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A novel method of preparing nano-sized gold and palladium particles dispersed in composites that uses the thermal relaxation technique

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Abstract. Stable nano–sized gold and palladium particles dispersed in composites were prepared by way of the thermal relaxation technique. Continuous formation and dispersion of metal particles into a nylon–11 oligomer film were achieved by the heating of the oligomer film to 46 °C during a vapor deposition of the metal. The mean particle size in the composite was 4.4 nm (S.D. = 1.7 nm) for the gold particles prepared by the deposition of about 3.6×10^{18} atoms cm^{-2}. For the palladium particles the particle size was 2.3 nm (S.D. = 0.67 nm) and the deposition 4.2×10^{18} atoms cm^{-2}. The obtained composite of gold or palladium particles was readily dissolved in CH_2Cl_2, producing stable colloidal solutions. The procedure reported here is very effective for preparing a great deal of metal particles dispersed in composites.

PACS. 81.20.Zx Other methods of materials synthesis and materials processing – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 07.30.-t Vacuum apparatus and techniques

1 Introduction

Many preparation methods for nano-sized metal particles have been developed because of the attractive optical properties caused by the quantum size effect [1–4]. These preparation methods can be grouped into two types. One is a gas phase process, and the other is a liquid phase one. A vacuum evaporation into running oil [5] is a typical example of the former type. This method provides finely dispersed particles in oil. The latter type includes some chemical methods such as reduction of metal precursors in a solution [6] and reverse micelles [7]. Surfactants are frequently required to stabilize the metal particles produced in the solution, since the nano-sized particles having large surface area show the tendency to agglomerate in order to lower the surface energy. Polymers are often used to protect the nano-sized particles from agglomeration by the steric repulsion effect [8]. They are very useful for obtaining solid composites containing nano-sized metal particles.

We proposed a preparation method for nano-sized metal particles that uses the thermal relaxation technique [9]. By using this technique, a composite consisting of polymer and homogeneously dispersed nano–sized metal particles is produced. Structural relaxation from a metastable state to a stable state of the polymer causes a dispersion of the nano-sized particles into the polymer. Recently, we found that the nylon–11 oligomer prepared through a thermal degradation was available for preparing the composite [10]. A dispersion of gold particles into the nylon–11 oligomer was confirmed in a vapor–deposited gold having a thickness of 20 nm, but a large amount of deposition of gold did not bring about the dispersion of the gold particles.

In this paper, we improved the preparation method by simultaneously heating the nylon–11 oligomer film during the vapor–deposition, and succeeded in preparing a great deal of gold particles and palladium particles dispersed in composites, which have attracted much interest in their catalytic properties [11, 12].

2 Experimental

Nylon–11 oligomer was prepared by a thermal degradation of nylon–11 (Toray Industries) [10]. Molecular weight was in the range of 600 to 800 and measured by a gel permeation chromatograph (Shimadzu LC-10A). The nylon–11 oligomer was mixed with diethylene glycol monoethyl ether, and was coated on a glass substrate to produce a thin film having a thickness of about 75 μm. Gold (99.999%) or palladium (99.999%) was vapor-deposited by the irradiation of an electron beam onto the nylon–11 oligomer films under a vacuum of about 6.7×10^{-3} Pa in a ULVAC

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EX-400 evaporator. The oligomer films were heated at 46 °C during the vapor deposition. A deposition rate of about 30 nm min^{-1} was monitored by a quartz–crystal microbalance. The metal-deposited oligomer films were heat-treated at 120 °C for 10 min so that the dispersion of the particles could be homogenized, and then they were dissolved in CH_2Cl_2. The solutions were filtrated through a 0.8 μm PTFE filter, and solids were obtained after the evaporation of CH_2Cl_2.

The samples were characterized by visible spectroscopy (VIS), X-ray diffraction (XRD), and transmission electron microscopy (TEM). VIS spectra were measured using Shimadzu 3100. XRD patterns were obtained through the use of Cu K_α radiation on Rigaku RINT-2000. TEM images were observed by Hitachi H-7100TE and JEOL JEM-2010, equipped with a Voyager microanalysis system of Noran Instruments. TEM specimens were prepared by the drying of drops of the CH_2Cl_2 solutions of the samples on carbon-coated Cu grids. Particle size distribution was obtained by measuring more than 1000 particles in TEM images.

