# Comparative study on the preparation of conductive copper pastes with copper nanoparticles prepared by electron beam irradiation and chemical reduction

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## ARTICLE INFO

## ABSTRACT

Copper nanoparticles with narrow size distribution of 5–7 nm were synthesized by using electron beam irradiation. The copper nanoparticles were stable in ambient air for two months. TGA showed that the copper nanoparticles prepared by using electron beam irradiation have the higher wt% of pure copper metal compared with the one prepared by chemical reduction using hydrazine hydrate($N_2H_4 \cdot xH_2O$). The conductive copper paste with copper nanoparticles prepared by electron beam irradiation showed higher conductivity than the paste with copper nanoparticles prepared by chemical reduction with $N_2H_4$ due to small size, less amount of surfactants on the surface and higher stability against the oxidation in ambient condition. The highest conductivity of copper paste was determined as $170\ S\ cm^{-1}$ at 90 wt% of copper nanoparticles in the paste.

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## 1. Introduction

Copper nanoparticles have been widely applied in many fields such as conductive materials, catalyst has been paid more attention because of the low cost (Woo et al., 2009; Zonezawa et al., 2008; Sarkar et al., 2008). The conductive paste has important applications in electronic field such as printed circuits and circuit repairing instead of soldering connection. The problem is that copper nanoparticles are easily oxidized in ambient air. It would be significant to find a method to prepare copper nanoparticles that are stable against oxidation.

Among many methods to synthesize copper nanoparticles such as chemical reducing process, thermal decomposition, polyol process and $\gamma$-irradiation (Su et al., 2007; Kim et al., 2006; Park et al., 2007; Zhou et al., 2008), electron beam irradiation is paid more attention because of the possible mass production with low cost. In this study, we reported the synthesis of copper nanoparticles in ethylene glycol (EG) as the medium by using electron beam irradiation. With polyvinyl pyrrolidone as dispersing agent, the average size of 5–7 nm of copper nanoparticles was obtained. After synthesis, the copper nanoparticles showed the stability under ambient air for two months. The nanoparticles were used to prepare conductive pastes and compared with the pastes of the copper nanoparticles prepared by chemical reduction as we reported in the previous work. The higher conductivity of the copper paste and stability of copper nanoparticles prepared by electron beam irradiation show the possibility to solve the problem of copper nanoparticles for the mass production and narrow size distribution of the particles.

## 2. Materials and methods

### 2.1. Materials

Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, 99.9%), copper chloride ($CuCl_2$, 97%), cetyltrimethylammonium bromide (CTAB, 95%), and hydrazine hydrate ($N_2H_4 \cdot xH_2O$, $x \sim 1.5$, 50–60%, 1.029 g/ml at 25 °C) were purchased from Aldrich. Ammonia solution (28–30%, 0.89 g/ml at 25 °C) was brought from Jin Chemical Pharmaceutical Co., Ltd, Korea. Ethylene glycol (EG) and polyvinyl pyrrolidone (PVP, Mw=10,000) were purchased from JUNSEI. Isopropyl alcohol (IPA, 99.7%, 0.784–0.786 g/ml) was obtained from Duksan Pure Chem. Co. Ltd. All chemicals were used without further purification. For the paste preparation, boron oxide ($B_2O_3$, 99.98%), $\alpha$-terpineol (tech. 90%), ethylcellulose and zinc oxide (ZnO, 99.999%) were obtained from Aldrich. Sodium silicate ($Na_2SiO_3$) was purchased from Samchung. All these materials were for making glass frit.

## 2.2. Synthesis of copper nanoparticles by electron beam irradiation

The copper nanoparticles were synthesized by using electron beam irradiation with different absorbed doses. In this process, the aqueous solution of 3 g PVP ($3 \times 10^{-4}$ mol) was dispersed in 100 ml ethylene glycol. Then, 5 g of $CuSO_4 \cdot 5H_2O$ (0.02 mol) and 15 ml isopropyl alcohol were added into the PVP solution. After stirring for 30 min, the solution was bubbled with nitrogen gas for 30 min to remove oxygen. Then the solution was irradiated with electron beam with various absorbed doses. Copper nanoparticles were collected by centrifugation and washed with ethanol 3 times. Then the sample was dried in vacuum for 3 h to get the final product. In this study, we used the electron beam accelerator from Korea Atomic Energy Research Institute (KAERI) for irradiation. The accelerator provided electrons with energy of 1 MeV and current of 1 mA for the sample irradiation and various absorbed doses in the atmosphere.

