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Production of gold nanoparticles-polymer composite by quite simple method

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Abstract. Recently, production methods of metal nanoparticles have been investigated extensively, not only for a research use in laboratory, but also for an industrial use. However, it is difficult to obtain metal nanoparticles in high amounts and concentrations with simple methods. In this study, a gold nanoparticle-polymer composite was prepared with a simple procedure using a gold salt and a melted polymer. The composite, which is in a wax state at room temperature, was highly soluble in water and lower alcohols, moreover the composite was melted at about 50 °C.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 81.07.-b Nanoscale materials and structures: fabrication and characterization – 81.16.-c Methods of nanofabrication and processing

1 Introduction

Metal nanoparticles are attracting attention as new materials for electronics, magnetics, optics, and catalysts because their chemical and physical properties are different from those of both bulk and atom [1–4]. It is well-known that the particular properties change mainly with the particle size [5,6]. Recently, metal nanoparticles have been used as an industrial material, such as catalyst and colorant [7,8]. Considering the industrialization of the application of metal nanoparticles, it is significant to produce them by simple methods.

Production methods can be grouped into two types. One is a gas phase process, and the other is a liquid phase process [9,10]. Reduction methods, in which metal ions are reduced to the metal nanoparticle easily and quickly, is suitable not only for a research use in laboratory but also for an industrial use in liquid phase processes. Production techniques of metal nanoparticles by using reduction methods have been investigated extensively [11–14]. In the case of a reduction method, a solvent, a reducing agent, a metal salt and a protective agent are generally used [10]. This method is easy, however, there are some problems such as impurities from the reducing agent and difficulties obtaining the high amount and concentration of nanoparticles with one-step operation. Moreover, it is difficult to handle because the product is in the liquid state.

In this communication, we present a new simple method, which produces a gold nanoparticle-polymer composite without the difficulties of current methods. This composite was produced from a gold salt and a polymer that melts at 50 °C. It is suggested that the polymer has the combined functions of a reducing agent, a protection agent and solvent.

2 Experimental

Polyethyleneoxide diamine terminated (PEO-NH_2; Mw = 2,000), polyetyleneglycol (PEO-OH; Mw = 2,000) and hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4$) were purchased from Scientific Polymer Products Inc. and Wako Chemical Inc. A certain amount of $HAuCl_4$ and PEO-NH_2 was mixed at 100 °C under air. The weight ratio of $HAuCl_4$/PEO-NH_2 was altered from 1/3000 to 1/15 to confirm the upper limit of the gold concentration in the produced composite.

In order to trace the formation of gold nanoparticles, ultraviolet-visible (UV-Vis) spectra of mixture of $HAuCl_4$ and PEO-NH_2 ($HAuCl_4$/PEO-NH_2 = 1/3000) were measured *in situ* at 100 °C for 60 min by stirring under air with a SHIMAZU UV-3100PC using a 50 mm quartz cell. A 4.0 mM $HAuCl_4$ aqueous solution and a mixture of $HAuCl_4$ and PEO-OH ($HAuCl_4$/PEO-OH = 1/3000) were also measured in place of the mixture of $HAuCl_4$ and PEO-NH_2 for reference. The gold nanoparticles in the composite were characterized by transmission electron

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Table 1. The weight ratio of $HAuCl_4$/PEO-NH_2 and the color after heat treatment for 1 and 30 min.

$HAuCl_4$/PEO-NH_2	1 min	30 min
1/3000	pale yellow	dark red
1/600	pale yellow	dark red
1/300	pale yellow	dark red
1/150	pale yellow	dark red
1/75	pale yellow	dark red
1/60	pale yellow	dark red
1/30	pale yellow	cloudy brown
1/15	pale yellow	cloudy brown

microscope (TEM) with a JEOL-2010 at 200 kV accelerating potential. After the mixture of $HAuCl_4$ and PEO-NH_2 ($HAuCl_4$/PEO-NH_2 = 1/600) was heated at 100 °C for 30 min, it was diluted with distilled water to definite concentration, and a drop of the diluted aqueous solution on an amorphous carbon-coated copper grid was dried to prepare the specimen for TEM observation. The mean diameter of gold nanoparticle was estimated from 100 particles found in an arbitrarily chosen area in the TEM images.

3 Results and discussion

Table 1 shows the weight ratio of $HAuCl_4$/PEO-NH_2 and the color after heat treatment for 1 min and 30 min. As soon as the mixtures were heated to 100 °C with stirring, the polymer melted and $HAuCl_4$ dissolved in the melted polymer. The color of the mixture changed from pale yellow into dark red or cloudy brown after 30 min of heating. There was a borderline in the colors between 1/60 and 1/30 of $HAuCl_4$/PEO-NH_2. It is suggested that the upper limit of gold concentration is approximately 1/60. After allowing to stand for a few hours at room temperature under air, the composites became wax state.

Figure 1 shows *in situ* UV-Vis spectra of the mixture of $HAuCl_4$ and PEO-NH_2 during heat treatment at 100 °C for 60 min in the quartz cell. After heating for a few minutes, a peak corresponding to the surface plasmon resonance absorption of gold nanoparticles appeared around 530 nm [15]. The intensity of the peak increased gradually as heating time. Figure 2 shows *in situ* UV-Vis spectra of 4.0 mM $HAuCl_4$ aqueous solution during heat treatment at 100 °C for 60 min in the quartz cell. The peak attributed to $[AuCl_4]^-$ ions should appear around 320 nm. The curve shows no change during heat treatment, which implies that $[AuCl_4]^-$ ions in water were not reduced solely by heat treatment. Figure 3 shows *in situ* UV-Vis spectra of the mixture of $HAuCl_4$ and PEO-OH during heat treatment at 100 °C for 60 min in the quartz cell. It was not possible to observe the $[AuCl_4]^-$ ion peak because of the absorption of PEO-OH. PEO-OH is used as the protective agent in reduction method of gold nanoparticle [16]. However, in this case without the solvent and the reducing agent, absorption around 530 nm was not completely confirmed during heat treatment, implying that there was no formation of gold nanoparticles in this system.

