

# Preparation of Sub-Micrometer Cu Particles by Green Hydrothermal Synthesis under Air

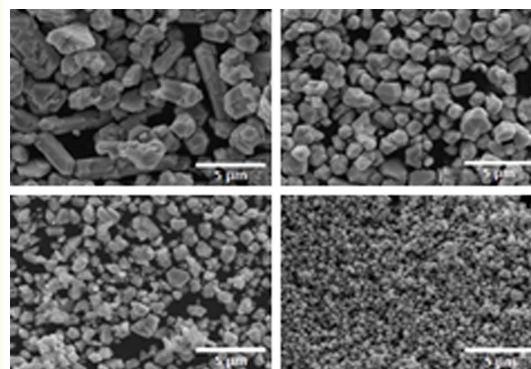
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Cu particles ranging in size from several micrometers to less than a micrometer were synthesized using an environmentally friendly hydrothermal process involving L-ascorbic acid as a reducing agent and gelatin. The size and synthetic yield of Cu particles was investigated at different gelatin additions and synthesis temperatures. With increasing gelatin content, the particle size decreased from 2.4  $\mu\text{m}$  to 0.4  $\mu\text{m}$  and the yield increased from 79.4% to 90.4%. With increasing synthesis temperature, the particle size changed significantly and the yield increased from 42.4% to 91.2%. The Cu particles synthesized at 85°C for 50 min with 12 g of gelatin showed the lowest average particle size of 0.4  $\mu\text{m}$  and a yield of 90.4%. The FR-IR spectra indicated that coordinating bonds between the N in the gelatin and the Cu were formed, and a sequential reaction mechanism was proposed. It was determined that the gelatin addition not only prevents the Cu particles from agglomerating but also enhances the reduction of Cu ions.

**Keywords:** Cu particle, sub-micrometer, green synthesis, gelatin, particle size, synthesis yield



## 1. INTRODUCTION

Over the years, Cu has been extensively studied as a possible alternative ingredient in various conductive pastes because of its excellent electrical conductivity, low electrochemical migration, and low cost.<sup>[1-5]</sup> However, pure Cu particles gradually oxidize in air, and the resulting oxide coatings increase the sintering temperature and degrade the conductivity.<sup>[6-8]</sup> To solve these critical problems, Ag has been proposed recently as a passivation material to be coated on the Cu particle surface, and a number of studies on the fabrication of Ag-coated Cu (Cu@Ag) particles have been carried out.<sup>[8-10]</sup>

Given the trend toward increasingly smaller electrodes, the line width of conductive paste regions in printed bezel electrodes has decreased to values below 50  $\mu\text{m}$ , and the size of filler particles such as Cu@Ag particles has been reduced to several micrometers.<sup>[11]</sup> Moreover, if the printed patterns

of conductive paste in the bezel electrodes are required to become even narrower, the particle size must be reduced to approximately one micrometer or less.

For preparation of the tiny Cu@Ag particles, single-micrometer or sub-micrometer Cu core particles should be preferentially synthesized. Until now, wet-chemical processes for the synthesis of small metal particles have been used, and the processes utilized various polymers as protective agents in order to acquire particles with little agglomeration.<sup>[12-14]</sup> Gelatin, obtained by the thermal or hydrolytic treatment of collagen, is a green capping agent that can prevent the oxidation and agglomeration of particles.<sup>[15]</sup> Zhang *et al.* reported that gelatin not only stabilizes the metal surface but also reduces the metal ions *via* oxidation of amines in nitriles.<sup>[16]</sup> In this study, we report a modified, simple hydrothermal process for synthesizing single-micrometer or sub-micrometer Cu particles as seeds for fabricating Cu@Ag particles. The process yield and powder size distribution changed according to the amount of gelatin used and the reaction temperature. The most advantageous aspect of the process is that it is eco-friendly process; it uses only an

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L-ascorbic acid reducing agent and distilled water reaction medium in addition to gelatin.

## 2. EXPERIMENTAL PROCEDURE

Cu(II) nitrate trihydrate [ $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , ~99%, Acros Organics] was used as the precursor agent for synthesizing the Cu particles, and gelatin (Duksan Pure Chemicals Co., Ltd.) and L-ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ , reagent grade, Sigma-Aldrich Co.) were used as a capping agent and reducing agent, respectively. Distilled water was used as the solvent during the reduction reaction. All chemicals were used without further processing or purification.

