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Synthesis and characterization of Cu_2O nanoparticles dispersed in NH_2-terminated poly(ethylene oxide)

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Small copper(I) oxide, Cu_2O, particles dispersed in diamine-terminated poly(ethylene oxide) (PEO-NH_2) matrices have been successfully prepared by vacuum evaporation of copper on to molten PEO-NH_2, followed by heat treatment. The obtained composites were characterized by TEM, electron diffraction, viscometry, TG–DTA and FT-IR spectroscopy. The mean size of the Cu_2O nanoparticles could be controlled from 2.5 to 3.5 nm in diameter by changing the amount of initial Cu deposition. The composites obtained here have a wax-like texture and are soluble in many organic solvents with no evidence for aggregation. The formation mechanism of Cu_2O nanoparticles and the interaction between the nanoparticles and the matrix is also discussed.

Introduction

Metal and semiconductor nanoparticles have recently attracted much attention as amongst the most important materials because of their specific properties based on quantum size effects,[1,2] and thus these materials have widely been studied in various fields, *e.g.*, electronics devices[3–5] and catalysis.[6,7] For such materials there have been a wide variety of preparation methods based on various chemical and physical techniques.[8–14] Liquid phase reduction of metal salts in the presence of protective agents is a well-known technique in colloid chemistry for the preparation of metal nanoparticles.[15] However, for practical use of nanoparticles as functional materials, the wet process has several problems. For instance, it is not readily amenable to mass production or removal of by-product (typically metal ions and/or residual organic solvent).

We have previously reported a novel method of preparing gold nanoparticles dispersed in amine-terminated poly(ethylene oxide) (PEO-NH_2) by a vacuum evaporation technique and subsequent heat treatment.[16] In this technique, the obtained composite can be dissolved into various types of solvents, allowing the composite to be useful as a starting material for various applications. In this previous work, we have suggested that the amine group may be responsible for the stabilization of the gold nanoparticles. However, details relating to the stabilization mechanism are still incomplete.

In this paper we report on the preparation of composite films consisting of Cu_2O nanoparticles dispersed in a PEO-NH_2 matrix. Cu_2O is known as a p-type semiconductor and exhibits characteristic exciton absorption at low temperature.[5,17–19] The preparation of Cu_2O nanoparticles without aggregation is usually difficult as compared with that of noble metal nanoparticles because the protective ability of stabilizing agents conventionally used for copper nanoparticles may be weaker than those for noble metal nanoparticles. Therefore, there are few studies related to the preparation of Cu_2O nanoparticles.[20–22] The characteristics of the composite films are investigated by using high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), cone–plate viscometry, thermogravimetry–differential thermal analysis (TG–DTA) and Fourier transform infrared (FT-IR) spectroscopy. The formation process of the composite and interaction between dispersed Cu_2O nanoparticles and the matrix will be discussed.

Experimental

Composite films containing Cu_2O nanoparticles were prepared by the vacuum evaporation technique. PEO-NH_2 (Scientific Polymer Products) was used as the matrix. The average molecular weight and the amine content were *ca.* 2000 and *ca.* 0.08 meq. g^{-1}, respectively. The melting point was *ca.* 50 °C as confirmed by differential thermal analysis. An ethanol solution containing 50 wt% PEO-NH_2 was spin-coated on a glass substrate and then heat-treated at 50 °C for 30 min in air to remove residual solvent. The thickness of the matrix film was *ca.* 7 μm.

The matrix films were set in a vacuum evaporator (ULVAC EX-400-006) and held at 50 °C. Cu metal (99.99%) was then vapour deposited (with a variety of thicknesses) on the matrix film from a tungsten basket at a pressure of $<5.0\times10^{-5}$ Torr with a deposition rate of 1.5 nm s^{-1} as monitored by a quartz crystal microbalance. The thickness of the deposited Cu ranged from 50 to 700 nm. The deposited film was then cooled to room temperature in vacuum. The obtained films were heat-treated at 110 °C for 30 min in air.

The size distribution and structure of the nanoparticles were determined by HRTEM and SAED, respectively, using a JEM-2010 (JEOL) transmission electron microscope operating at 200 kV. The samples for TEM observations were prepared by

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dropping methanol solutions of the composite films on carbon coated copper grids. The Cu_2O content of the PEO-NH_2 in the composite films was determined by TG–DTA (Rigaku TAS-300 system). The viscoelastic behaviour of the composites and the PEO-NH_2 was characterized using a cone–plate viscometer (HAAKE VT550) at 50 °C. A plate of 10 mm in diameter and cone angle of 0.1 rad were used. The shear rate was gradually increased from 0.5 to 30 s^{-1} for 180 s, and the viscosity value at a shear rate of 30 s^{-1} was employed as the standard viscosity. IR spectra were measured using FT-IR (FT/IR 615R, Japan Spectroscopic Co.) in the diffuse reflectance mode to elucidate the interaction between the nanoparticles and PEO-NH_2.

