

## Preparation of copper nanoparticles with an organic coating by a pulsed wire discharge method

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**In the pulsed wire discharge method, a coating technique to prepare metal nanoparticles covered with organic matter has been investigated. Copper nanoparticles covered with organic matter have been successfully prepared by evaporation of a copper wire in an oleic acid vapor/mist. The thickness of the coating layer was a few nanometres. The median diameter of the powder was 25 nm, and became 10 nm smaller than that without the coating because of the inhibition of particle growth by the formation of the coating. From phase identification by transmission electron microscopy and X-ray diffraction analysis, it was found that the copper nanoparticles have been passivated and have not been oxidized in over 2 months.**

**Key words: Nanoparticles, Pulsed wire discharge, Copper, Passivation.**

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### Introduction

Solid particles with an average grain size in the range of 1 to 100 nm are called nanoparticles. Various unique characteristics can be exhibited by the reduction of the particle size [1, 2]. Since some of these characteristics are attributed to the high surface activity of the nanoparticles, maintaining the activity is important as on effective use of these characteristics. One of the major deteriorations of the activity is caused by oxidation in the case of base metals. The base metal nanoparticles react easily with oxygen in air even at room temperature and form an oxide phase on the surface, which has an undesirable effect on usage. Consequently, special isolation and passivation techniques of the nanoparticles prepared are required. Along with a recent remarkable growth of nanotechnology, nanoparticles as a raw material with superior or additional properties are in strong demand. A hybridization of the base metal nanoparticles is the most realistic way to obtain these properties. There is a possibility of a useful effect development at the hybridizing interface, and increasing the degree of mixing of the nanoscale mixture seems to result in a better composite effect. To passivate and hybridize nanoparticles, a coating appears to be a promising method.

Physical vapor deposition (PVD) is a major synthesis method of nanoparticles in gas phases. In this method, nanoparticles are prepared by a homogeneous nucleation from the evaporated raw material, namely by condensation and coagulation. It is possible to prepare high

purity powder by PVD. However, the particle size distribution is too broad compared with monodispersed particles [3]. In PVD, some ways to overcome the problems mentioned above have been reported by many researchers over the past years. An older method of particle passivation is the formation of a thin and dense oxide layer on the surface of the particle immediately after its preparation. Though the oxide layer plays a role as an oxidation-resistant coating, in some cases, it is difficult to remove the oxide layer later on for usage. Yatsuya et al. successfully prepared isolated aluminum and silver particles on the surface of substrate coated with oil by vacuum evaporation on a running oil substrate (VEROS) method [4]. Kwon et al. added a stearic acid solution to prepared tungsten powder before contact with air, and passivated it [5]. Nakayama et al. evaporated metal and organic matter simultaneously, and made special isolated deposits of several kinds of metal particles with organic matter on a substrate [6]. These techniques are more like immersion than coating. A limitation of the organic matter species is not so severe in the PVD method, compared with the solution phase synthesis method.

The pulsed wire discharge (PWD) method, where the exploding wire technique is applied, is one of the methods for preparing nanoparticles [7-9]. In PWD, a solid wire is evaporated by a pulsed current to produce a vapor, which is then cooled by an ambient gas to form nanoparticles. Preparations of metal, oxide and nitride nanoparticles by PWD have been reported [7-11]. This method has potentially a high production rate and a high energy efficiency. Furthermore, the nanoparticles are prepared in a simple apparatus consisting of a vacuum chamber, a powder collection filter and a discharging circuit. Therefore, PWD is considered to

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be suitable for mass-production of nanoparticles at low cost.

In this study, a coating technique to prepare metal nanoparticles covered with organic matter has been examined. Specifically, the influence of the coating on the particle size and the proceeding oxidation have been investigated.