The synthesis of the Cu particles proceeds as follows: An initial aqueous solution was prepared by dissolving different amounts of gelatin in 100 mL of distilled water under magnetic stirring for 10 min, and 0.01 M of Cu(II) nitrate trihydrate was added to this solution. After 10 min, 0.11 M of L-ascorbic acid was added to the aqueous solution, which was stirred for 10 additional min. Finally, the mixed solution was heated to different reaction temperatures under continuous stirring for 50 min in a mantle and cooled for 40 min to room temperature. All aforementioned processes were performed under air. The detailed procedure is represented schematically in Fig. 1.

The particles dispersed in the solution were washed three times using DI water and centrifugation at 7000 rpm for 15 min to remove residual species, and the DI water in the final centrifugation step was replaced with methanol. The particles suspended in methanol were dried in a low-vacuum chamber at room temperature. The size and morphology of the synthesized particles were analyzed using a scanning electron microscope (SEM, VEGA 3 LMU, TESCAN Ltd.). The size distribution of the synthesized particles was determined from the SEM images. The composition of the particles was confirmed using x-ray diffraction (XRD, X'pert PRO-MPD, PANalytical). The yield of the Cu particle synthesis was calculated by dividing the weight of the obtained Cu particles by the weight of Cu in the Cu

precursor. Furthermore, the gelatin-capped Cu particles were analyzed using Fourier transform infrared (FT-IR) spectroscopy (Vertex 80 v, Bruker Optics Co.) to identify any coordination between nitrogen atoms in the amine groups of the gelatin and the Cu particles.

## 3. RESULTS AND DISCUSSION

Figures 2 and 3 show the SEM images and measured sizes, respectively, of the particles synthesized at 85°C for 50 min with different amounts of gelatin. For gelatin additions ranging from 0.5 g to 12 g, the average particle size continuously decreased from 2.4 to 0.4  $\mu\text{m}$ , and the size distribution narrowed with increasing gelatin content. Figure 2(g) shows the particles synthesized with 12 g of gelatin, which were well-dispersed polygonal particles with an average size of 0.4  $\mu\text{m}$ . Considering the reducing capabilities of gelatin,<sup>[16]</sup> these data suggested that an increase in the gelatin content promoted nucleation, resulting in the formation of more fine particles. It was also expected that the increase in solution viscosity with increasing gelatin content decreased the collision frequency between the as-synthesized particles, resulting in reduced agglomeration. When 15 g of gelatin was added, however, the particle size increased to 0.7  $\mu\text{m}$ , and irregularities in size and aggregation of the obtained particles also increased. This result indicated that too much gelatin is unsuitable for forming fine, non-aggregated particles. Too many metal particles formed on a cross-linked gelatin molecule structure might lead to coarsening during growth of the particles. (The as-synthesized structure will be discussed in the last part of this work.) Consequently, it was determined that a 12 g gelatin addition was optimal.

Figure 4 shows SEM images of the particles synthesized with 12 g of gelatin at different temperatures. The average size of synthesized particles was 1  $\mu\text{m}$  at 75°C, 0.4  $\mu\text{m}$  at 85°C, and 0.8  $\mu\text{m}$  at 95°C; this means that even a slight temperature change had a strong influence on the final particle size. The reduction of copper ions is slow at low temperature, and the number of nuclei formed during the