Results and discussion

Fig. 1 shows typical HRTEM images of the samples with the lowest (50 nm in thickness) and highest (700 nm) amount of deposited Cu. In both images, we can see that small nearly spherical particles are uniformly dispersed and isolated individually. The structure of these nanoparticles was assigned to the cubic Cu_2O crystalline modification with lattice parameters corresponding to those of bulk Cu_2O from SAED patterns (inset in Fig. 1). TEM observation was performed for all the samples with different amounts of deposited Cu and similar results were obtained. Bulk copper oxide is known to be stable as CuO below 1100 °C in air atmosphere. Palkar *et al.* have reported that a decrease in particle size (below 25 nm) favors the Cu_2O phase relative to CuO.[23] They have proposed that the ionic character of a solid tends to increase with reduction in particle size. From similar consideration, the particles obtained in this study are Cu_2O because the particle size is almost below 10 nm. The color of the matrix film gradually changed from transparent to ruby red during the vapour deposition process, which is characteristic of the surface plasmon resonance of small Cu particles.[24] However, when the samples were taken out from the vacuum chamber and exposed to air, they become green due to oxidation of the copper metal (presumably the particle surface is oxidized). After heat treatment, it seems likely that the particles are completely oxidized and Cu_2O nanoparticles are formed.

In the present preparation technique, the content of the Cu_2O nanoparticles in the matrix increased as the amount of initial Cu deposition increases. From the results of TG–DTA measurements (not shown), the Cu_2O content of the sample with deposited Cu thickness of 700 nm (Fig. 1b) is *ca.* 40 wt%. This value is much higher than that of composites prepared by other conventional methods (typical metal content is a few wt% for the liquid phase reduction method).[10,12] In addition, since the Cu_2O content increases in proportion to deposited Cu thickness, the content can be controlled over a wide range by varying the amount of initial Cu deposition. The obtained Cu_2O/PEO-NH_2 composite was a dark brown solid with a wax-like texture at room temperature. The composite is soluble in various solvents, forming stable dispersions in water, methanol, toluene and chloroform. The composite and its solutions are very stable at room temperature with no indication of aggregation or coalescence occurring for the Cu_2O nanoparticles over several weeks. The obtained nanoparticles can therefore be useful as a starting material in various applications.

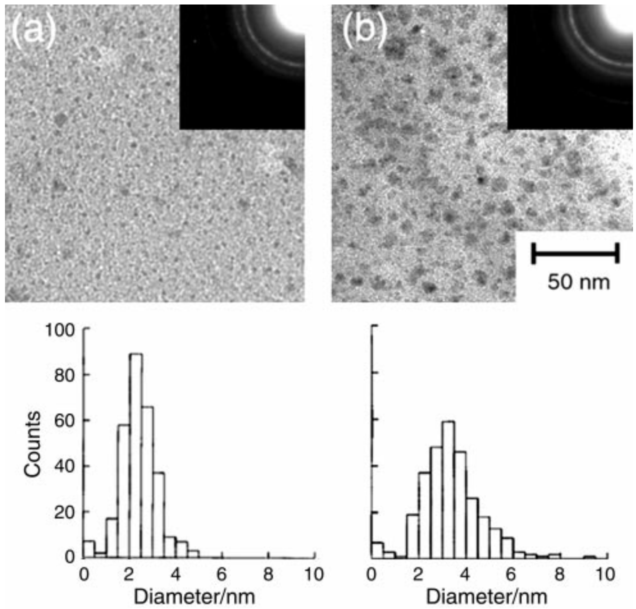

Fig. 1 TEM images, SAED patterns and corresponding size histograms of the composites. The thickness of deposited Cu is (a) 50, (b) 700 nm.

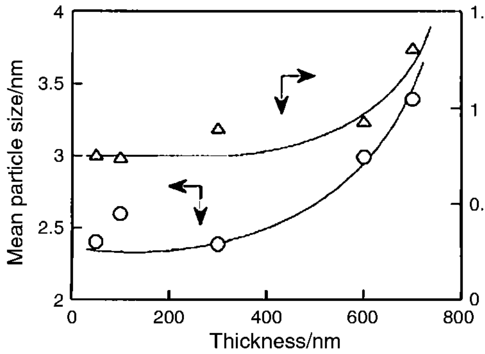

Fig. 2 Variations of mean size and standard deviation of dispersed Cu_2O particles with the thickness of deposited Cu.

