Oxidation-resistive copper nanoparticles: photoreduction synthesis and their oxidation state measurements by XAFS and HRTEM

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Abstract. We examined the synthesis of copper nanoparticles by photoreduction, and characterized them using optical spectroscopy, XAFS measurement, and electron microscopy. Ethanol solution of copper acetate with TiO₂ nanoparticles was photoirradiated. Optical absorption observation indicated that copper nanoparticles were formed in the solution. XAFS measurement indicated that the nanoparticles were metallic, not oxidized. Electron microscopy observation exhibited that the nanoparticles kept metallic even under exposure to air.

1. Introduction
Copper nanoparticles have attracted much attention because they have a potential for substitution of precious and worth metal nanoparticles such as gold nanoparticles [1-2]. In fact, various synthesis methods have been studied, but they usually use radical and hazardous reagents such as hydrazine in order to reduce copper ions which are more difficult to reduce than noble metal ions [3-4]. In addition, they are usually obtained more or less oxidized because of their high reactivity [5]. In these points of view, it is important to establish the environmental-friendly synthesis method and to confirm the oxidation state of produced nanoparticles.

In this study, we have examined synthesis of copper nanoparticles by environmental-friendly photoreduction method, which has been developed for synthesis of silver nanoplates [6]. The synthesized nanoparticles were characterized by optical absorption and electron microscopy. Additionally, oxidation state of the synthesized nanoparticles was measured by XAFS measurements.

2. Experimental
The synthesis of copper nanoparticles was carried out using a similar method to that reported previously [6-7]. In brief, copper acetate ((CH₃COO)₂Cu·H₂O, Wako Pure Chemical Industries) was
dissolved in ethanol solution which was diluted 10-fold with water, and its concentration was adjusted to 8 mmolL⁻¹. TiO₂ nanoparticles dispersion was added to the copper acetate solution without any degassing processes, and was sealed. The mixed solution was photoirradiated using a high-pressure Hg lamp (USH-500SC, Ushio) equipped with a wavelength-selective mirror (UV365, Ushio) for 24 h at room temperature.

The obtained dispersion was analyzed by optical absorption, and Cu K-edge XAFS (JASRI, Hyogo, Japan). The Cu K-edge XAFS spectra were measured at beam line BL01B1 with fluorescence mode. The XAFS spectra were analyzed by the program package REX2000 (Rigaku Co.). Model parameters for curve-fitting analysis (back scattering amplitude and phase shift) was extended from an EXAFS oscillations observed for Cu foil. Additionally, the dispersion was deposited onto a collodion-coated Cu grid under air, and was observed by high resolution TEM (spherical aberration corrected HD-2700 Type A, HITACHI High-Technologies Co.) operated at 200 kV equipped with EELS (electron energy-loss spectroscopy) analyzer.

3. Results and discussion

3.1. Optical spectroscopy measurements

When the initial dispersion started to be photoirradiated by Hg lamp, its color changed light blue to dark red rapidly. In its optical absorption spectrum, a peak ascribed to surface plasmon band for Cu nanoparticles was observed. This photosynthesis process of Cu nanoparticles is probably considered to be proceeded by two-step reaction as follows: pairs of electron and hole were induced by photons emitted from Hg lamp by help of TiO₂, and Cu²⁺ ions are reduced into Cu metal by the electrons. On the other hand, when the photoirradiated dispersion was exposed to air, its color changed dark red to light blue gradually. Furthermore, this light-blue dispersion was photoirradiated again, its color turned to dark red. These observations were almost the same as those previously reported [7], and this similarity indicates that reproducible copper nanoparticles were synthesized by the present method.

**Figure 1.** XANES spectrum for (a) Cu nanoparticles and (b) Cu foil. Fourier-transformed EXAFS spectrum for (c) Cu nanoparticles and (d) Cu foil.
3.2. XAFS measurements

Figure 1 shows XANES and Fourier-transformed EXAFS spectra for Cu nanoparticles and Cu foil. Since absorption edge and peak profile in the XANES spectrum are found to be almost coincident, the oxidation state of the Cu nanoparticles is considered to be metallic. In the EXAFS spectrum, as the highest peak is distributed in the same range for both, this peak can be assigned to the scattering from the first nearest-neighbor Cu atoms.

Table 1 shows summary of curve-fitting analysis for Cu nanoparticles. The coordination number of 11.9 for the Cu nanoparticles agrees well with that for the Cu foil, and this suggests that the Cu atoms in the nanoparticles are fully coordinated with the first nearest-neighbor Cu atoms as the fcc structure. In addition, the coordination distance of 0.259 for the Cu nanoparticles agrees well with that for the Cu foil. These results indicate that the Cu nanoparticles are composed of metallic Cu in solution. In addition, since the energy difference of 3 eV and R factor of 0.38 % are small enough, the curve-fitting process was considered to be well conducted.

| Samples    | Coordination | Number  | Distance | $dE^a$ | $\sigma^b$ | $R^c$ |
|------------|--------------|---------|----------|--------|-----------|-------|
| Cu NPs     | Cu-Cu        | 11.9±0.9| 0.259±0.001| 3±2    | 0.0060    | 0.38  |
| Cu foil    | Cu-Cu        | 12.0    | 0.256    | 0      | 0.0060    | -     |

$^a$ Energy difference in the absorption threshold between the model compounds and Cu NPs.

$^b$ Debye-Waller factor (fixed).

$^c$ R factor.

Figure 2. High-resolution TEM image for Cu NPs.
3.3. HRTEM observations

Figure 2 shows the HRTEM image for the Cu nanoparticles. Spacing of the lattice fringes is 0.21 nm, and this corresponds well with that for Cu metal. This can be confirmed by EELS spectrum shown in Figure 3(a). This profile is almost the same for metallic Cu, neither CuO nor Cu_{2}O [8]. In addition, even in the surface of nanoparticle in Figure 2, no oxides are observed. In fact, as shown in Figure 3(b), no distribution indicates that there are no substances relevant to oxygen. Considering the treatment of the specimen under exposure to air, the Cu nanoparticles synthesized by the present method are oxidation resistive.

![Figure 3. Electron energy loss spectra for Cu NPs. (a) Cu L and (b) O K absorption edge.](image)

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