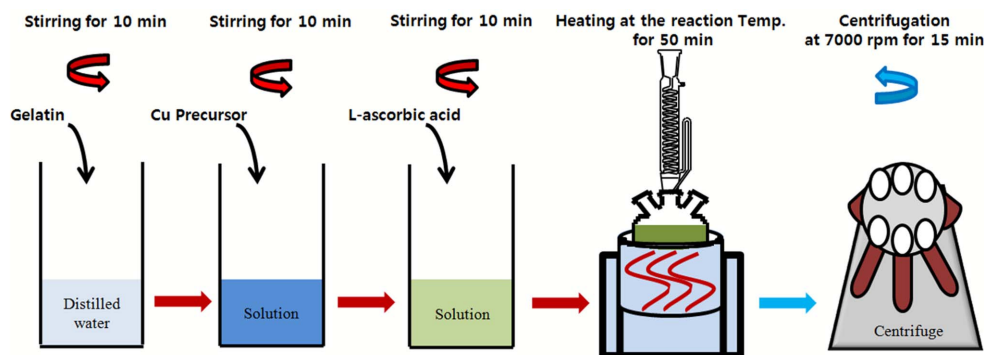
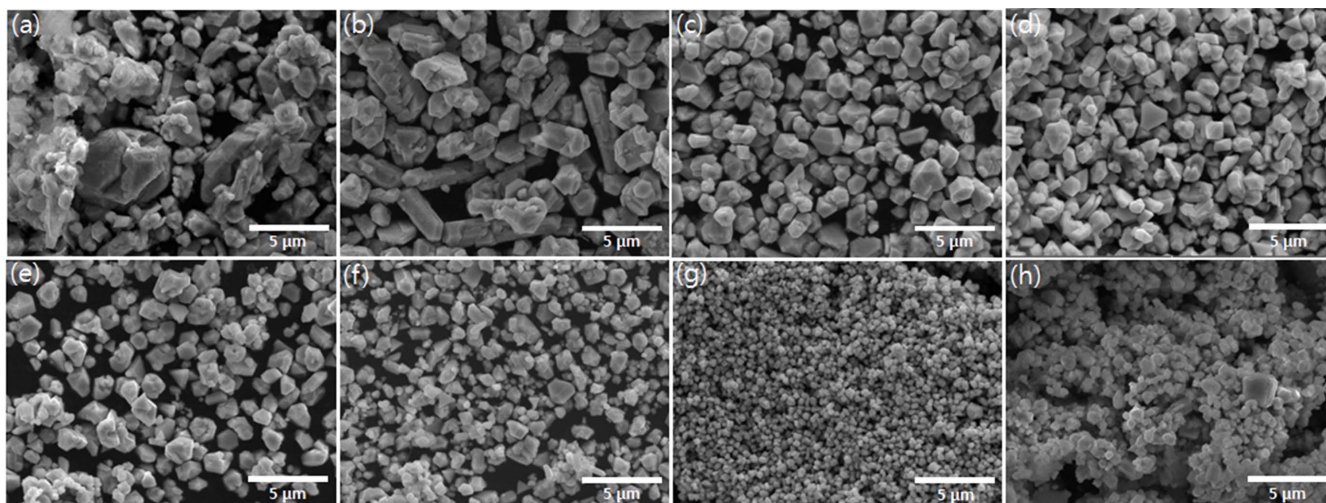
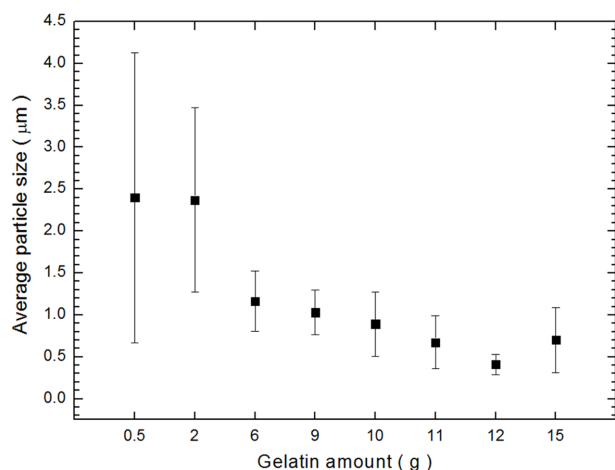


Fig. 1. Procedure for synthesizing Cu powders with particle sizes  $\leq 1$   $\mu\text{m}$ .



**Fig. 2.** SEM images of the Cu powders synthesized at 85°C for 50 min with different gelatin additions of: (a) 0.5, (b) 2, (c) 6, (d) 9, (e) 10, (f) 11, (g) 12, and (h) 15 g.



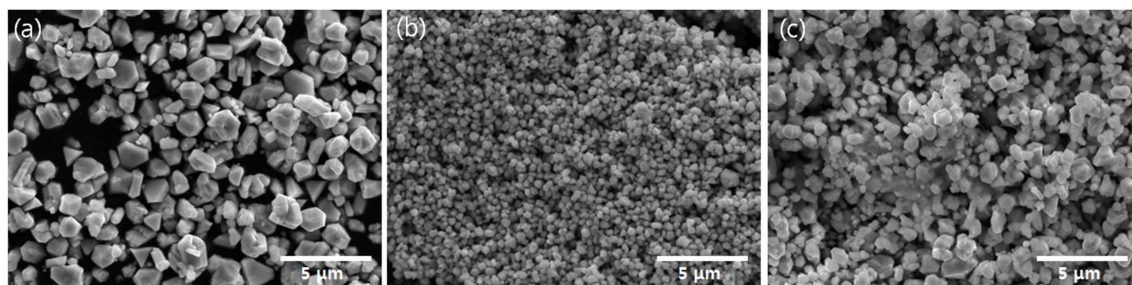
**Fig. 3.** Sizes of the Cu particles synthesized at 85°C for 50 min with different gelatin additions.