## 2.3. Synthesis of copper nanoparticles by reducing agent

In this work, two equal volume solutions of reactants were prepared: solution A was prepared by adding copper (II) chloride into 25 ml aqueous solution of 0.1 M CTAB and $4 \times 10^{-4}$ M PVP to form a 0.04 M copper (II) solution. This solution was bubbled with argon gas to remove oxygen. Then, 0.5 ml of ammonia solution was added to solution A to adjust pH up to 10. In solution B, 25 ml aqueous solution of CTAB and PVP with the same concentrations as solution A was bubbled with argon gas in a capping reactor to remove oxygen. Then, 1 ml of hydrazine hydrate was injected to form a 0.64 M solution of hydrazine. For the chemical reduction reaction, solution B was heated to 60 °C and then solution A was injected dropwise and stirred vigorously for 6 h. Reaction temperature was maintained at 60 °C during reaction time. Copper nanoparticles were separated by centrifugation and washed 3 times with water and ethanol alternately to remove reactants and capping agents, then dried in vacuum at room temperature for 3 h to yield the final product.

## 2.4. Preparation of copper paste

For the preparation of copper paste the method of Tani et al. (1994) was followed. Copper nanoparticles were mixed with glass frit and organic vehicle with different wt% of copper. The amount of glass frit and vehicle was fixed for all of the preparations. Glass frit contains 50 wt% of $B_2O_3$, 30 wt% of ZnO and 20 wt% of sodium silicate. After the grinding and sieving process (180 μm mesh), the copper pastes were screen printed on alumina substrates ($1 \times 1$ cm$^2$). Annealing process was done under 500 °C for 1 h with fluxing of $N_2/H_2$ (97/3 v/v).

## 2.5. Characterizations and measurements

Copper nanoparticles were characterized by using X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). Resistivity of copper paste was measured using the four point probe method and cross-sectional image of paste film was checked by scanning electron microscopy (SEM) to determine the thickness. The XRD patterns were recorded with a PHILIPS (Netherland) X'Pert-MPD diffractometer using Cu Kα irradiation at 40 kV and 150 mA at scanning rate of 0.02° per step in the range of $10° < 2\theta < 80°$. The morphologies of copper nanoparticles were investigated by using transmission electron microscopy of Philips Technai F20. Thermogravimetric analysis was carried out on a TGA 2050 CE analyzer (TA Instruments). SEM was performed on the field emission scanning electron microscope (FE-SEM) Hitachi S-4300. Resistance of paste
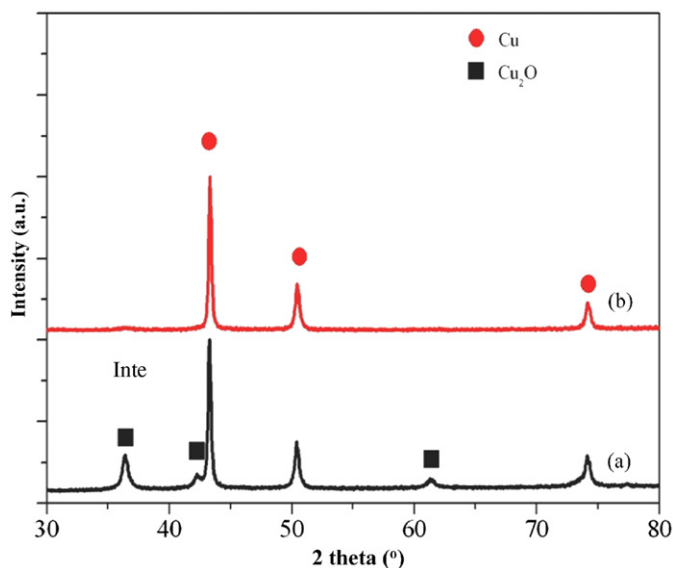


