Editor's Choice

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One-pot Preparation of Antioxidized Copper Fine Particles with a Unique Structure by Chemical Reduction at Room Temperature

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A one-pot and single-step reduction process for producing antioxidized copper fine particles will be described. This process can be carried out at room temperature, and size range is quite wide, from 190 nm to 1 µm by varying the amount of gelatin, the stabilizing reagent. From SEM images it is revealed that higher loading of gelatin gave larger but relatively uniform particles. However, XRD patterns indicated that the large particles were composed of smaller particles; that is, they had a "particle-in-particle" structure. Cross-sectional TEM image strongly supports this structure and indicates that gelatin is a good antioxidizing coating material which kept 5-nm copper metallic.

Metal nano- and fine particles show a wide variety of unique spectroscopic, electronic, chemical, and physical properties.[1–3] They have significant potential for a wide range of applications, such as catalysts, magnetic recording media, optoelectronic materials, magnetic fluids, materials for surface-enhanced Raman scattering, fuel cells, photovoltaic materials, pigments, and sensors. Such unique properties arise from their sizes which correspond to their high ratio of surface area to volume. Among these interesting phenomena of metal nano- and fine particles, their lower sintering temperature is one of the most important properties for industrial application. Due to continued improvements in printing technology, demand for fine and size-controlled metallic particles keeps increasing. For example, the use of copper interconnects on semiconductor chips for modern computers is a widespread use of copper nano- or fine-particles. Alternation of nickel inner electrodes of multilayered ceramic capacitors (MLCC) to copper is another good motivation to develop fine copper particles[4] because nickel poses a cancer risk to humans.[5] Not only nanoparticles but also submicron-sized particles are highly demanded for cosintering with ceramics. Moreover, in the gigahertz range, nonmagnetic electrodes and wiring systems are always in demand. From this point of view, copper is probably the single solution for this purpose because of its high electroconductivity, relatively low melting temperature, low price, and lower propensity to migrate.

Various techniques, such as chemical reduction,[6–9] evaporation, atomization, and plasma[10] have been proposed to produce copper particles. Among them, chemical reduction processes are quite familiar because of their easiness, variability of the conditions, and low cost. We have recently proposed relatively uniform sized copper particles stabilized by gelatin by chemical reduction of cupric oxide.[6] With this process, we could successfully control the particle diameter from 50 to 200 nm. Addition of a thiol compound as a complexing reagent during the hydrazine reduction of CuO makes the particle size larger, and the amount of the thiol controls their size. However, to our best knowledge, larger particles up to micron size with a uniform size cannot be achieved by chemical reduction so far.

In this study, we would like to propose a preparation procedure for metallic copper particle in a wide range from 190 nm to 1 µm. The single control parameter is the amount of gelatin, which is introduced as an antioxidizing stabilizing reagent. The reduction conditions are mild, that is, at room temperature. Gelatin is a unique biopolymer and has been used as a functional polymer in the photoindustry for a long time. Moreover, plastic capsules for medicines are made of gelatin in order to prevent oxidation.

As the metal precursor, cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, 99.5%, Wako) was selected. Sodium L-tartrate ($Na_2C_4H_4O_6 \cdot 2H_2O$, complex reagent), sodium hydroxide (NaOH, pH adjuster), and hydrazine monohydrate ($N_2H_4 \cdot H_2O$) were supplied by Wako. Gelatin used here is supplied from Nitta Gelatin, Inc. Water (>18.2 MΩ) was doubly distilled water by a Millipore system.

Preparation is a modified hydrazine-reduction system at r.t.; 5 g of $CuSO_4 \cdot 5H_2O$ and 4.6 g of $Na_2C_4H_4O_6 \cdot 2H_2O$ were dissolved into 100 cm^3 of water. Then, a designated amount of gelatin (8, 40, 80, 200, and 800 mg) was introduced into this mixed solution, and pH was adjusted by addition of 6 g of NaOH. After stirring for 10 min in order to dissolve the reagent completely, 30 mL of 10 M aqueous $N_2H_4 \cdot H_2O$ solution was added slowly dropwise into the solution, which is kept stirred for 1.5 h. The obtained dark-brown precipitates were collected by filtration over a membrane filter (Millipore, Omnipore 0.45 µmϕ) and rinsed intensively with water.

