Preparation of Cu Nanoparticles from Cu Powder Dispersed in 2-Propanol by Laser Ablation

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Received July 21, 2006

Key Words : Cu nanoparticle, Laser ablation, 2-Propanol

Intensive investigations on metal nanoparticles suspended in solutions have been undertaken because of their unique size-dependent electronic, optical, magnetic and chemical properties.[1-4] Silver and gold nanoparticles have been extensively studied as they show a strong absorption band in the visible region, which is due to the excitation of the surface plasmon resonance.[5-10] Recently, attention has been focused on Cu nanoparticles due to their catalytic and electrocatalytic properties.[11,12] Since copper nanoparticles are highly unstable for oxidation compared with Au and Ag, Cu nanoparticles precipitate immediately after the exposure into the air, and an inert gas environment is required to stabilize copper colloids solution.[13,14]

A number of different methods have been developed to prepare metal nanoparticles, such as chemical,[15] photochemical,[16] electrochemical,[17] and radiolytic reduction.[18] In order to acquire stable colloidal suspensions, the stabilizing agents such as polymers and surfactants are usually employed in preparation. However, for the optimal application, a pure metal colloid solution is preferred because the additives can interfere with the interaction between reactants and metal surface, and eliminate or reduce the catalytic effect.

The ablation technique has been applied to form metal colloidal solution in various solvents under protective-agent-free conditions by irradiating metal plate.[19,20] According to Neddersen *et al.*,[21] since copper metal is highly reactive, it is difficult to prepare stable colloids in the water and a solution with olive-green color was obtained by irradiating copper plate in an aerobic environment, indicating oxidation from copper to copper oxide. However, Yeh *et al.* reported a generation of stable Cu colloids from CuO powder in 2-propanol by laser ablation under the aerobic and protective-agent-free conditions.[22] Although they did not provide a detailed explanation, they demonstrated the reducing power of 2-propanol from the production of acetone during the ablation of CuO powder.

In this study, we demonstrate a method to generate stable Cu nanoparticles from Cu powder dispersed in 2-propanol by the laser ablation technique under aerobic condition. In case of using the metal plate as the ablation target, it is difficult to adjust the focus of laser light on the metal surface immersed in solvent, and the turbulence of fluid which is generated by plume expansion can protect next laser pulse to arrive at metal surface, and the metal plate has to be continuously rotated to prevent the irradiation of laser light on the same position of the metal plate. Furthermore, if the concentration of nanoparticles increases as the ablation proceed, the laser light become more difficult to arrive at the metal surface by self absorption of nanoparticles. The use of Cu powder dispersed in solution can be simple alternatives to maintain the homogeneity of the sample during the ablation.

Experimental Section

Cu metal powder (99.9%) with a size range of 80-100 mesh was purchased from Aldrich chemicals. HPLC grade 2-propanol was used without further purification. The Cu powder (0.5 g) was dispersed in 2-propanol (25 mL) and the solution was sonicated to prevent the precipitation of Cu powder under the ultrasonic frequency of 25 kHz using a commercial ultrasonic cleaner during the ablation. The solution was irradiated with the second harmonic (532 nm) output of a pulsed Nd:YAG laser (Quantel, Brilliant II) focused by a lens having the focal length of 50 mm. A spot size of the laser beam on the surface of the solution was adjusted within 0.5-1 mm in diameter by changing the distance between the lens and the surface of the solution. The solution became red-colored under irradiation of the laser due to typical surface plasmon band of nanoparticles in the wavelength range of 560-580 nm, indicating the formation of Cu nanoparticles. The solution was centrifuged at 3500 rpm for 30 min to remove the residual Cu powder unreacted after ablation.

The UV-VIS absorption spectrum of the clean portion was measured by a Shimadzu UV-3600 spectrometer. An electron micrograph was observed by a transmission electron micrograph (Hitachi H-7600). A drop of the sample was placed on a copper grid coated with an amorphous carbon film, and it was dried at room temperature. X-ray powder diffraction data were collected on a (MacScience Co. MXP-3V) diffractometer using Cu-K$_\alpha$ radiation (λ = 1.54056 A) at a 30 kV and 20 mA.

