nucleation and growth mechanism. At high rate of reduction reaction; i.e., high NaOH concentration, the copper nuclei could numerously formed during the short-time nucleation stage which eventually resulted in small powders at the end of the reaction. This may be because the increase of the pH value by the addition of NaOH results in increasing the different reduction potential (ΔE) which give rise to elevate the equilibrium constant (K_{eq}) [16] as shown in Eq. (1):

$$\ln K_{eq} = nF\Delta E / RT \qquad (1)$$

(where K_{eq} = equilibrium constant, n = number of electrons in a reaction equation, F = Faraday's constant, R = gas constant).

Therefore the driving force of the reaction was increased. The more spontaneous reaction hence occurred and consequently brought about to the generation of a large amount of nuclei.
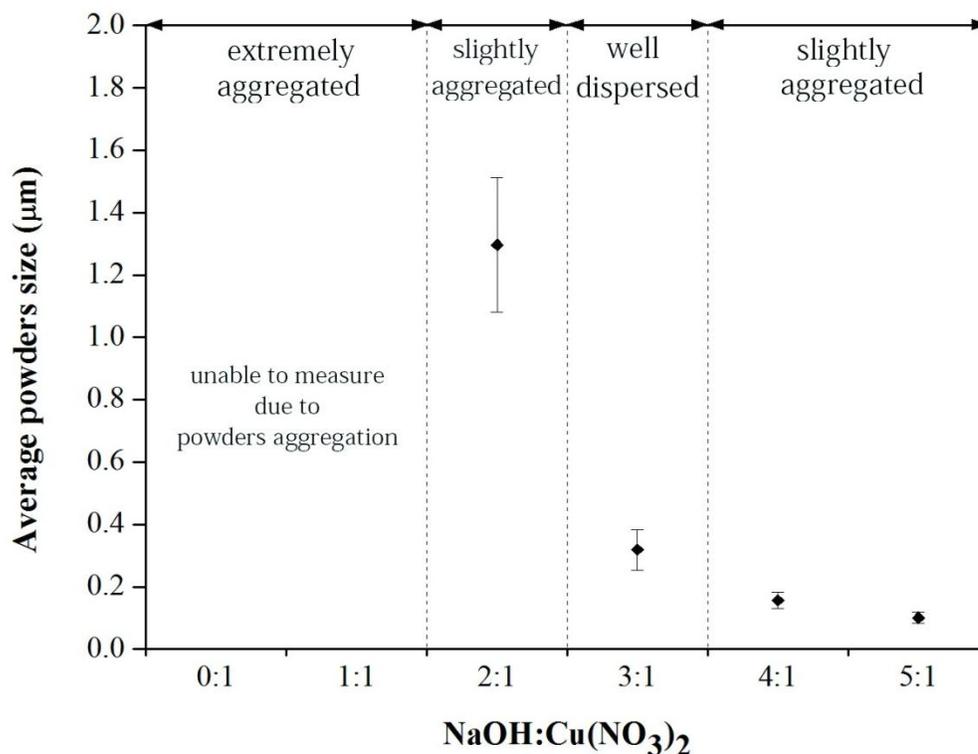

Fig. 5.   Average powder sizes as a function of the concentration of sodium hydroxide.

3.3. The Effect of Reaction Temperature

The reaction temperature was also a crucial parameter in particle synthesis by chemical reduction route. As seen from the Table 2, using the reduction temperature of 120, 140 and 160 °C at the constant molar ratio of NaOH:Cu(NO$_3$)$_2$ equal to 3:1, the reduction reactions were completed in 90, 27 and 15 minutes, respectively. An increase in the reaction temperature results in increasing the rate of reaction and consequently shortening the complete reaction time. In addition size of the obtained powders also decreased from 0.40 to 0.06 μm as the reaction temperature increased from 120 to 160 °C. The solubility limit of Cu$_2$O in the glycerol increased with higher reaction temperature. This gives rise to higher chemical potential (μ) as the driving force to reduce Cu$^+$ ion to Cu particles. However, when the molar ratio was increased to 5:1, the copper powders were decreased in size and became more aggregated.

Table 2.   The effect of reaction temperature on particle size and complete reaction time.

Reaction temperature (°C)	Average particle size value (μm)	Standard deviation (μm)	Complete reaction time (minutes)
120	0.40	0.06	90
140	0.32	0.06	27
160	0.06	0.01	15

(a) **(b)** **(c)**
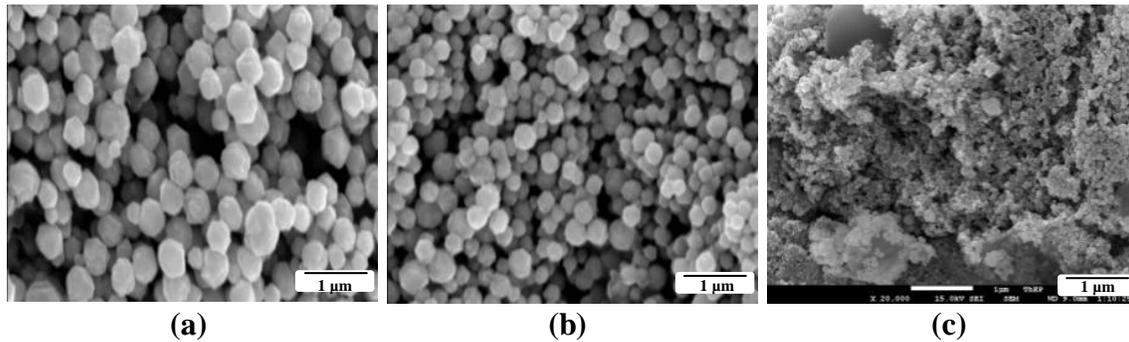
Fig. 6.   The morphology of the copper powders prepared using the constant molar ratio of NaOH:Cu(NO$_3$)$_2$ = 3:1 at various reaction temperatures (a) 120 °C, (b) 140 °C, and (c) 160 °C.

4. Conclusion

The ultrafine copper particles with controllable size can be effectively synthesized by simple polyol process. The size, size distribution, shape and complete reaction time of the copper powders were regulated by the concentration of NaOH and the reaction temperature. The size of the copper powders and the complete reaction time were both decreased as the NaOH concentration and reaction temperature were increased. The morphology of the copper powders depended upon the NaOH concentration; namely, the crystal-like powders were precipitated in the range of molar ratio from 0:1 to 2:1 while, at higher molar ratio of more than 3:1, the powders provided equiaxed shape. The powders synthesized at the molar ratio of 3:1 produced the suitable uniform size and well-dispersed powders. The aggregation of copper powders slightly occurred when the concentration of NaOH was increased to the molar ratio of 4:1 and 5:1.

Acknowledgement

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