Formation of Cu Nanoparticles from CuO Powder by Laser Ablation in 2-Propanol

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Laser ablation technique has been employed to generate Cu nanoparticles from CuO powder in 2-propanol. The resulting copper colloids are conspicuously stable under aerobic and protective agent-free conditions. Larger particles have also been produced through the photoinduced aggregation.

Due to their novel characters being different from their bulk properties and the variety for applications as lubricants, catalysts, and magnetic recording media,[1-3] nanoscale particles have been an exciting subject of investigation. The coinage metal elements, Cu, Ag, and Au, are studied most extensively, to our knowledge. These nanometallic particles strongly absorb the visible light because of the collective oscillation of free electrons.[4,5]

In order to acquire colloidal dispersions, it is known that stabilizing reagents are usually employed in preparation. In comparison with Ag and Au, copper particles are very unstable for air oxidation. According to the previous studies,[5-9] the color of colloids turned to a yellow or green and Cu precipitated immediately after exposure to air. Therefore, an inert gas environment is required to stabilize copper solution, as well.

Henglein first used the 694 nm light of a ruby laser to perform laser ablation of metal films immersed in various solvents to form colloidal solutions, such as Au and Ni.[10] Later, Cotton used a similar preparation technique to irradiate a copper plate in water.[11] Without any precautions taken, such as protective agents and oxygen-free conditions, a colloidal solution with olive green color was obtained, indicating that the oxidization had occurred. Additionally, surface plasmon band was down to 625 nm which was red shifted from the reported values, 570 - 580 nm. In this letter, we demonstrate a method to generate Cu particles from CuO powder in 2-propanol by laser ablation technique under aerobic conditions without any surfactant or protecting polymer presented. The resulting copper metal colloids are salient by their stability.

HPLC grade 2-propanol was used as received. Pyrex vials as containers were rinsed with nitric acid followed by sonication in distilled water prior to preparation. The nanosized Cu particulates were produced by using a Nd:YAG laser (Quantel Brilliant) operated at 10 Hz. The fundamental 1064 nm light without focusing was conducted through the opening into the vial containing 0.02 g CuO powder (99.999%) and 5 mL of 2-propanol.

Figure 1 shows the UV-Vis spectra of copper colloids in 2-propanol. It was found that a laser fluence of 509 mJ/cm^2 for only 5 min resulted in deep wine-red solutions. An absorption band appeared at 580 nm is due to the surface plasmon of Cu nanoparticles. Prior to measuring absorption spectra, the ablated solutions were centrifuged to remove the rest of CuO powder. We have also irradiated the colloidal solutions, which no longer contained CuO powder, of Figure 1a with the same laser power for an additional five min. The color of the solutions did not change and the surface plasmon band remained at 580 nm, while the absorbance decreased, as illustrated in Figure 1b.

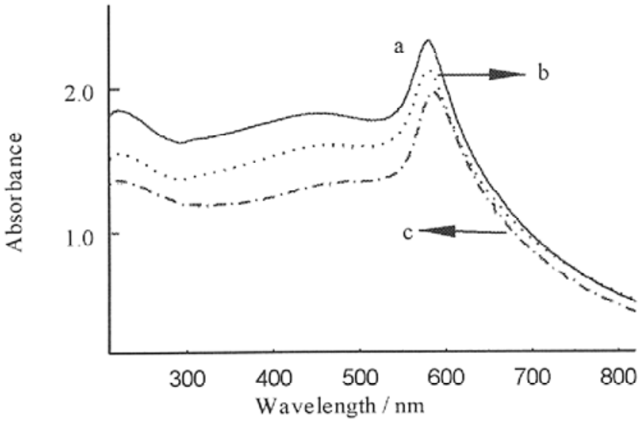

Figure 1. UV-Vis absorption spectra of copper colloids prepared in 2-propanol by 1064 nm laser light with 509 mJ/cm^2 of laser intensity: (a) 5 min of irradiation time, (b) additional 5 min of irradiation time for (a) colloidal solution, (c) after aging of (b) colloidal solution for 5 days.

