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Preparation of Copper Nanoparticles in Liquid by Matrix Sputtering Process

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Abstract. As a new method for nanoparticles preparation, magnetron sputtering of metal atoms and clusters into organic liquids has been intensively used recently. In this study, metallic copper nanoparticles dispersed in pentaerythritol ethoxylate were prepared by this process. Their size control was achieved by controlling the sputtering current. Specific absorption at *ca.* 580 nm was detected by UV-Vis measurement which is attributed to the specific plasmon absorption of metallic copper. TEM observation also revealed the formation of metallic nanoparticles.

1. Introduction

Metal nanoparticles (MNPs) have been attracted significant attention from the scientific and engineering community as their specific physicochemical properties which are different from bulk materials and atomic materials, and it is considered that they play an important role in developing new scientific approaches. MNPs are now considered as a key material of modern nanotechnology. Their unique properties, including nonlinear optics, plasmon phenomena, photo luminescence, catalysis, electronics, biomedicine, magnetic phenomena, as well as energy conversion, are varied with their sizes, especially in a single digit nm region, and with their shape and surface condition. [1-4] For optical properties, extremely small MNPs with their sizes close to Fermi wave length of electron have photoluminescence characterized by quantum size effect. [5-7]

In most cases, recently, especially in laboratories, MNP dispersions were prepared by chemical reduction or decomposition of the corresponding metal compounds by using external reduction agents or solvents. [1, 8-10] Initial cost of wet chemical processes is usually much smaller than vacuum processes and the particle sizes can be controlled by the selection of metal sources, protective reagents, reducing reagents as well as their concentrations.

On the other hand, NP preparation by vacuum process is considered as an industrial process which generates naked MNPs or oxide coated MNPs. Initial cost of vacuum processes is usually much more expensive than chemical reduction processes, but vacuum processes are usually continuous manufacturing ones, whose running cost can be smaller than that of chemical processes, which are batch processes, generally. From this point of view, a new route to prepare MNPs by using a relatively non-expensive apparatus has been demanded. Recently, magnetron sputtering, which is usually focused on the preparation of thin films on solid substrates, has been applied for NP preparation. Ye et al. reported the preparation of rough thin films of Ag on silicon oil. [11] After this work, this magnetron sputtering procedure to prepare MNPs in liquid was extended to other liquids, such as ionic liquids, [12-15] oils, [16] liquid polymers [17] and so on. Size and structure control of Au NPs by

changing sputtering parameters has been also discussed. [17-19] The Authors' group proposed to use a thiol organic salt, being solid at room temperature, as the matrix to sputtering preparation of Au NPs by heating the matrix molecules. [20] Other thiol liquid molecules were also used as the matrix for Au NP preparation by sputtering, and this NP dispersion could be polymerized to form a transparent fluorescent resin.[21]

However, these papers published so far reported only Au or Ag NPs as MNPs, which are stable in ambient condition. Quite recently, Suzuki et al. reported metal oxide NPs by sputter deposition into ILs and heat treatment under air. [22,23] In this study, we firstly prepared metallic Cu NPs in liquid organic molecules by magnetron sputtering process.

2. Experimental Section

2.1. Materials

As an organic liquid, pentaerythritol ethoxylate (PEEL, Aldrich, $C(CH_2(OCH_2CH_2)_nOH)_4$) was selected and used as purchased. It is one of the monomers of urethane. Target copper (99.96 %, diameter = 50 mm) was purchased from Nilaco, Japan.

2.2. Preparation of copper nanoparticle dispersion by sputtering process

In order to remove water molecules and other ingredient molecules in PEEL, it was kept at 90 °C under vacuum for more than 2 h. Some bubbles formed from PEEL. The vacuum chamber was evacuated first to ~ 10^{-3} Pa and Ar gas was admitted in until the system was stabilized at a pressure of 2 Pa. Before sputtering, this gas exchange procedure was repeated more than twice in order to evacuate oxygen gas completely. The vacuum pressure was kept at 2 Pa during the sputtering. All samples were obtained by dc-magnetron sputtering of a Cu target over a cylindrical glass petri plate (~ 6 cm diameter × ~ 1 cm height) containing 7.0 g of PEEL. The temperature of PEEL was kept at 20 °C by using a cooling apparatus under the petri plate. Sputtering current was varied in the range of 10 – 100 mA, and sputtering time was 8 or 60 min.

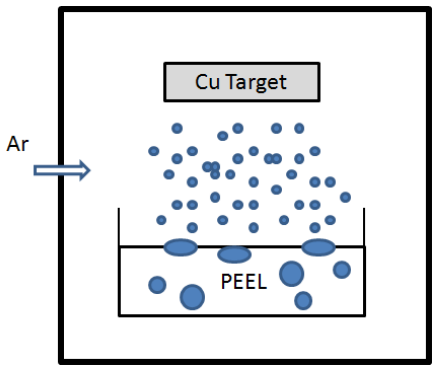


Fig. 1 Schematic illustration of Cu NPs preparation by magnetron sputtering on PEEL.