**Fig. 1.** XRD patterns of copper nanoparticles prepared by electron beam irradiation with absorbed doses of (a) 100 and (b) 300 kGy.
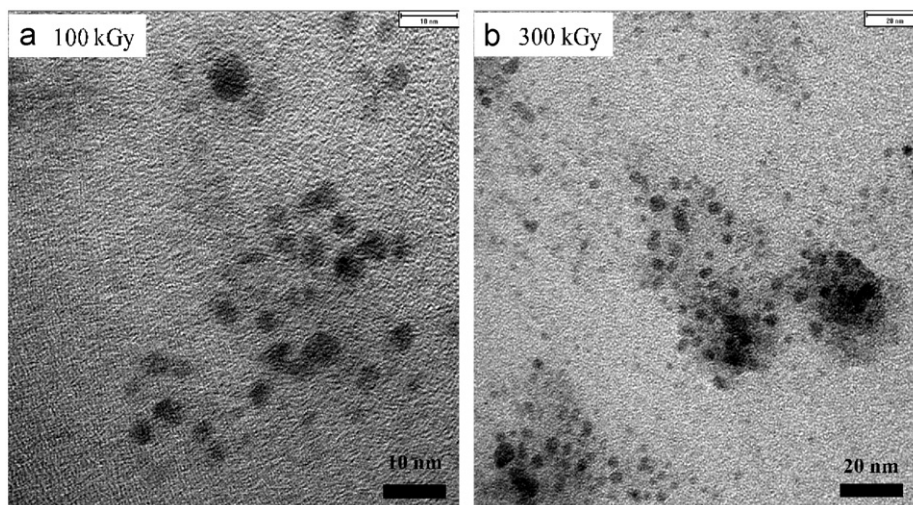


**Fig. 2.** TEM images of copper nanoparticles prepared by electron beam irradiation with absorbed doses of (a) 100 and (b) 300 kGy.

was measured on a 2420 3A Source Meter with four point probes. The conductivity of paste was calculated with the following equation (Schuetze et al., 2004):

$$C = \frac{ln2}{2\pi tR}$$

where, $C$ is the specific conductivity ($S\,cm^{-1}$), $t$ is the thickness of the paste (cm) and $R$ is the resistance of the paste ($\Omega$).

## 3. Results and discussion

### 3.1. Characterizations of copper nanoparticles

Fig. 1 shows the XRD patterns of copper samples prepared by using electron beam irradiation with different doses. The diffraction peaks at $2\theta = 43.2°$, $50.2°$ and $73.8°$ correspond to the (1 1 1), (2 0 0) and (2 2 0) planes of Cu nanoparticle crystal, respectively. With the dose of 100 kGy, the peaks at $\theta = 36.4°$, $42.3°$ and $52.4°$ in XRD pattern indicate the formation of $Cu_2O$ in the sample. The radiolysis of water generates several intermediate products. Among these active particles, the solvated electron ($e_{sol}^-$) and hydrogen atoms are strong reductive species (Dey, 2005). Then, this electron reduces copper ion to copper as shown in:

$$Cu^{2+} \overset{e_{sol}^-}{\rightarrow} Cu^+ \overset{e_{sol}^-}{\rightarrow} Cu$$
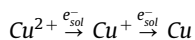
When the dose is increased from 100 to 300 kGy, there is no peak of $Cu_2O$ crystal in the XRD pattern. This means that $Cu^{2+}$ ion is reduced completely. Radicals such as hydrogen atom ($H^\bullet$) and hydroxyl radical ($^\bullet OH$) are formed during the irradiation. It is stated that copper nanoparticles can be oxidized by these radicals. The hydrogen atom is a strong reducing radical. To solve this problem, IPA is used as a radical scavenger (Ramnani et al., 2007). Fig. 2 shows TEM images of the copper nanoparticles prepared by electron beam irradiation with different absorbed doses. TEM images displayed the spherical shape of copper nanoparticles. The size of obtained copper nanoparticles was in the range of 5–7 nm. In this process, PVP acts as the dispersing agent and capping agent to protect copper nanoparticles from oxidation. Zhou et al. (2008) also synthesized copper nanoparticles using electron beam irradiation with polyvinyl alcohol as surfactant. The reaction medium was water. In their case, the optimized

