

Preparation of Cu₂O nanoparticles dispersed in NH₂-terminated polyethyleneoxide matrix

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Abstract. Small Copper (I) oxide, Cu₂O, nanoparticles dispersed in diamine-terminated polyethyleneoxide (PEO-NH₂) matrix have been successfully prepared by vacuum evaporation of copper onto the molten PEO-NH₂. The obtained composite were characterized by TEM, electron diffraction, TG-DTA and FT-IR spectroscopy. The stable composite, in which the Cu₂O nanoparticles are stabilized through interaction between NH₂ chain end groups of PEO molecules and Cu₂O nanoparticles was obtained when the samples were heat-treated at 110 °C. The mean size of the Cu₂O nanoparticles increased from 2.5 to 3.5 nm in diameter upon increasing the amount of initial Cu deposition. The obtained composite material having a waxy texture was soluble in many solvents without aggregation and can be handled as a simple chemical compound for starting material in various applications.

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1 Introduction

For the past two decades, metal and semiconductor nanoparticles have attracted much attention because of their unique properties such as plasmon absorption and nonlinear optical susceptibility [1–3], and have potential towards application as electronics device as well as catalyst. In such materials there have been a wide variety of preparation methods that involves various chemical and physical techniques. The method of liquid phase reduction of metal salts by chemical reaction in the presence of protective agents is a well-known techniques in colloid chemistry for preparation of metal nanoparticles [4]. By using the wet process preparation of various kinds of nanoparticles have been reported and the obtained nanoparticles can be uniformly dispersed in the solution with relatively narrow size distribution. However, there are some problems with this wet process, *e.g.*, difficulty of mass production and removal of by-product (metal ions and/or residual organic solvent).

Vapor synthesis technique, the majority of which utilize the condensation of atomic metal vapor into a dispersing medium or an inert gas, is another successful physical technique for preparation of nanoparticles [5,6]. The phys-

ical method has an advantage that if one select a suitable kind of materials it can make stable metal particle dispersion without any stabilizing agent such as ions, polymers or surfactants as is usually the case in liquid phase reduction methods.

We have previously reported the preparation of highly concentrated gold nanoparticles dispersed in NH₂-terminated polyethyleneoxide (PEO-NH₂) by using vacuum evaporation technique followed by heat treatment [7]. In this technique, stable composite materials consisting of PEO containing uniformly dispersed Au nanoparticles have been successfully prepared, and the obtained composite can be dissolved into various kinds of solvents. Thus, the composite prepared by this technique can be useful as a starting material for various applications.

In this paper we report on preparation of the composite films consisting of Cu₂O nanoparticles dispersed in PEO-NH₂ matrix. Cu₂O is known as p-type semiconductor and exhibit characteristic exciton absorption at low temperature [8–10]. Although characteristics of Cu₂O films have been studied in detail [11–15], there are few studies related to preparation of copper (I) oxide nanoparticles [16,17]. For the characterization of the composite films, transmission electron microscope (TEM), thermogravimetry-differential thermal analysis (TG-DTA), and Fourier-transform infrared (FT-IR) spectroscopy were used. We

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also discuss the formation process of the composite and interaction between dispersed Cu_2O nanoparticles and the matrix.

2 Experimental

The $\text{Cu}_2\text{O}/\text{PEO-NH}_2$ composite films were prepared by vacuum evaporation technique. The average molecular weight and the amine content of the PEO-NH_2 was *ca.* 2000 and *ca.* 0.08 Meq/g, respectively. The melting temperature (T_m) was *ca.* 50 °C as confirmed by differential thermal analysis. The ethanol solution containing 50 wt% PEO-NH_2 was prepared at room temperature. The solution was then spin-coated on a glass substrate (1500 rpm) and heat-treated at 50 °C for 30 min in air to remove residual solvent. The thickness of the matrix film was *ca.* 7 μm .

Cu metal (99.99%) was vapor deposited on the matrix film heated at 50 °C with various thickness from a tungsten basket at a pressure of 5.0×10^{-1} torr. The deposition rate was set to 1.5 nm s^{-1} as monitored by a quartz-crystal microbalance. After the deposition, the films were heat-treated at 110 °C for 30 min in air.