2.3. Characterization

UV-Vis absorption spectra were obtained with a Jasco V-630 using a 1-mm or 10-mm quartz cuvette. The particle structure and size were observed by TEM with a Hitachi H-9500 at the acceleration voltage of 300 kV. The sample grid (Cu, 3 mmϕ) was prepared by putting a drop of Cu nanoparticle dispersion in PEEL and followed by dipping into ethanol for 10 min to wash excess PEEL.

3. Results and Discussion

3.1. Preparation of Cu nanoparticles by Sputtering

As previously reported, Au NPs can be readily obtained by magnetron sputtering into ionic liquids, oils, *etc*. Discussions of the relationships between sputtering parameters and sizes and shapes of the obtained Au NPs were also discussed. Here, we tried to obtain Cu NPs by sputtering. First, we evacuate the sputtering chamber to 10^{-3} Pa and then filled it with Ar gas up to 2 Pa. This evacuation/Ar introduction process was carefully repeated at least twice in order to remove oxygen gas. Othewise, CuO or Cu_2O NPs can be obtained.

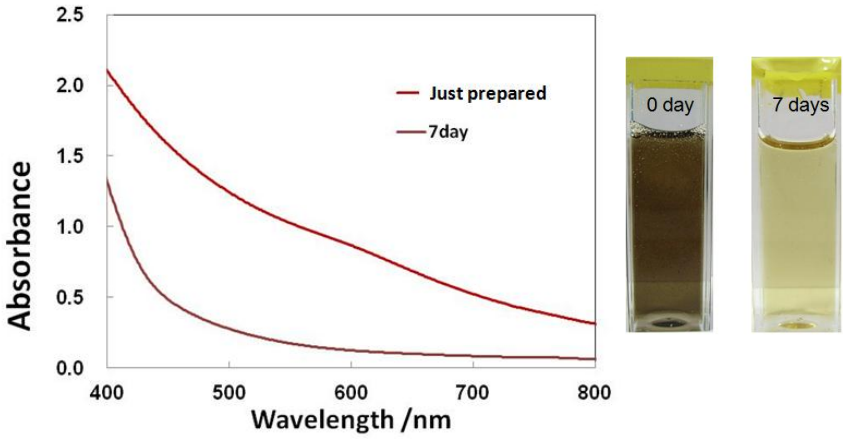


Fig. 2. UV-Vis spectra of Cu NPs in PEEL prepared by sputtering (50 mA, 8 min). Red: Just prepared, Brown: 7 days after preparation. Specific plasmon absorption peak can be observed in the spectrum just after preparation. Images (right) show the Cu NP dispersion in PEEL (just prepared and 7 days after preparation) in a cuvette.

When we carefully changed the chamber gas to Ar, we have successfully obtained CuNPs in PEEL. Figure 2 shows the UV-Vis absorption spectra of Cu NPs obtained by magnetron sputtering at 50 mA for 8 min and the spectra were measured at just after preparation and 7 days after preparation. After preparation, one can find a small absorption shoulder peak at ca. 580 nm, which is corresponding to the specific plasmon absorption of metallic copper NPs. [24] However, after keeping 7 days under ambient condition, the absorbance of the Cu NPs in PEEL dramatically decreased in whole area. In Figure 2, the photographs of the dispersion in a quartz cell are also collected. The color of the dispersion diminished dramatically during 7 days, and the sample after 7 days is slightly yellow. This situation should be attributed to oxidation of Cu NPs in PEEL dispersion. On the other hand, this color change suggests that no aggregation or flocculation of Cu NPs occurred in PEEL.

3.2. Cu NPs in PEEL Prepared by Sputtering with Different Sputtering Parameters

As discussed in the introduction section, precise control of particle size is very important technique to obtain MNPs. Hatakeyama *et al.* changed various sputtering parameters to obtain Au NPs in poly(ethylene glycol) (PEG). [17-19] Temperature, concentration can be parameters which control the size and shape of Au NPs. Here, we have tried to control Cu NPs in PEEL by changing the sputtering current. In order to emphasize the effect of the changing sputtering current, the sputtering time was kept at 60 min. UV-Vis spectra and TEM images of Cu NPs obtained in PEEL by sputtering Cu at various currents in the range between 10 – 100 mA are collected in Figs. 3 and 4, respectively. No plasmon absorption peak is found in the spectrum of Cu NPs in PEEL prepared with sputtering current

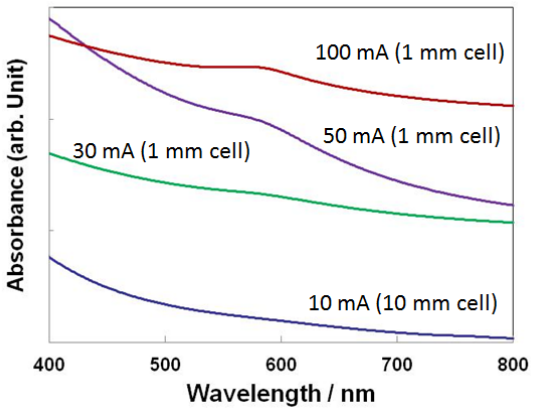


Fig. 3 UV-Vis spectra of Cu NPs prepared by sputtering at various sputtering currents. Sputtering currents used and optical path lengths of the quartz cells are indicated in the Figure (10, 30, 50 and 100 mA; 1 mm or 10 mm cell). The Sputtering time = 30 min.

of 10 mA. More than 30 mA, the plasmon absorption peak at ca. 580 nm can be observed. After being sputtered from the Cu target, Cu atoms and clusters bombarded onto PEEL surface and interact with PEEL molecules. In the surface region, growth of Cu atoms and clusters to Cu NPs proceeds. [16] Therefore, when the sputtering current is higher, the amount of generated Cu atoms and clusters increased. Then, the growth of the particles becomes rapid to generate larger NPs.