electron beam absorbed dose to completely reduce copper ion to copper was 350 kGy (Zhou et al., 2008). Fig. 3 shows the XRD patterns of prepared copper nanoparticles with different delay times. The copper oxide peaks did not appear in XRD patterns. This result revealed that the copper nanoparticles prepared by using electron beam irradiation with absorbed dose of 300 kGy were not oxidized easily. Fig. 4 shows the TEM image of copper nanoparticles synthesized by chemical reduction with hydrazine hydrate. The average particle size is below 100 nm. Although the optimized surfactant proportion used in the reducing process is higher than the surfactant proportion used in the electron beam irradiation process, the size of copper nanoparticles prepared by chemical reduction is significantly bigger than the size of copper nanoparticles synthesized by electron beam irradiation. This point is very important in paste preparation because small size particles will increase the dispersity of copper nanoparticles in the glass frit. This results in the better conductivity of paste
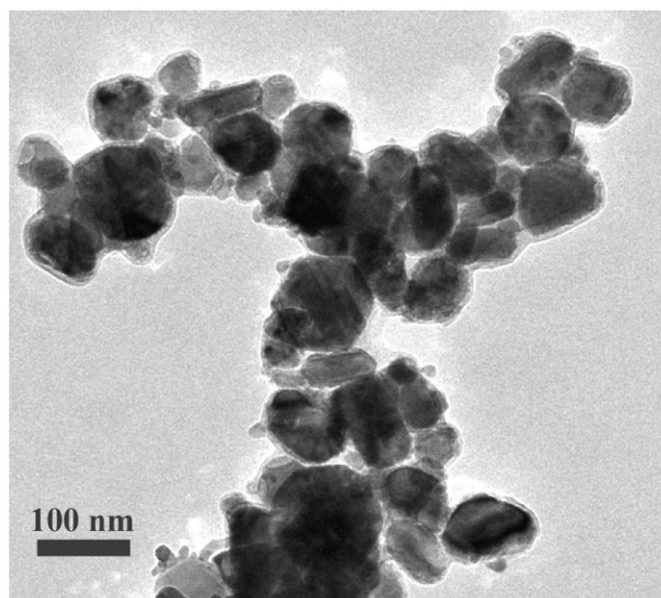


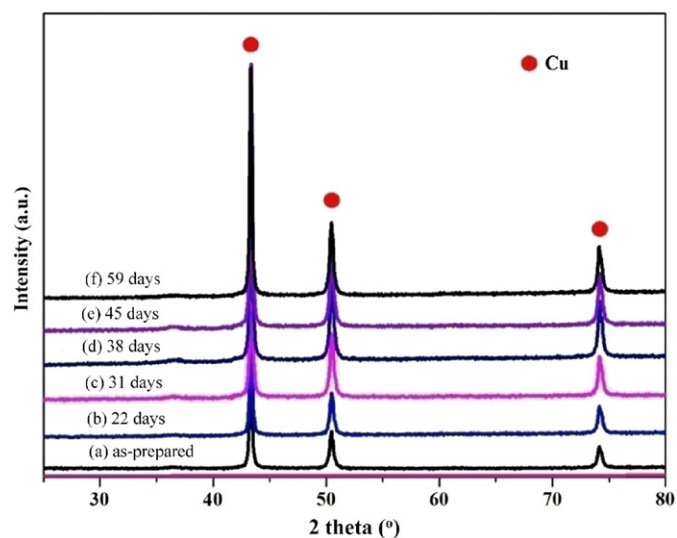**Fig. 4.** TEM image of copper nanoparticles prepared by chemical reduction.