### Experimental Setup

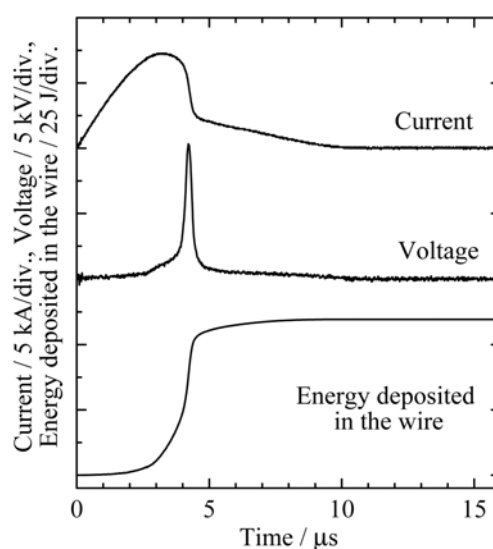
The experimental setup is shown in Figure 1. The system consisted of a chamber (2.5 l in volume), an oil-free dry vacuum pump, a powder collection filter (which includes a cold trap and a filter), and a simple discharge circuit (which included a high-voltage power supply, a capacitor, and a spark gap switch). A copper wire (99.9% in purity, Nilaco) with length of 25 mm and diameter of 0.25 mm was placed in the chamber which was filled with nitrogen gas. The ambient gas pressure was kept at 100 kPa. Before the discharge, 15 mg of oleic acid (Tech. 90%, SIGMA-ALDRICH) was heated and evaporated into the chamber by an electrical heater at a temperature of 473 K. This temperature is the boiling point of the oleic acid used in this experiment, which was measured by a thermobalance. A pulsed current was generated from a 10  $\mu$ F capacitor which was charged up to 5.2 kV. In order to evaporate the copper wire, an energy of 68 J is required theoretically [12]. The stored energy in the capacitor was therefore enough to evaporate the wire. The current was driven through the wire by a triggering pulse input to the spark gap switch, i.e. closing the switch. The amount of energy deposited in the wire was calculated from the current and voltage waveforms. After the discharge, the chamber was evacuated through a membrane filter (pore size 0.1  $\mu$ m, Millipore) for powder collection. The cold trap, which was cooled by liquid nitrogen, in front of the filter plays a role as an organic matter vapor/mist collector. The efficiency of trapping the organic vapor was estimated by the weight change of the filter in an experiment without PWD. With the cold trap at 77 K, only 0.1 mg of oleic acid existed on the filter.

Additionally, the copper powder without the coating was prepared using almost the same conditions but without the evaporation of oleic acid for comparison.

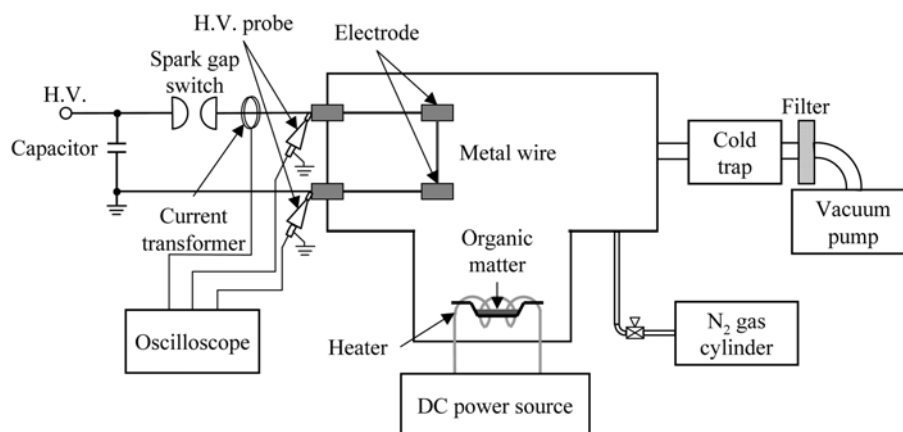
The powder morphology was observed by a transmission electron microscope (TEM; JEOL JEM2010, at an accelerating voltage of 200 kV). The particle size distribution was analyzed by measuring the diameter of more than 1000 nanoparticles on bright field images (BFIs). The crystal structure of the powders was identified with a powder X-ray diffractometer (XRD; Rigaku RINT2000, Cu-K $\alpha$  radiation of 0.15418 nm, 50 kV, 300 mA). The identification of the organic matter was carried out by a Fourier transform infrared spectroscopy (FT-IR; Nicolet IMPACT410) using the infrared reflection method.

### Experimental Results

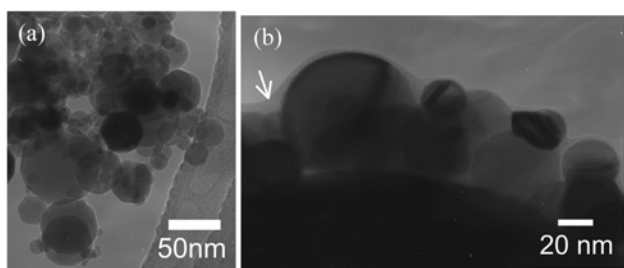
Shown in Fig. 2 are the waveforms from the current and voltage measurements. The energy deposited in the



**Fig. 2.** Current and voltage waveforms, and energy deposited in the wire. Here, 0  $\mu$ s is a point in time at which the spark gap switch was closed.