Hydrazine is often used as a reducing reagent to prepare particles of light transition metals such as copper, nickel, and cobalt. It reduces cupric ions to metallic copper under alkaline conditions. Hydrazine is oxidized and generates nitrogen gas as shown in reaction (1), and cupric ions are reduced as shown in reaction (2):

$$N_2H_4 + 4OH^- \rightarrow N_2\uparrow + 4H_2O + 4e^- \tag{1}$$

$$Cu^{2+} + 2e^- \rightarrow Cu(0) \tag{2}$$

However, usually, hydrazine reduction is carried out at high temperature. In this study on the other hand, we kept the reaction solution for 1.5 h at room temperature to obtain metallic copper particles. Even in this mild condition, reduction of cupric ions to metallic copper could proceed. Reduction of cupric ions at r.t. by hydrazine has some advantages. (1) Nitrogen evolution occurs slowly (see reaction 1). Nitrogen bubble generation can keep the reaction solution homogeneous. But gelatin is amphiphilic and the reaction solution becomes foamy. Then, it may overflow the flask when the reaction rate is very high. (2) Copper can precipitate onto copper nuclei slowly but smoothly, that gives uniform sized large particles.

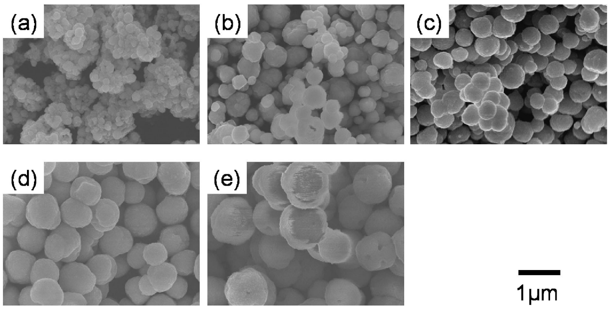

Figure 1. SEM images of gelatin-stabilized copper particles prepared with different amounts of gelatin. (a) 8, (b) 40, (c) 80, (d) 200, and (e) 800 mg.

Scanning electron microscopic (SEM, JEOL JSM-6500F) images of the obtained copper particles prepared with various amount of gelatin are shown in Figure 1. The average sizes of the obtained copper particles are in the range between 190 nm to 1 μm depending on the amount of gelatin. The particles are spherical and their size is relatively uniform. As no projection was observed on the surface, we can assume that no considerable oxidation of the particles proceeded. There have already been several papers concerning the size control of metal nanoparticles by varying the amount of stabilizing reagents added during the reduction of the corresponding metal ions. In such cases, the size becomes smaller when the amount of the stabilizer is larger. In this case, the situation is completely opposite.

Careful observation of these images, the particles in Figures 1d–1e, shows that particle surfaces are not smooth but some small round structures can be found. We have also compared the X-ray diffractograms. In Figure 2, the XRD patterns of the copper particles with the diameter of 190 nm (a) and 1 μm (b) are shown. The particles are polycrystalline. It is obvious that these patterns exhibit the characteristic peaks of crystalline metallic copper corresponding to (111), (200), and (220) planes. These characteristic peaks show the formation of a face-centered cubic (FCC) copper phase without copper oxides or other impurity phases. Comparing these two patterns, it should be noted that although the whole particle size became larger with the amount of gelatin (Figure 2b), the XRD peaks becomes wider, indicating that these copper particles are composed of very small metallic copper nanoparticles.