first nucleation step decreased accordingly. This principle leads to the formation of large particles<sup>[17]</sup> and large deviations in the size of the particles. Therefore, the average size and size deviation of particles synthesized at 75°C were larger than those at 85°C and 95°C. However, the sizes of the

particles synthesized at 95°C were larger than those synthesized at 85°C. This is because the dense formation of many metal particles on a cross-linked gelatin molecule structure by the enhanced reduction reaction, which is identical to the reason for the size increase in the particles synthesized with 15 g gelatin, shown in Figs. 2 and 3. Hence, the structure of aggregated, irregular particles shown in Fig. 4(c) was similar to the structure observed in Fig. 2(h).

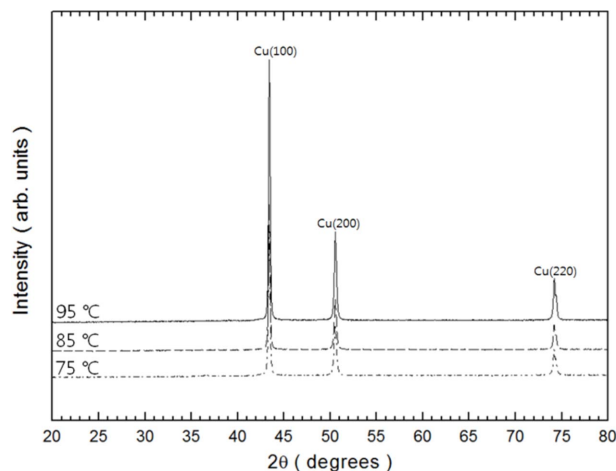
In order to identify the phases in the synthesized particles, the samples synthesized with 12 g of gelatin at different temperatures were analyzed using XRD. The (100), (200), and (220) lattice planes of Cu were detected in all samples, as shown in Fig. 5; this suggested that all synthesized particles were a phase-pure Cu.

The Cu particle yields for different gelatin additions and synthesis temperatures are given in Fig. 6. The synthesis yield increased with an increase in the amount of gelatin at all temperatures. When the Cu was synthesized at 85°C, the yields with respect to 0.5 and 12 g of gelatin were 79.4% and 90.4%, respectively. This yield was maintained with a slight increase at 95°C. Hence, it appeared that the yield saturated above 85°C. The yield at 75°C was significantly lower. For example, the yield at 75°C was just 42.4%, in spite of the

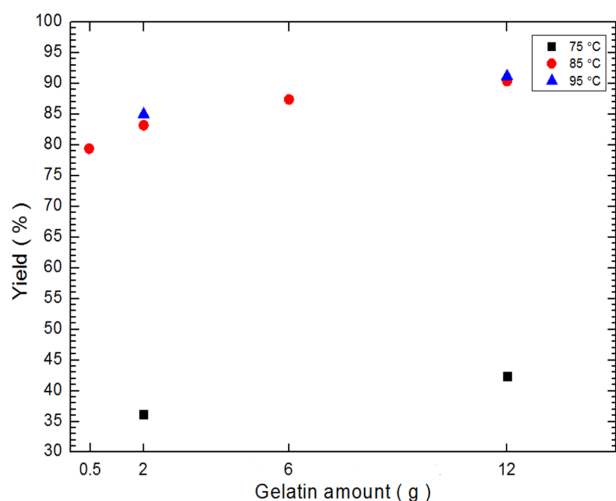


**Fig. 4.** SEM images of the Cu particles synthesized with 12 g of gelatin over 50 min at different temperatures: (a) 75, (b) 85, and (c) 95°C.





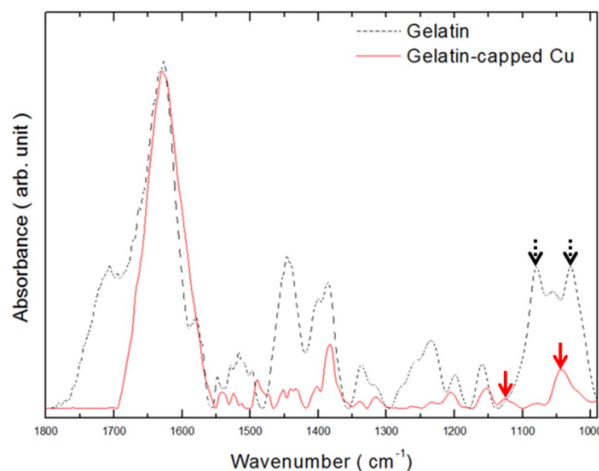
**Fig. 5.** Results of the XRD results of Cu powders synthesized with 12 g of gelatin for 50 min at different temperatures.