**Fig. 1.** Experimental setup.



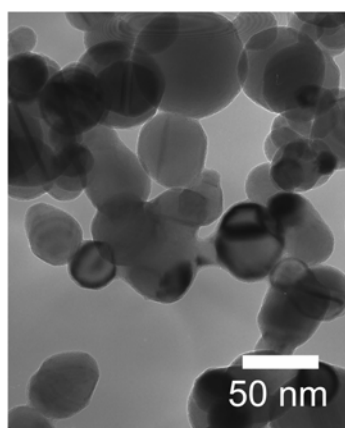
**Fig. 3.** Bright field TEM images of copper particles prepared in an oleic acid vapor/mist (a) with/(b) without an acetone dispersion treatment. The arrow in Fig. 3(b) shows a coating layer.

wire is plotted in the same figure. These results are almost the same as those previously which were measured with the same electric experimental conditions but without the evaporation of oleic acid [13]. It can be seen that the evaporation of oleic acid does not influence the discharge under these conditions. Since several investigations concerning the discharge in the exploding wire phenomenon have been reported [13, 14], this will not be discussed in detail here.

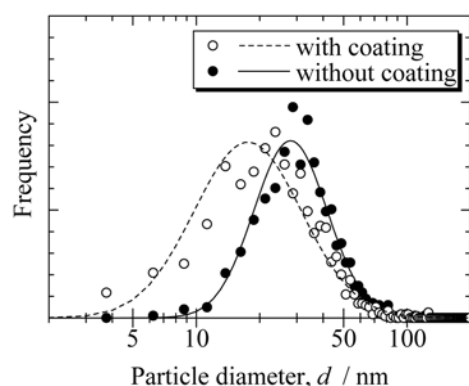
Bright field TEM images of particles prepared in the oleic acid vapor/mist are shown in Fig. 3. Here, Fig. 3(a) is an image of particles after the dispersion treatment to measure particle diameters. Figure 3(b) is an image of prepared particles without the dispersion treatment, to observe the surface condition. Most nanoparticles do not have diameters above 100 nm. The shape of nanoparticles is spherical, and the nanoparticles are aggregated. Thin coating layers were observed on all particles, and the thickness was a few nm.

Figure 4 shows a typical bright field TEM image of particles prepared in nitrogen gas without the oleic acid vapor/mist. The shape of these particles is clearly different from that shown in Fig. 3(a). Specifically, inter-particle neck growth due to particle collision/coalescence was observed frequently.

Figure 5 shows size distributions of particles prepared with/without the coating. These distributions were



**Fig. 4.** Typical bright field TEM image of particles prepared in nitrogen gas without the oleic acid vapor/mist.



**Fig. 5.** Size distributions of particles prepared with/without coating.

obtained from multiple images including those shown in Figs. 3(a) and 4. The frequency was fitted to solid or dashed curves based on the following log-normal distribution function,

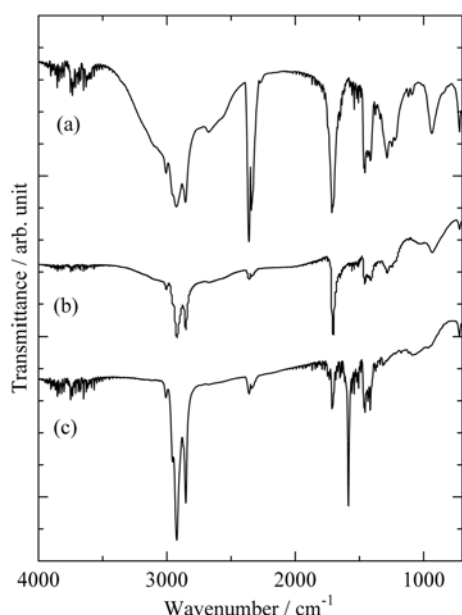
$$f(d) = \frac{1}{\sqrt{2\pi} \log \sigma_g} \exp \left( -\frac{(\log d - \log D_{50})^2}{2 \log^2 \sigma_g} \right), \quad (1)$$

where

$$\log \sigma_g = \sqrt{\frac{\sum n_i \cdot (\log d_i - \log D_{50})^2}{\sum n_i}}, \quad \log D_{50} = \frac{\sum n_i \cdot \log d_i}{\sum n_i}.$$

Here,  $f(d)$  denotes the log-normal distribution function,  $d$  is the particle diameter,  $n_i$  is the number of the nanoparticle with diameter of  $d_i$ ,  $D_{50}$  is the median diameter, and  $\sigma_g$  is the geometric standard deviation. It was found that the  $D_{50}$  and  $\sigma_g$  of the particles with the coating were 25.0 nm and 1.79, while those of the particles without the coating were 35.0 nm and 1.49, respectively. As a trend, the particle diameter with the coating was smaller and the divergence from the log-normal distribution function was larger than those of particles without the coating.