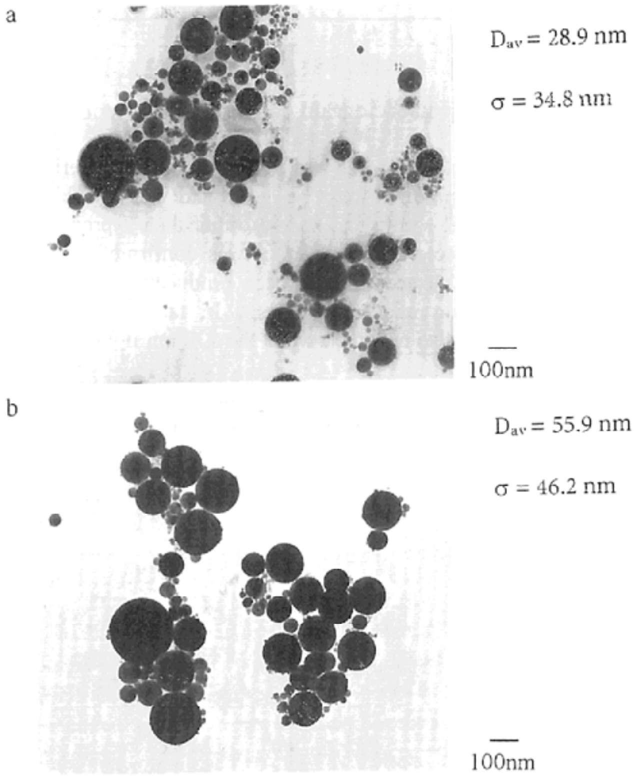

Figure 2. TEM images, a and b, corresponding to Figure 1a and 1b, respectively.

Figures 2a and 2b reveal the corresponding transmission electron microscopic (Hitachi FE-2000) images of the colloids shown in Figures 1a and 1b, respectively. From the transmission electron micrographs, it is apparent that the number of small particles with diameter less than 2 nm became much fewer and the average diameter increased from 28.9 nm to 55.9 nm upon going to Figure 2b from Figure 2a. These results suggest that the photoinduced aggregation occurred to produce larger particles from single stage irradiation (Figure 1a) to two-stage irradiation (Figure 1b). Figure 3 shows the XRD pattern acquired from the sample after the two-stage irradiation. The diffraction peaks at 43.2° (43.3°), 50.3° (50.3°), and 74° (73.8°) correspond to the formation of metallic copper, where the numbers in parentheses are 2θ of standard Cu.

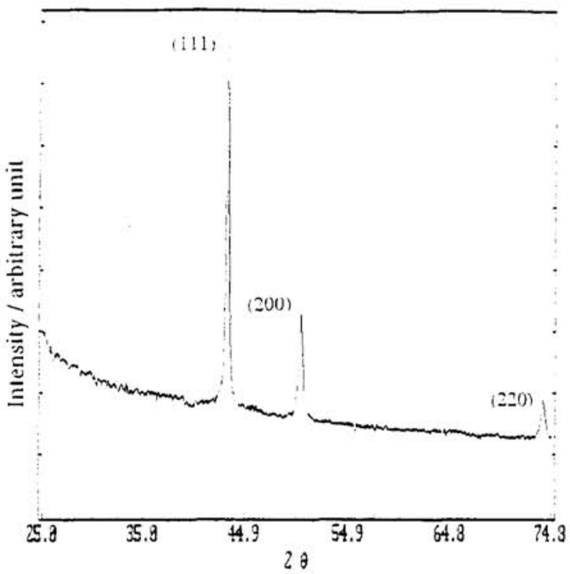

Figure 3. X-ray diffractogram of copper nanoparticles.

Because high laser power was employed in this experiment, a side reaction product may be generated during ablation. Based on ^{1}H-NMR results, no species other than 2-propanol in solution were detected. However, it was confirmed by a gas chromatography that acetone had been produced, accompanied with the formation of Cu particles. In fact, formation of acetone had been also observed when the 532 nm light was used as the source.[12]

It is surprising that copper colloids made either by one-stage or two-stage irradiation exhibited much better stability than those of previous reports.[5-9] After aging for five days, the absorbance (Figure 1c) was decreased by only 7% and the surface plasmon peak was red-shifted about 6 - 8 nm relative to the spectrum of the Figure 1b. The colloidal solutions still showed a wine-red color, while some precipitates were observed. The particle sizes presented here are significantly larger than those of previous studies; although a few conditions generated sizes around 20 nm, most of the cases displayed particle diameters of less than 10 nm.[5-9] The unusual stability of the present Cu colloids may be attributed to larger sizes, which are less active. Another possibility is the alcohol, which may be responsible for the stabilization of Cu nanoparticles.[13] Toshima has synthesized Cu-containing colloids without protective reagent, which were stable against air in the presence of glycol.[14] We have also found that the oxidized colloids, after aging, can be reversed back to the solution with λ_{max} (surface plasmon band) at 580 nm by employing a laser light.[12]

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