In fact, the particle diameter was depending on the sputtering current. Sputtered at 10 or 20 mA, the average particle size is between 2 – 3 nm. However, higher current gave larger particles, especially Cu NPs prepared at 100 mA, showed two peaks in the size distribution, one is 5.5 nm, and the other is larger, about 8 nm.

Precise observation of the UV-Vis spectra in Fig. 3 indicates a slight blue shift in the spectrum of Cu NPs prepared at 100 mA comparing with that prepared at 50 mA, even the particle sizes became larger. It can be explained by the difference of the baselines. However, further experiments with different sputtering conditions are needed.

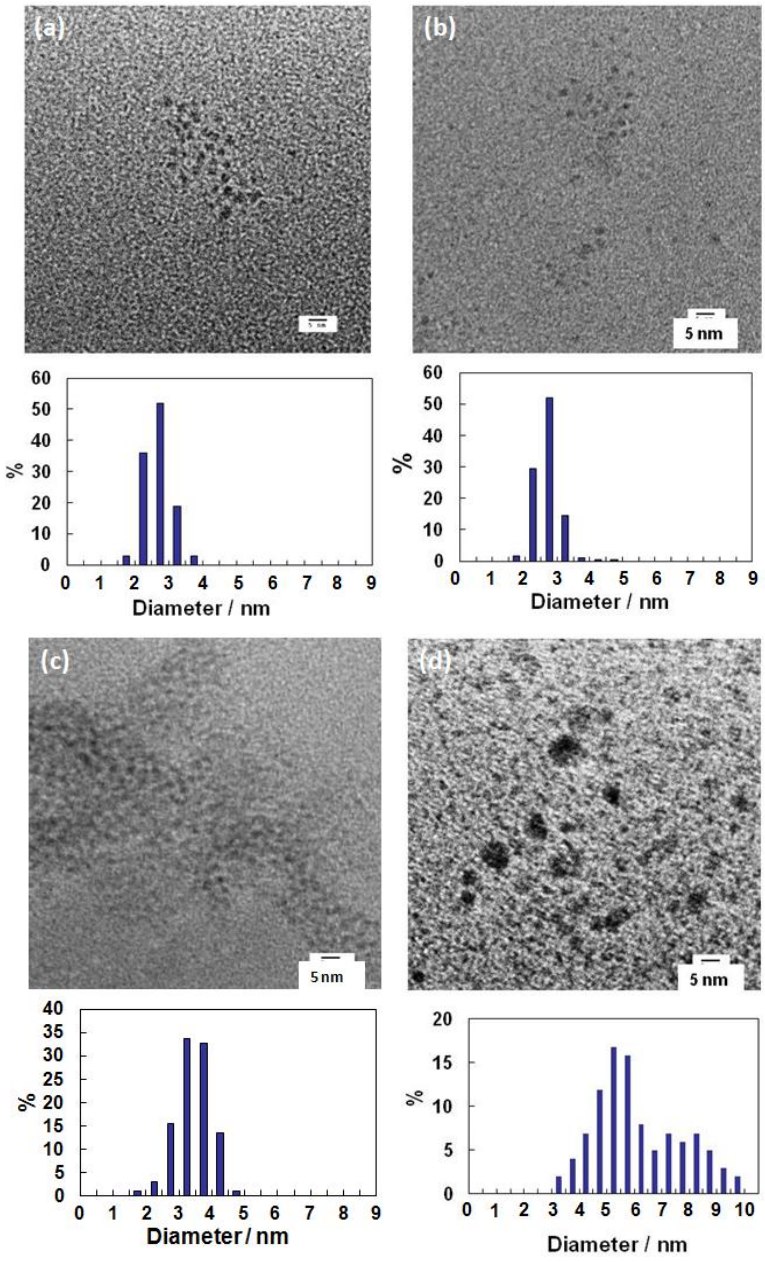


Fig. 4 TEM images and particle size distributions of Cu NPs in PEEL prepared by sputtering process. Sputtering current: (a) 10 mA, (b) 30 mA, (c) 50 mA, (d) 100 mA. Sputtering time = 30 min.

4. Conclusion

Spherical metallic Cu NPs with a diameter of single digit nm were obtained by Ar sputtering onto organic oil, PEEL and Cu NP dispersions were obtained. No aggregation or flocculation of NPs has been observed but oxidation of Cu NPs proceeded when the dispersion was kept under ambient condition. Their particle size has been controlled by sputtering current, and plasmon absorption corresponding to metallic Cu NPs has been clearly detected.

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