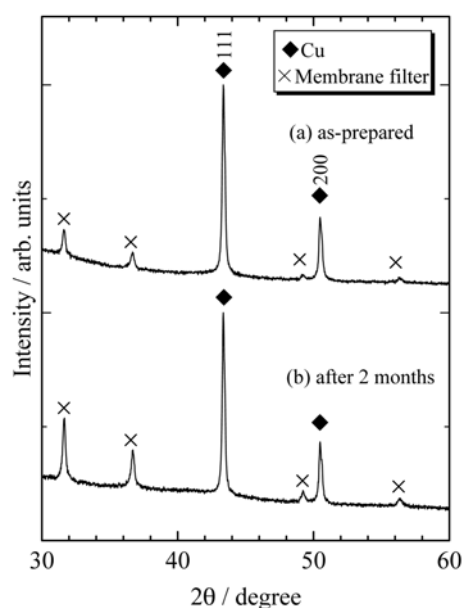
Figure 6 shows FT-IR spectra of (a) the oleic acid, (b) the evaporated oleic acid and (c) the prepared particles with the coating. In order to obtain the FT-IR spectrum of the coating matter, a solution was prepared by dissolving the matter from the powder in acetone. A test sample for the FT-IR measurement was prepared by condensing the matter from this solution. It was confirmed that the molecular structure of the oleic acid had been retained after the evaporation. However, there are some differences on comparing Fig. 6(a) with Fig. 6(c). Specifically, the disappearance of a broad spectrum due to the O-H stretching vibration ( $3500\text{--}2500\text{ cm}^{-1}$ ), the disappearance of some spectral characteristics due to the C-O stretching and O-H deformation vibration ( $1300\text{--}1200\text{ cm}^{-1}$ ), and an intensity reduction of the spectral characteristics due to the C=O stretching vibration ( $1700\text{ cm}^{-1}$ ) were observed after the coating. As can be seen from these differences, the coated matter did not retain its original molecular structure of the oleic acid. Since



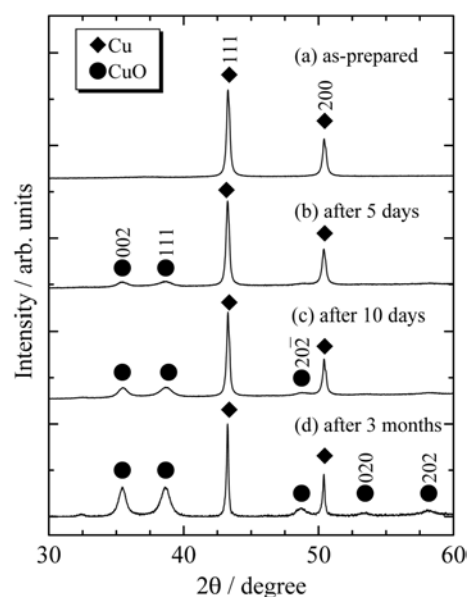
**Fig. 6.** FT-IR spectra of (a) oleic acid, (b) evaporated oleic acid and (c) the coating matter on the prepared particles.

some peaks due to C-H stretching and deformation vibrations ( $3000\text{--}2800\text{ cm}^{-1}$  and  $1500\text{--}1400\text{ cm}^{-1}$ , respectively) remain in the spectrum in Fig. 6(c), the coated matter consisted of some types of organic matter, (i.e. it did not consist mainly of soot).

Figures 7 and 8 show XRD patterns of particles prepared with/without the coating, respectively. In the first case, since the measurements were carried out for particles prepared and adhered to the membrane filter, there are several diffraction lines from the filter in Fig. 7. It was seen that the crystallized particles immediately after the preparation consisted only of copper. It was found that the copper nanoparticles with the coating have been



**Fig. 7.** Change of XRD patterns of particles prepared with the coating over time ((a) as-prepared, (b) after 2 months).