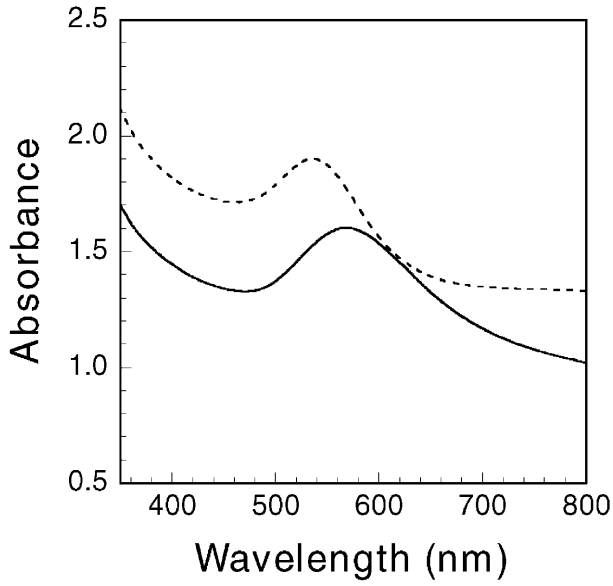

Fig. 1. VIS spectra of the gold (1.2×10^{17} atoms cm^{-2}) deposited nylon–11 oligomer film at 46 °C before (solid line) and after (dashed line) the heat treatment at 120 °C for 10 min.

3 Results and discussion

3.1 Preparation of the nano-sized gold particles

In the thermal relaxation technique using the nylon–11 oligomer, gold particles are dispersed into a film of the nylon–11 oligomer from a thin layer of gold particles formed on the oligomer film [10]. However, a large amount metal deposition causes undesirable aggregation or film formation, and therefore the dispersion of the gold particles does not occur. For the the thermal relaxation technique to be applied to a preparation of a large amount of metal particles, an improvement is required. We found that heating a matrix to a temperature at which a molecular motion of a matrix begins, in the thermal relaxation technique [13], was effective for dispersing metal particles during a vapor deposition.

When gold was vapor-deposited with a thickness of 20 nm (ca. 1.2×10^{17} atoms cm^{-2}) onto a nylon–11 oligomer film kept at room temperature, a sample (gold/nylon–11 oligomer film) showed gold color on the surface. The thickness of 20 nm was the upper limit of the dispersion of gold, deposited at room temperature, into the oligomer film; above this limit, gold conglomerates were left on the surface of the oligomer film. The gold color indicated that the vapor-deposited gold was localized on the surface of the oligomer film.

On the other hand, when the gold/nylon–11 oligomer film was prepared with the same deposition of gold onto the nylon-11 oligomer kept at 46 °C, the film exhibited a transparent deep blue color immediately after the preparation. The temperature of 46 °C was selected from the thermal behavior of the nylon–11 oligomer measured by a differential thermal analysis. The transparent deep blue color indicated that gold vapor–deposited at 46 °C was not localized on the surface of the oligomer film.

Figure 1 shows VIS spectra of the gold-deposited oligomer film prepared at 46 °C. The film shows a single absorption band at 567 nm; the band shifted to 535 nm after the heat treatment at 120 °C, which was chosen to be the point where the nylon–11 oligomer begins to melt partially. The difference among the backgrounds of the spectra are a result of the difference in the scattering of light of the films. Nano-sized gold particles show a plasmon resonance absorption band in visible light region [14]. The band at 567 nm indicates that the vapor-deposited gold was totally embedded in the form of the nano-sized particles in the nylon–11 oligomer. However, it was too high as the plasmon band for fairly isolated gold particles [14]. Coagulation or a filling factor of the particles in the matrix affects the absorption of the gold particles, but the former usually brings about a double peak structure. In addition, TEM observation of the film after the heat treatment indicates that nano-sized gold particles having a mean size of 4.5 nm (S.D. = 1.1 nm) were dispersed separately from each other in the nylon–11 oligomer film. Therefore, the high peak position of the plasmon band is a result of the large filling factor per unit volume, which suggests that the gold particles were localized in a narrow region of the nylon–11 oligomer film. The shift of the plasmon band after the heat treatment indicates that the filling factor per unit volume decreased as the result of the dispersion of the gold particles into the inside of the oligomer film.