In Fig. 2, the mean sizes and standard deviations of Cu_2O nanoparticles produced after heat treatment are plotted against the initial amount of Cu deposition. The mean sizes are nearly constant for up to 300 nm deposition thickness and then increase as the amount of Cu deposition increases. A similar tendency is observed for the profile of the standard deviation. Fig. 3 shows plots of viscosity values for the composites with deposition thicknesses of 50, 100 and 300 nm. Samples with deposition thickness of more than 500 nm showed too high a viscosity to measure under the experimental conditions (50 °C). All the plots exhibit non-linear viscoelastic behaviour. It is well known that composites consisting of polymer and colloidal particles exhibit non-linear viscoelastic behaviour such as shear thinning, thixotropy, rheopexy and dilatancy.[25,26] Such behaviour is generally explained in terms of the breaking up of aggregates of colloidal particles under a shear field. In all the samples, the shear viscosity decreases with increasing the shear rate below 10 s^{-1} and the behaviour is characterized by thixotropy.[27,28] This indicates that the Cu_2O nanoparticles show chemical interactions with the matrix. Moreover, the samples can be regarded as a typical model for a suspension because the size distribution of the particles is relatively narrow

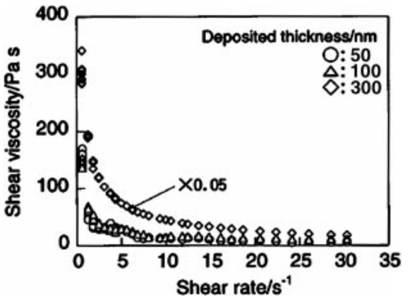

Fig. 3 Plots of shear viscosity as a function of shear stress for the composites at 50 °C.

Table 1 Relationship between deposited Cu thickness and standard viscosity of the composites: data obtained at 50 °C

Cu thickness/nm	0	50	100	300
Standard viscosity/Pa s	4.3	6.5	10.9	357.0

and each nanoparticle is completely dispersed with no evidence for aggregation, *i.e.*, only the size and the amount of the Cu_2O nanoparticles affect the viscoelastic behaviour. Further detailed study is, however, required and results will be reported elsewhere. In this study we employed the viscosity value obtained at a shear rate of 30 s^{-1} as the standard viscosity, and results are listed in Table 1. The values up to 100 nm in the deposited Cu thickness are comparable with that of the bulk matrix. The standard viscosity remarkably increased for a deposition thickness of 300 nm.

We note that the matrix melts during Cu deposition since the matrix is heated at 50 °C (the melting point is *ca.* 50 °C), and the standard viscosity of the composites is comparable with that of the bulk matrix. Therefore the matrix behaves as a viscous fluid which may allow a diffusion of deposited atoms and/or clusters.[29,30] It is proposed that deposited Cu atoms are condensed to form small clusters at the surface region of the molten PEO-NH_2, where the particles are stabilized by the matrix and further diffuse into the bulk phase of the matrix. Under these conditions, nuclei are predominantly formed, and thus the mean size is mostly unchanged at the early stage of the deposition.

In Fig. 3, for the sample with a deposited Cu thickness of 300 nm, the viscosity is extremely high ($>$ 6000 Pa s) at around zero shear rate (*i.e.*, condition at which the Cu deposition was performed). We suggest that, as the deposited Cu thickness increases, the deposited Cu is localized near the matrix surface due to an increase of the viscosity of composites, and the coalescence of the Cu nanoparticles proceeds non-homogeneously in the matrix. As a result, the local volume fraction of the particles remarkably increases near the surface region so that the particles undergo coalescence, which leads to an increase in the mean size of the particles.

Fig. 4 shows FT-IR spectra of the composite and PEO-NH_2 matrix. The spectrum of the matrix is well characterized by bands attributed to the backbone modes of PEO together with the –NH_2 end groups. In Fig. 4b, for the spectra of Cu_2O/PEO-NH_2 sample, the peaks assigned to N–H asymmetric (3400–3600 cm^{-1}) and deformation 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 changes are increasingly pronounced for the sample with increased amount of Cu deposition (Fig. 4c). These results suggest that the Cu_2O nanoparticles are stabilized through an interaction between the –NH_2 end groups and the Cu_2O surface.

Conclusion

By using a vacuum evaporation technique, composites consisting of Cu_2O nanoparticles dispersed in NH_2-terminated poly(ethylene oxide) matrices have been reproducibly prepared. The mean size and the concentration of the particles were found to be highly controllable in a wide range by changing the initial amount of Cu deposition. IR studies of the composites revealed that the NH_2 end groups of the matrix molecule are responsible for stabilization of the dispersed Cu_2O particles. The composites obtained here were very stable and can be dissolved in many organic solvents and re-precipitated.

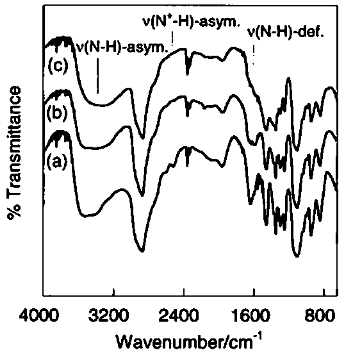

Fig. 4 FT-IR spectra of the composites. The thickness of deposited Cu is (a) 0, (b) 100, (c) 700 nm.

It is thus envisaged that the present composites containing highly concentrated Cu_2O nanoparticles will be useful for a wide range of applications, *e.g.*, catalysis, sensors and microelectronics.

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