Results and Discussion

Figure 1 reveals the typical transmission electron micro-

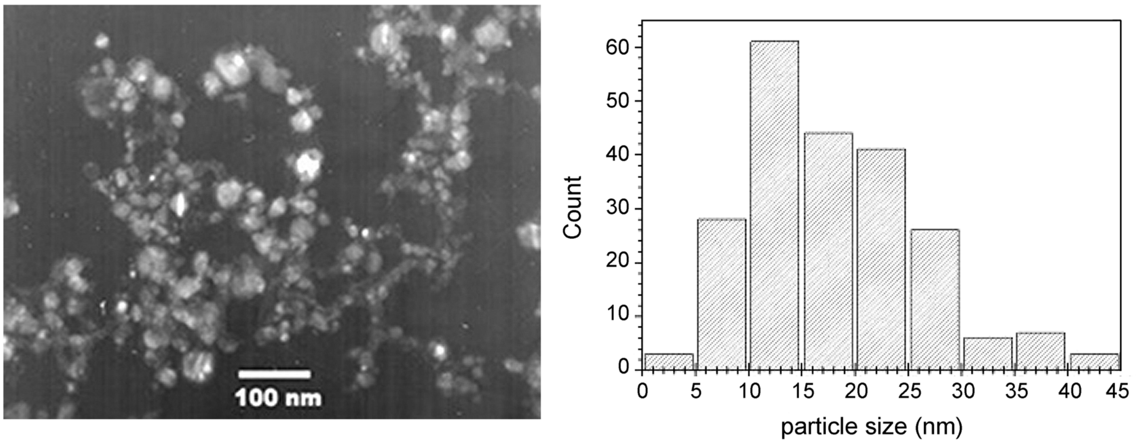


Figure 1. Electron micrographs and size distributions of the Cu nanoparticles produced by laser ablation (532 nm, 100 mJ/pulse, 30 min) of Cu powder dispersed in 2-propanol.

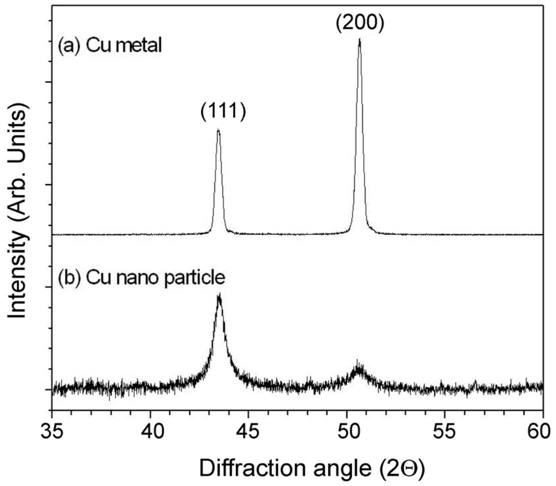


Figure 2. X-ray diffraction profiles of dried suspensions obtained by laser ablation of Cu powder dispersed in 2-propanol.

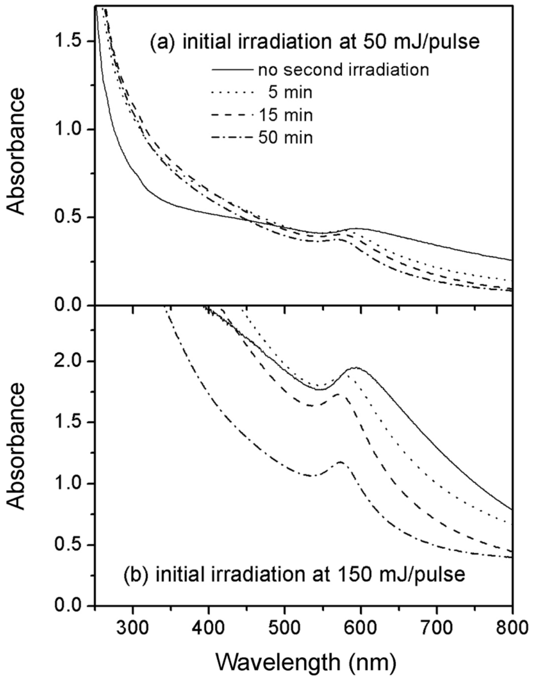


Figure 3. Optical absorption spectra of the Cu nanoparticles prepared in 2-propanol by 532 nm laser ablation at various irradiation condition. Solid lines denote the absorption spectra after only initial irradiation at 50 mJ/pulse (panel a) and 150 mJ/pulse (panel b) for 30 min. Broken lines denote the absorption spectra after the second stage irradiation at 250 mJ/pulse for 5 min (dotted line), 15 min (dashed line), and 50 min (dash-dotted line).