**Fig. 6.** Yields of Cu particles synthesized with different amounts of gelatin and at temperatures for 50 min.

gelatin addition of 12 g. The exceedingly low yield at 75 °C was attributed to weakening of the reduction reaction by the temperature decrease.<sup>[18]</sup>

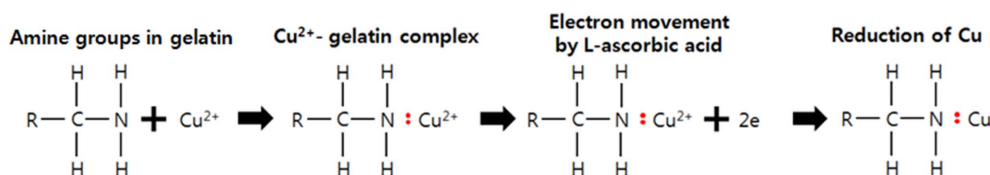
Figure 7 shows the FT-IR spectra of pure gelatin and gelatin-capped Cu particles. In the spectrum of pure gelatin, C-N absorption peaks at 1030 and 1080  $\text{cm}^{-1}$  were observed, whereas these peaks were red-shifted to 1040 and 1126  $\text{cm}^{-1}$  in the gelatin-capped Cu particles. This change in the spectra means that coordination bonding between N in the gelatin



**Fig. 7.** FT-IR spectra of pure gelatin and of Cu particles synthesized with 12 g gelatin at 85 °C for 50 min.

and Cu was transformed.<sup>[19]</sup> Zhang *et al.* reported that the donated lone pairs of nitrogen atoms in the polar groups of a polyvinyl pyrrolidone unit may occupy two *sp* orbitals of the Ag ion to form a complex compound.<sup>[20]</sup> Therefore, it was inferred that the coordinating bonds between N and Cu were formed in this case for a similar reason. Since the ligand of C-N in the PVP complex contributes electronic density to the *sp* orbital of metal ions, the metal ions in the complex may obtain electrons more easily, which promotes the reduction of metal ions.

Schematic illustrations of the reaction mechanism between Cu ions and N atoms in the gelatin, including the coordination bonding, are presented in Fig. 8. Gelatin molecules are initially dispersed in solvent, and then Cu ions combine with nitrogen atoms in the amine groups, forming  $\text{Cu}^{2+}$ -gelatin complexes. Next, electrons provided by the L-ascorbic acid reduce the Cu ions in the complexes into Cu atoms during heating. At a magnified scale, the structure that the metal nuclei form on the cross-linked gelatin molecule can be obtained. It is anticipated that this sequential reaction pathway decreases the Gibbs free energy difference for Cu-ion reduction in comparison to the direct reduction of Cu ions, resulting in easier generation of Cu metal. Hence, the increase in yield with increasing gelatin content shown in Fig. 6 can be considered indirect evidence for the effective reduction of Cu ions by this sequential reaction. Therefore, the gelatin in our system not only prevents Cu particles from



**Fig. 8.** Schematic illustration of the synthesis procedure of Cu particles using gelatin and L-ascorbic acid.

the agglomerating but also contributes to the facile reduction of Cu ions.

#### 4. CONCLUSIONS

Cu particles were synthesized using a modified hydrothermal process using L-ascorbic acid as a reducing agent with different amounts of gelatin addition. With increasing gelatin content, the particle size decreased from 2.4  $\mu\text{m}$  to 0.4  $\mu\text{m}$ , and the yield of Cu particles increased from 79.4% to 90.4%. The synthesis temperature was also an important parameter; the yield increased from 42.4% to 91.2% when the synthesis temperature was increased from 75°C to 95°C at the optimal gelatin content of 12 g. A saturation point in the yield was observed at 85°C. Fine Cu particles of 0.4  $\mu\text{m}$  were formed during synthesis at 85°C for 50 min, and the synthesis yield was 90.4%. The sub-micrometer size (0.9  $\mu\text{m}$ ) of Cu particles was maintained up to additions of 10 g of gelatin. The FR-IR spectra indicated that coordinating bonds between N and Cu were formed, and a sequential reaction mechanism for the reduction of Cu ions was proposed. It was determined that gelatin not only prevents Cu particles from the agglomerating but also contributes to the easy reduction of Cu ions.

#### ACKNOWLEDGMENT

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