The size distribution and the structure of dispersed nanoparticles were determined by HRTEM and SAED, respectively, with a JEOL JEM-2010 electron microscope operating at 200 kV. The samples for TEM observation were prepared by dropping methanol solution of the composite on thin carbon films supported on Cu grids. The Cu contents and the decomposition temperature of the matrix were determined by TG-DTA (Rigaku TAS-300). FT-IR spectra were measured by diffuse reflectance method using FT-IR instrument (FT/IR 615R, Japan Spectroscopic Co.). The spectra were recorded in a range of 700–4000 cm^{-1} at a resolution of 2 cm^{-1} .

3 Results and discussion

Figure 1 shows TEM images of the samples with the lowest (100 nm in thickness) and highest (700 nm) amount of deposited Cu. We can see in both images that small particles with nearly spherical in shape are uniformly dispersed and isolated individually. As shown in Fig. 2, SAED patterns for these samples were completely indexed as cubic Cu_2O with lattice parameters corresponding to those of bulk Cu_2O . TEM observation was performed for all the samples with different amount of deposited Cu. Consequently, it was confirmed that Cu_2O nanoparticles can be uniformly dispersed in the matrix, irrespective of initial amount of deposited Cu. Palkar *et al.* has reported that a decrease in particle size (below 25 nm) is to favor the Cu_2O phase over CuO due to increase in ionic character with decreasing particle size [18]. It seems thus likely that the particles in the present study are Cu_2O (not CuO) because the particle size is almost below 10 nm. In Fig. 3, the mean sizes dispersed of Cu_2O nanoparticles produced after heat treatment are plotted against initial amount of

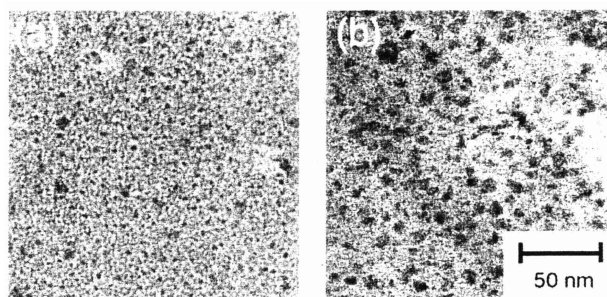


Fig. 1. TEM images of the dispersed particles in PEO-NH_2 matrix. Amount of initial Cu deposition: (a) 100 nm, (b) 700 nm.

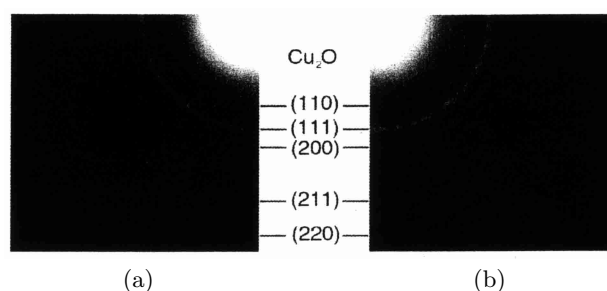


Fig. 2. Selected area electron diffraction patterns of the samples shown in Fig. 1. Amount of initial Cu deposition: (a) 100 nm, (b) 700 nm.

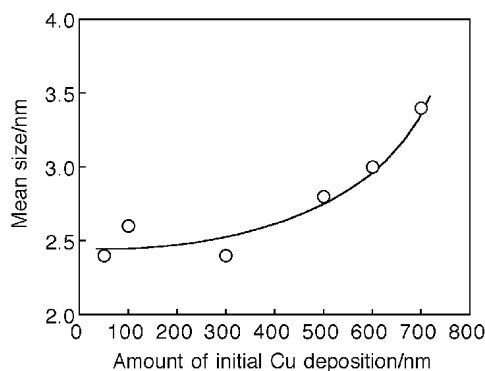


Fig. 3. Variations of mean sizes of the dispersed Cu_2O nanoparticles with the amount of initial Cu deposition.

Cu deposition. The particle size was obtained by counting 500 particles on the TEM images. The mean size is found to increase gradually as the amount of initial Cu deposition increases.

The Cu_2O content of the sample with highest amount of deposited Cu was *ca.* 40 wt% (calculated by TG-DTA measurement). This value is extremely higher than those prepared by other conventional methods (typical metal content is few wt% for liquid phase reduction method). The obtained $\text{Cu}_2\text{O}/\text{PEO-NH}_2$ composite was dark brown solid having wax-like texture at room temperature. It can