graph and the size distribution of copper nanoparticles produced by laser ablation (532 nm, 100 mJ/pulse, 30 min) with sonication of a copper powder dispersed in 2-propanol. Copper nanoparticles show the near spherical shapes with irregular edges, and they exhibit the broad size distribution predominantly ranging from less than 5 nm to about 30 nm in diameter with the average diameter of 15 nm. Yeh *et al.* reported the production of copper-nanoparticle with the average diameter of 24.7 ± 34.8 nm and a tendency to coagulate by laser ablation of CuO powder in 2-propanol without sonication. In this experiments, when the magnetic stirrer was used to make a dispersion of Cu metal powder in 2-propanol, the Cu metal powder was not fully dispersed due to high gravitational density of Cu, and the nanoparticles of Cu were not produced. It has been well established that ultrasound irradiation in liquids has a variety of physical and chemical effects derived from an acoustic cavitation. The acoustic cavitation and the associated streaming, micro-streaming and shock waves lead to a very efficient stirring of the solution and may assist the size of the particles to be fine. Our results also show that sonication leads to the production of copper nanoparticles with smaller size and narrower distribution.

The XRD pattern of nanoparticles obtained from dried suspension of the colloidal solutions is shown in Figure 2. The diffraction peaks at 43.5° and 50.4° correspond to the formation of metallic copper, which are well consistent with the position of XRD diffraction peaks of Cu metal plate (Figure 2a). The FWHM of diffraction peaks of the powder is 0.67°, which is much broader than 0.36° of metal Cu, indicating that the size of Cu particle produced by laser ablation is small enough to show the size effect.

Figure 3 shows the UV-VIS absorption spectra of copper colloids in 2-propanol produced at various irradiation condition. A characteristic peak of absorbance near 580 nm grew progressively by increasing laser fluence and exposure time. After initial irradiation, the copper plasmon bands near 590 nm show broadening and tailing toward longer wavelengths. This red-shifted plasmon band compared with 570 nm of that of isolated copper colloid indicates that aggregates are presented as the result of oxidation.[14] The broadening and tailing of Cu plasmon band is much stronger at 50 mJ/pulse of initial irradiation than that at 150 mJ/pulse of initial irradiation. The colloids solution produced after initial irradiation was unstable. So, red color gradually changed to brown and the colloids precipitated completely within 2-3 days. It was reported that the irradiation on gold nanoparticle suspension modifies the shape and size of nanoparticles and increase the stability of nanoparticles.[22,23] After the second irradiation at laser fluence of 250 mJ/pulse on Cu nanoparticle solutions produced from initial irradiation, the UV spectra of Cu nanoparticle solutions show the decrease of broadening and tailing in the region of longer wavelengths and the red color of solution tuned deeper. Yeh *et al.* reported the detection of acetone in Cu colloidal suspension after the laser ablation of CuO powder in 2-propanol and suggested the possibility of reduction from CuO to Cu in bulk phase.[24] In this study, the trace of CuO might be produced from residual oxygen dissolved in 2-propanol during initial irradiation and might be reduced back to Cu by the second irradiation at higher laser fluence of 250 mJ/pulse than that of initial irradiation. As the second irradiation time increases, the peak wavelength of 590 nm after first irradiation might shift up to 571 nm, which indicates the surface plasmon band of isolated Cu colloids. This is consistent with Yeh's results that a high power laser beam was required for the second irradiation to produce a wine-red solution containing Cu colloids from ablation of CuO powder.