**Fig. 3.** XRD patterns of copper nanoparticles prepared by electron beam irradiation at 300 kGy under exposure time in ambient air.
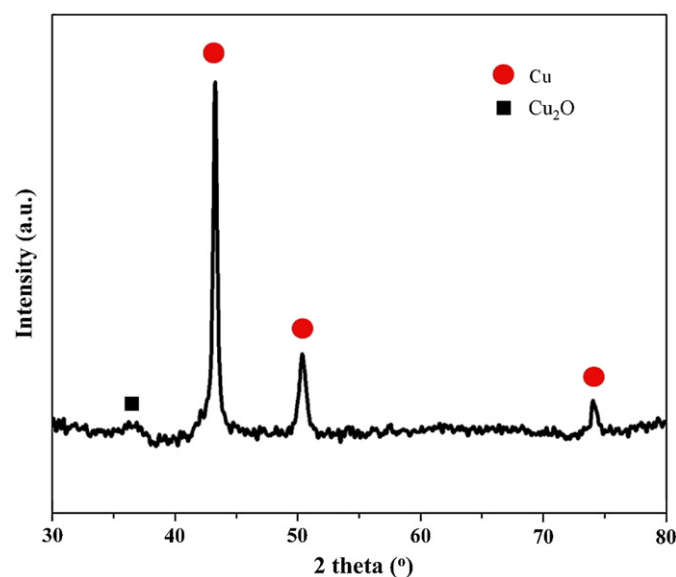


**Fig. 5.** XRD pattern of copper nanoparticles prepared by chemical reduction.

(Zhao et al., 2007). XRD pattern in Fig. 5 shows the high crystallinity of copper nanoparticles with trace amount of $Cu_2O$. The presence of $Cu_2O$ also reduces conductivity of copper paste.
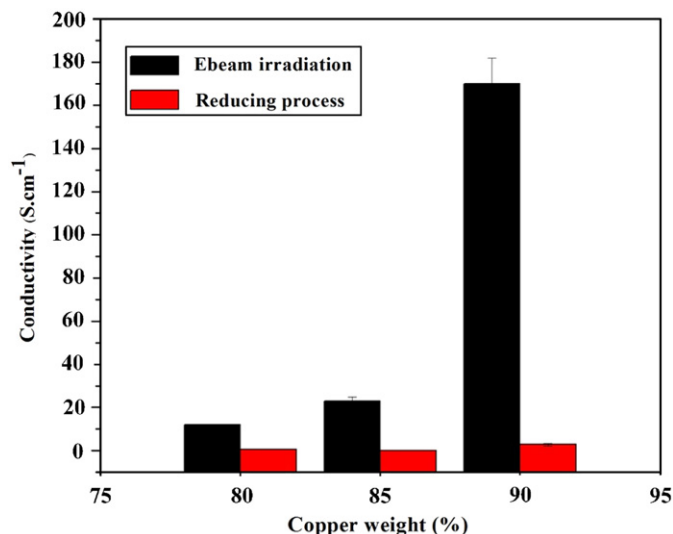


**Fig. 6.** Relationship between conductivity of copper paste and wt% of copper nanoparticles. The samples were calcinated at 500 °C in $N_2/H_2$ flux (97:3 v/v).
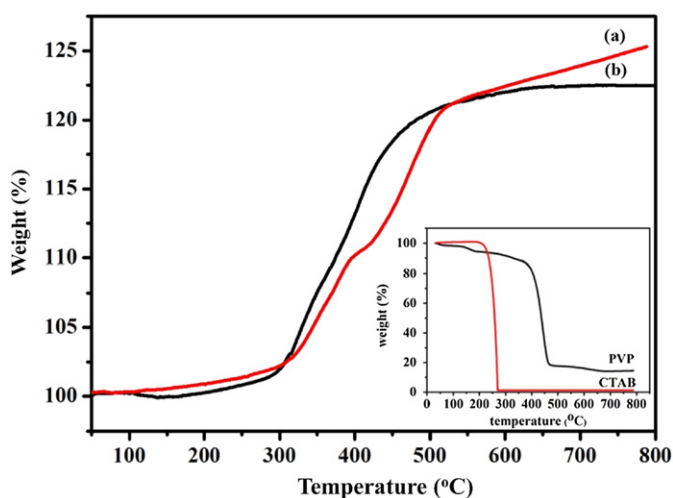


**Fig. 7.** TGA of copper nanoparticles synthesized by (a) electron beam irradiation and (b) chemical reduction in the presence of oxygen. The inset picture is the TGA of PVP and CTAB under $N_2$ flux. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### 3.2. Preparation of conductive pastes