For the preparation of the gold-deposited oligomer film with gold about 600 nm thick (about 3.6×10^{18} atoms cm^{-2}), the vapor deposition began at 46 °C, and the temperature was elevated to 60–70 °C by irradiation from the evaporation source. Appearance of the product was almost black, but thinner parts exhibited transparent ruby red color. Deposited gold had completely dispersed into the matrix as nano-sized particles. The content of the gold particles was 14.9 wt % after they were calcined at 900 °C

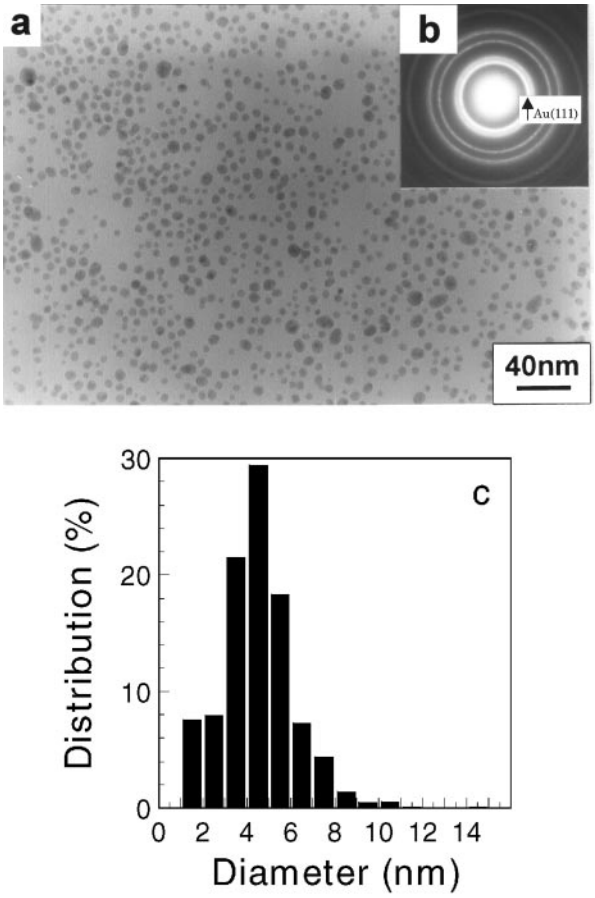

Fig. 2. (a) TEM image and (b) electron diffraction of the gold particles in the nylon–11 oligomer prepared at 46 °C. (c) Particles size distribution of the gold particles. Deposition of gold was ca. 3.6×10^{18} atoms cm^{-2}.

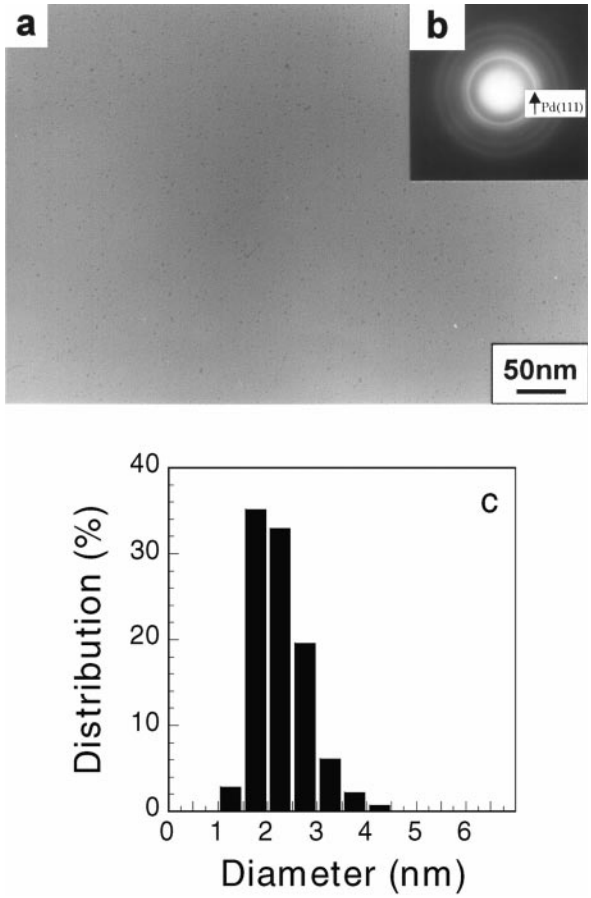

Fig. 3. (a) TEM micrograph. (b) Electron diffraction of the palladium particles in the nylon–11 oligomer prepared at 46 °C. (c) Particle size distribution of the palladium particles. Deposition of palladium was about 1.4×10^{17} atoms cm^{-2}.