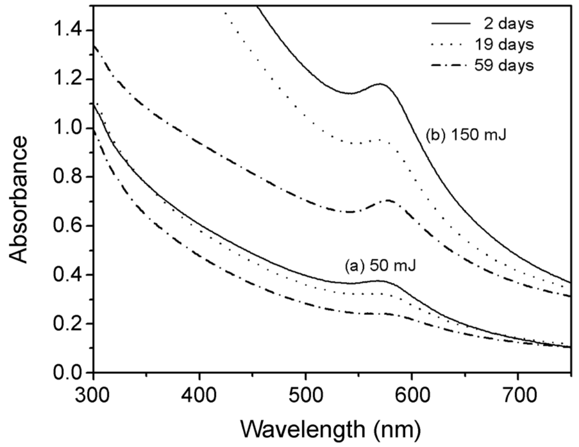
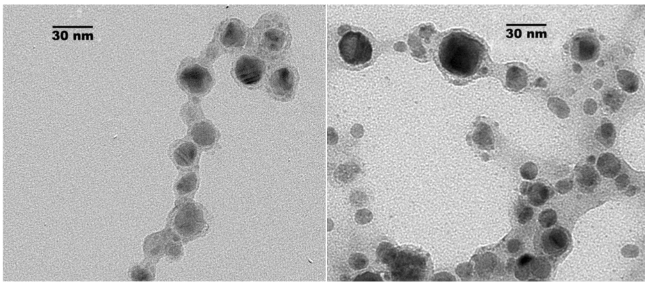


Figure 4. The absorption spectra of Cu nanoparticle solution produced by the second stage irradiation; after 2 days (solid lines), 19 days (dotted lines), and 59 days (dash-dotted lines). The conditions of initial irradiation are 50 mJ/pulse (part a) and 150 mJ/pulse (part b) for 30 min, and that of the second irradiation is 250 mJ/pulse for 50 min.



(a) (b)

Figure 5. TEM images of Cu nanoparticles after aging 60 days. The conditions of initial irradiation are 50 mJ/pulse (a) and 150 mJ/pulse (b) for 30 min, and that of the second irradiation is 250 mJ/pulse for 50 min.

Figure 4 shows the stability of the Cu nanoparticles produced in 2-propanol after the second irradiation. After aging for 60 days, the intensity of the surface plasmon band decreases just to half compared with the initial intensity of the solution after the second irradiation, and the peak was shifted only 5-6 nm without distinct broadening. The colloidal solution still exhibited red-wine color, while some precipitates were observed. It has been found that the laser light irradiation on the colloidal suspension also causes coagulation or dispersion of the particles. Takeuchi *et al.*[23] suggested that the dispersion phenomenon of flocculates is due to the increment in the ζ-potential of the particles which prevent mutual access of charged particles. The value of ζ-potential increases after the laser irradiation and the repulsive Coulomb force becomes stronger than before, causing the particles to aggregate slowly. The size distributions after aging for 60 days are shown in Figure 5 of TEM photographs of Cu nanoparticles produced under the same irradiation condition with Figure 4. The particles with the size less than 10 nm nearly disappeared and most of the living particles have the diameter about 10-20 nm nearly in spherical shape, with an occasional particle as large as 40 nm. This stability of Cu nanoparticles might result from the size and shape effect. The presented particles, whose diameter is larger than 10 nm, are less active, and the near-spherical shape with least surface tension is the most thermodynamically stable configuration. As shown in Figure 5, it looks Cu nanoparticles imbedded into some amorphous cloud. The formation of nanoparticles by the laser ablation in liquid environment has been much investigated in various solvents since suggested by Mafune[8] although the mechanism is not clearly understood. It is known that the graphitic film is deposited on the nanoparticles produced, or that the glassy carbon is formed during the ablation in the aromatic carbon solvents such as benzene and toluene.[25] However, oxygen-rich solvents such as water and aliphatic alcohol are known to have little effects on composition of nanoparticles except incorporation of oxygen in forming of the reactive metal nanoparticles.[26] Since Cu is relatively active metal compared to Au and Ag, we can not perfectly exclude the possibility of reaction with solvent although 2-propanol is the only chemical used as solvent in this study. The reaction between Cu and the solvent in ablation and the investigation of amorphous cloud will be further studied.

We have prepared stable Cu nanoparticles from the laser ablation of Cu powder dispersed in 2-propanol. The method described here may provide an alternative and simple route to prepare stable Cu nanoscale materials from the bulk phase metal. The colloids prepared in this experiment offer an opportunity to be utilized as a catalyst in interesting reactions.

Acknowledgment. This work was supported by the Soongsil University Research Fund, Seoul RNBD program, and the Ministry of Commerce, Industry, and Energy of Korea (No. 10022953).

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