In this process, the glass frit was used to bind the copper nanoparticles with alumina substrate. Without glass frit, the copper nanoparticles were easily removed from the alumina substrate. α-Terpineol acted as temporary binder and was removed during the calcination. The copper pastes were calcinated at 500 °C and the surfactants could be removed from the pastes and increased the conductivity (Wang et al., 2009). Fig. 6 shows the relationship between conductivity of the paste and wt% of copper nanoparticles. The highest conductivity of the paste was obtained at 90 wt% of copper nanoparticles. Then the conductivity decreased when the content of glass frit increased. The copper paste with copper nanoparticles prepared by electron beam irradiation shows higher conductivity than the one obtained from chemical reduction. As we can see in Fig. 7, TGA of copper nanoparticles shows the oxidation during heat treatment in the presence of oxygen. The increase in sample wt% corresponding to the going-up curve is due to the reaction of copper nanoparticles with oxygen as shown in the following equation:

$$Cu \overset{+O_2}{\rightarrow} Cu_2O \overset{+O_2}{\rightarrow} CuO$$
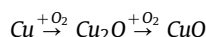
The sample wt% of copper nanoparticles prepared by chemical reduction (black curve) becomes constant at 125 wt% at 600 °C. The copper nanoparticles are totally oxidized. While the sample wt% of copper nanoparticles prepared by electron beam irradiation (red curve) increases above 125 wt% at 800 °C. In TGA measurement, we maintained equal weight of copper samples to make comparison. From this result, we can conclude that the proportion of surfactants in the copper sample prepared by chemical reduction is higher than that in the copper sample prepared by electron beam irradiation. This means that the copper samples prepared by electron beam irradiation have a higher wt% of pure copper metal. The inset picture shows the TGA of pure PVP and CTAB. As shown in the inset, CTAB decomposed at 270 °C while 12% of the initial weight of the PVP sample remained even at 469 °C. As we can see in Fig. 8, after calcinations, there are more residues of surfactants in the copper paste with copper nanoparticles prepared by chemical reduction (Fig. 8b) than those with electron beam irradiation (Fig. 8a). These residues will reduce the connections between copper particles. This results in the lower conductivity (Wang et al., 2009).

### 4. Conclusion

In this work, we reported the synthesis of copper nanoparticles using electron beam irradiation. The prepared copper nanoparticles have narrow size distribution and small diameter in the range of 5–7 nm. The copper nanoparticles prepared by electron beam irradiation have shown stability against oxidation when exposed
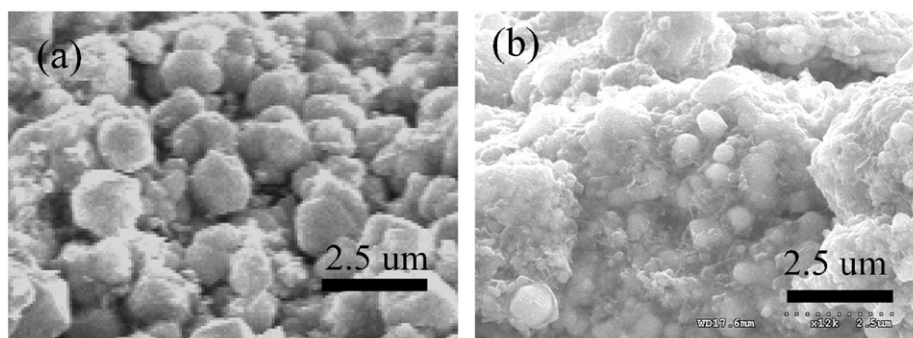


**Fig. 8.** SEM images of cross-section of copper pastes with 90 wt% copper nanoparticles prepared by (a) electron beam irradiation and (b) chemical reduction. The samples were calcinated at 500 °C in $N_2/H_2$ flux (97:3 v/v).

to ambient air for two months. The size of copper nanoparticles prepared by electron beam irradiation is smaller than the size of copper nanoparticles prepared by chemical reduction. At the same condition, the higher conductivity of copper paste with copper nanoparticles prepared by electron beam irradiation is due to small size particles, less amount of surfactants on the surface and higher stability against oxidation in ambient condition.

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