for 1 hr in air. The product was stable, and no condensation of metallic gold has been observed for more than a year.

The product with gold deposition of about 3.6×10^{18} atoms cm^{-2} easily dissolved into organic solvents and gave a transparent ruby red solution. VIS spectra of the solution having the plasmon band at 524 nm proved the formation of the colloids of unaggregated gold particles. The colloids were very stable for more than one month. This suggested that the nylon–11 oligomer stabilized the gold particles in the solution.

A TEM image of this product showed the well-dispersed nano-sized particles (Fig. 2a). Elemental microanalysis and electron diffraction (Fig. 2b) indicated that the particles were gold crystal. The mean size of 4.4 nm (S.D. = 1.7 nm) in Fig. 2c was almost as same as 4.5 nm (S.D. = 1.1 nm) for the deposition of 1.2×10^{17} atoms cm^{-2}, and it was independent of the amount of the deposition.

3.2 Preparation of the nano-sized palladium particles

Palladium particles were able to be prepared by the same method described above. The color of the product prepared with 20 nm deposition of palladium (1.4×10^{17} atoms cm^{-2}) was black, and the color became more dark with the increase in the deposited thickness to 600 nm (4.2×10^{18} atoms cm^{-2}). The XRD pattern was very broad, even for the product with a 100 nm deposition of palladium, and indicated that very small crystallites were formed [15].

These products were readily dissolved into organic solvents, giving stable colloidal solutions. In absorption spectra, absorbance increased with an increase in the amount of the deposition.

Figure 3a shows a TEM image of the product prepared with a palladium deposition of 1.4×10^{17} atoms cm^{-2}. The existence of palladium crystals was confirmed by the elemental microanalysis and electron diffraction (Fig. 3b). An isolated distribution of very small particles was observed, and the mean size was 2.2 nm (S.D. = 0.56 nm), as is shown in Fig. 3c.

The size distribution of the nano-sized palladium particles became a little broad when 30 times the amount of palladium was deposited. However, the mean diameter of 2.3 nm (S.D. = 0.67 nm) was almost the same as that for the sample shown in Fig. 3, and comparable with the particles prepared by the other method [16].

Table 1. The mean size and the standard deviation (S.D.) of the metal particles dispersed in the nylon–11 oligomer.

metal	thickness (nm)	amount of deposition (atoms cm^{-2})	mean size (nm)	S.D. (nm)
gold	20	1.2×10^{17}	4.5	1.1
	600	3.6×10^{18}	4.4	1.7
palladium	20	1.4×10^{17}	2.2	0.56
	100	7.0×10^{17}	2.2	0.57
	600	4.2×10^{18}	2.3	0.67

4 Summary

The mean sizes and the standard deviations (S.D.) of the metal particles prepared by the thermal relaxation technique are summarized in Table 1. We suppose that the particle size of the nano-sized metal particles, which were prepared by the thermal relaxation technique, is dependent on the deposition rate of metal and the dispersion rate of metal particles produced. The particle size of each metal was almost the same value, independent of the amount of metal deposition. Therefore, we consider that the deposition rate of metal and the dispersion rate of metal particles into the nylon–11 oligomer film were almost constant in the experimental condition adopted in this study.

Preparations of the nano-sized particles were successfully achieved by simultaneous heating during the vapor deposition of gold. This procedure has a great deal of advantages compared to previous methods [14]. It is applicable to a mass the nano-sized metal particles produced in a very short time, even when the content of the metal particles is very large. The composites prepared by this procedure are very stable in not only the solids but also the solutions. The metal particles do not aggregate, even if the composites are solidified from the colloidal solutions; the solidified composites are readily re-dissolved in the solvents.

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