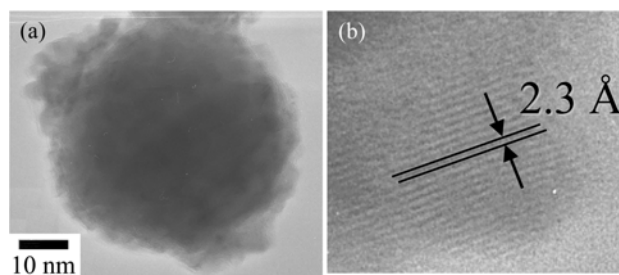
**Fig. 8.** Change of XRD patterns of particles prepared without the coating over time ((a) as-prepared, (b) after 5 days, (c) after 10 days and (d) after 3 months).

passivated and have not been oxidized in over 2 months. Since it is clear from Fig. 8 and an other study [8] that the copper nanoparticles without the coating oxidize gradually, it was demonstrated that the organic coating on the metal nanoparticles is effective in preventing the oxidation of them.

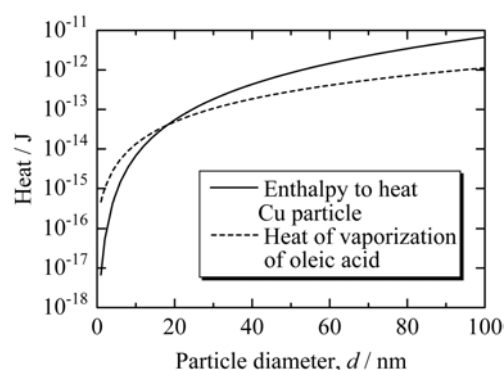
High resolution electron microscope (HR-TEM) images of a particle without a coating 5 days after the preparation and its closeup are shown in Figs. 9(a) and 9(b). Many grains with the size of a few nm are observed on the particle. Lattice fringes of  $2.3\text{ Å}$  in Fig. 9(b) are seen on the surface, which is in good agreement with the interplanar spacings of CuO (111).

## Discussion

First, the place and time of the coating are investigated. As mentioned above, oleic acid vapor which has not adhered to the particles is supposed to be condensed completely by the cold trap. From Fig. 3(b), the coating must not be formed on the filter during the collection but must be generated in the chamber during PWD.



**Fig. 9.** HR-TEM images of a particle without the coating 5 days after the preparation ((a) overall, (b) close-up view).



**Fig. 10.** Comparison of the theoretical enthalpy to heat a copper particle from the boiling point of oleic acid to the boiling point of copper with the heat of vaporization of the oleic acid layer.

Secondly, the reason for the particle size distribution observed is discussed. There are significant differences of particle size distributions between the particles prepared with and without the coating. These differences can be explained by the influence of the oleic acid vapor/mist on the particle growth process. The formation of the coating due to the condensation on the particle surface occurred during the particle growth process. It is expected that the coating acts as an impediment to collision/coalescence, so that a decrease of the neck formation and grain growth processes occurs. At the time of collision/coalescence, re-vaporization of the coating due to the heat of the particle probably has also occurred. Figure 10 shows a comparison of the theoretical enthalpy to heat a copper particle from the boiling point of oleic acid to the boiling point of copper [12] with the heat of vaporization of the oleic acid layer [15]. These were calculated by multiplication of the enthalpy and volume as a function of particle diameter. Here, the temperature of a copper particle is 2843 K. It is assumed that the thickness of the oleic acid layer is 1 nm. From Fig. 10, with copper particles in the range of 1 to 20 nm in diameter, it is shown that the heat content of a copper particle is not enough to vaporize the oleic acid layer, i.e. the coating remains. On the other hand, with copper particles of 20 nm-diameter or more, it is possible to re-vaporize the oleic acid coating layer, considering the heat available. From these computational results, it appears that the coating prevents grain growth in particular on smaller particles, and this tendency can explain the difference in the sizes shown in Fig. 5. In copper particles of 20 nm-diameter or more, it seems that the excessive heat results in decomposition of the oleic acid coating, as shown in Fig. 6(c).

## Conclusions

Preparation of copper nanoparticles covered with organic matter was carried out and analyses of the morphology, the molecular structure and the crystal structure were

conducted to investigate such a nanoparticle synthesis process. The following conclusions have been obtained.

(1) Copper nanoparticles covered with organic matter have been successfully prepared by evaporation of copper wire in an oleic acid vapor/mist. The thickness of the coating layer was a few nanometres.

(2) The median diameter of the powder was 25 nm, and became 10 nm smaller than that without the coating.

(3) The coating matter has not kept its original molecular structure, because of the decomposition by the heat from a growing particle.

(4) The copper nanoparticles covered with organic matter have not oxidized several months after the preparation.

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