Figure 3 shows the cross-sectional TEM (Hitachi H-9500, 300 kV) image of the 1 μm-sized copper particles. The sample was prepared by using an FIB process with a Hitachi FB-2000A. Careful observation of this image reveals that the particles are composed of small-sized primary particles about 5 nm in diameter and that the particles are covered by gelatin layer of a few nm (indicated in Figure 3). Surprisingly, from the XRD pattern and the TEM image, even the primary particles as small as 5 nm are not covered by inorganic condensed layers such as metal oxides but just coated by gelatin molecules.

From these results we can assume the formation mechanism of this "particle-in-particle" structure. Addition of larger amounts of gelatin gives smaller copper particles by this mild reduction. Then, these small copper nanoparticles are gathered with excess gelatin molecules by intermolecular interaction by peptide groups to form larger but uniform secondary particles (see Graphical Abstract).

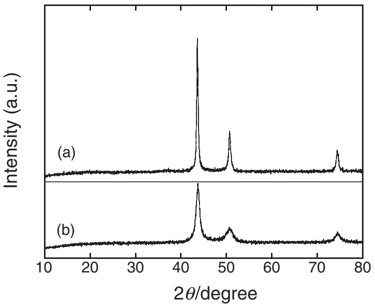

Figure 2. X-ray diffractions of gelatin-stabilized copper particles prepared with different amounts of gelatin. (a) 8 and (b) 400 mg.

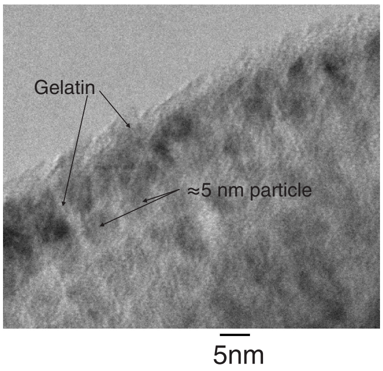

Figure 3. Cross-sectional TEM image of a gelatin-stabilized copper particle prepared with 800 mg of gelatin. Uniform copper nanoparticles (ca. 5 nm) are aggregated with gelatin layers to form a large particle.

In this study, we have proposed one-pot preparation of antioxidized metallic copper fine particles with a diameter from 190 nm to 1 μm. SEM observation revealed the size of the particles is relatively uniform. XRD and cross-sectional TEM image revealed that the 1 μm-sized particles consisted of 5-nm metallic copper particles covered and connected by gelatin.

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References and Notes

1 C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.* **2005**, *105*, 1025.
2 N. Toshima, T. Yonezawa, *New J. Chem.* **1998**, *22*, 1179.
3 R. L. Whetten, M. N. Shafigullin, J. T. Khoury, T. G. Schaaff, I. Vezmar, M. M. Alvarez, A. Wilkinson, *Acc. Chem. Res.* **1999**, *32*, 397.
4 T. Yonezawa, S. Takeoka, H. Kishi, K. Ida, M. Tomonari, *Nanotechnology* **2008**, *19*, 145706.
5 IARC Monographs Database on Carcinogenic Risks to Humans, http://monographs.iarc.fr/ENG/Classification/crthalllist.php.
6 M. Tomonari, K. Ida, H. Yamashita, T. Yonezawa, *J. Nanosci. Nanotechnol.* **2008**, *8*, 2468.
7 J.-G. Yang, T. Okamoto, R. Ichino, T. Bessho, S. Satake, M. Okido, *Chem. Lett.* **2006**, *35*, 648.
8 H. H. Huang, F. Q. Yan, Y. M. Kek, C. H. Chew, G. Q. Xu, W. Ji, P. S. Oh, S. H. Tang, *Langmuir* **1997**, *13*, 172.
9 Y. Lee, J. Choi, K. J. Lee, N. E. Stott, D. Kim, *Nanotechnology* **2008**, *19*, 415604.
10 S. Sulaimankulova, E. Omurzak, J. Jasnakunov, A. Abdykerimova, H. Gafforova, A. Mametova, *J. Cluster Sci.* **2009**, *20*, 37.