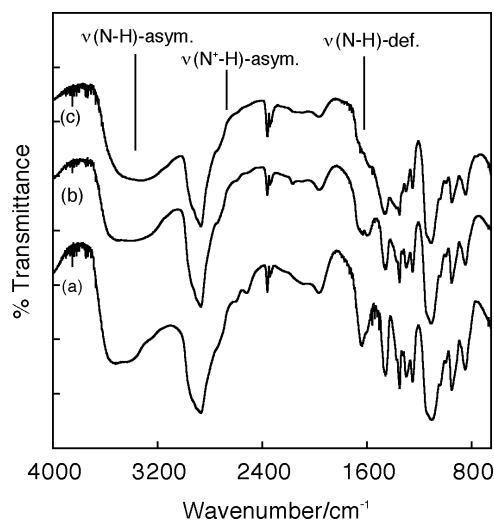


Fig. 4. FT-IR spectra of the matrix and composites. (a) PEO-NH₂ matrix, (b) sample with 100 nm of deposited Cu, (c) sample with 700 nm of deposited Cu.

be handled as a chemical compound and is soluble in various kinds of solvents, *e.g.*, stable dispersions such as water, methanol, toluene and chloroform are readily obtained. The composite and solution were very stable at room temperature with no indication of aggregation or coalescence occurring of the Cu₂O nanoparticles over several weeks. Figure 4 shows FT-IR spectra of the composite and PEO-NH₂ matrix. The spectrum of the matrix is well characterized by a bands attributed to the backbone modes of PEO together with the NH₂ end groups. In Fig. 4b, for the spectra of Cu₂O/PEO-NH₂ sample, the peaks assigned to N-H asymmetric (3400-3600 cm⁻¹) and defective vibration (1650 cm⁻¹) becomes broader towards lower wavenumber and decrease in intensity, respectively. In addition, the N⁺-H asymmetric vibration mode (2600 cm⁻¹) associated with the interaction among molecular chains disappears. These tendency is found to be much enhanced for the sample with increasing the amount of Cu deposition (Fig. 4c). These results suggest that the Cu₂O nanoparticles are stabilized through an interaction between the NH₂ end group and the Cu₂O surface.

In the case that the deposition of Cu was performed at room temperature (without heating of the PEO-NH₂ matrix), Cu thin film with metallic luster was formed on the matrix surface. In addition, when the polyethyleneglycol (having a OH end chain group) with same molecular weight was used as matrix, Cu thin film was also formed. These results indicate that both melting behavior of the matrix and amine group of the PEO molecules play an important role in the formation of the particles. During Cu deposition, since the substrate was heated at 50 °C (higher than melting temperature of the PEO-NH₂ matrix), the matrix behaved as viscous fluid which may allow a diffusion of deposited atoms and/or clusters [19–21].

It is proposed that deposited Cu atoms are condensed to form small clusters at the surface region of the molten PEO-NH₂, where the particles are stabilized by adsorbed amine groups of the PEO molecules and further diffuse into the bulk phase of the matrix. In fact, during vapor deposition process, the color of the matrix film gradually changed from transparent to ruby red which is characteristic of the surface plasmon resonance of small Cu particles [22]. However, when the samples were taken out from vacuum chamber and exposed to air, the samples became green since the copper metal is generally liable to be oxidized by air (presumably particle surface are oxidized). After the heat treatment, it seems likely that they are completely oxidized and copper (I) oxide nanoparticles are formed.

Since the condensation kinetics are expected to be associated with Cu vapor flux, particle size can be varied not only by the amount of deposition but also by the deposition rate determined by the temperature of the Cu evaporation source. The temperature of the molten PEO-NH₂ matrix may also be a size determining factor because viscosity of the matrix changes according to its temperature. The studies related to these effects are currently under way and results will be reported elsewhere.

4 Conclusion

Using a vacuum evaporation technique, the composites consisting of Cu₂O nanoparticles dispersed in NH₂-terminated polyethyleneoxide matrix were reproducibly prepared. It is suggested that the deposited Cu atoms or clusters diffuse into the bulk phase of the molten matrix during deposition process to form Cu nanoparticles, and oxidation of the Cu particles is achieved when the deposited samples are exposed to air and heat-treated at 110 °C. IR studies of the composites revealed that the NH₂ end group of the matrix molecule are responsible for stabilization of the dispersed Cu₂O particles. The dispersed Cu₂O nanoparticles were relatively homogeneous in size, and the mean size of the particles was found to increase simultaneously as the amount of initial Cu deposition increases. The composites are very stable and can be dissolved in many organic solvents and re-precipitated. It is thus envisaged that the present composite containing highly concentrated Cu₂O nanoparticles are useful for a wide range of applications, *e.g.*, catalysis, sensors and microelectronics.

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