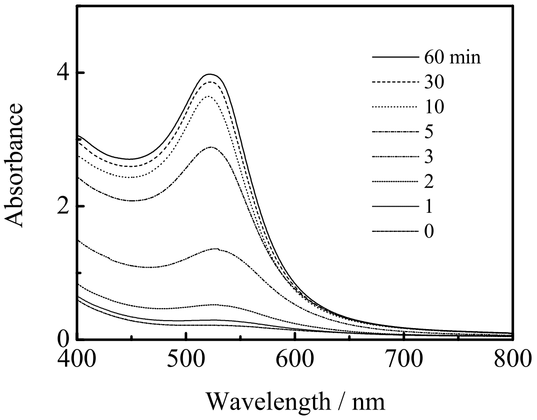

Fig. 1. *In situ* UV-Vis spectra of the mixture of $HAuCl_4$ and PEO-NH_2 ($HAuCl_4$/PEO-NH_2 = 1/3000) during heat treatment at 100 °C for 60 min in the quartz cell.

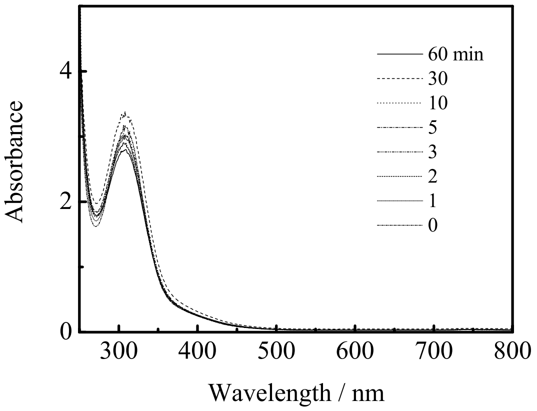

Fig. 2. *In situ* UV-Vis spectra of 4.0 mM $HAuCl_4$ aqueous solution during heat treatment at 100 °C for 60 min in the quartz cell.

As shown in Figure 4, the gold nanoparticles were confirmed in $HAuCl_4$/PEO-NH_2 system by TEM observation and the mean diameter of the particles was estimated to be 16.3 nm. This result clearly indicates that the reduction of $[AuCl_4]^-$ ions was promoted and gold nanoparticles were formed only in the case of the $HAuCl_4$/PEO-NH_2 system.

The generation process of metal nanoparticle in a reducing method is believed to be as follows: (1) a complex between a metal ion and a ligand, that is the functional group of a protection polymer, is formed in solution. (2) The metal ion is reduced to a metal atom with a reducing agent. (3) The metal atoms aggregate and grow into a nanoparticle. Because the protector that forms the complex with the metal ion or atom surrounds the metal nanoparticle, the growth of the particle is prevented and stops at a size on the order of a nanometer [17]. It is surmised that this gold nanoparticle-polymer (PEO-NH_2) composite is also formed by the same process. In this case, a complex between gold ion and the -NH_2 group

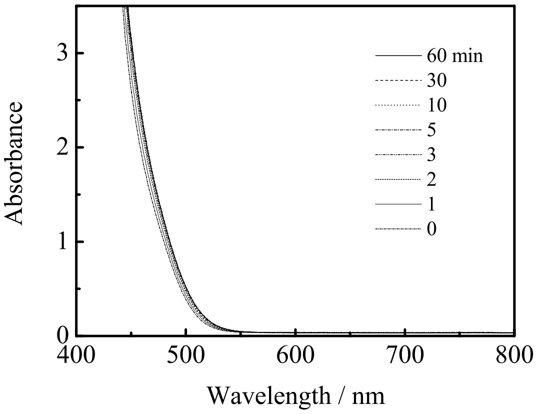

Fig. 3. *In situ* UV-Vis spectra of the mixture of $HAuCl_4$ and PEO-OH ($HAuCl_4$/PEO-OH = 1/3000) during heat treatment at 100 °C for 60 min in the quartz cell.

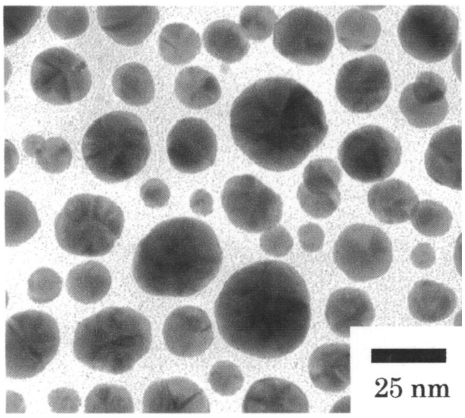

Fig. 4. TEM image of gold nanoparticles in PEO-NH_2 ($HAuCl_4$/PEO-NH_2 = 1/600, mean particle size: 16.3 nm).

of PEO-NH_2 is formed, and the gold ion is reduced to gold atom with the -NH_2 group. Then, the gold atoms aggregate and form a nanoparticle. It is also noted that gold nanoparticles cannot be formed by the -OH group of PEO-OH.

In general, the metal nanoparticles are made from four materials, which are a solvent, a reducing agent, a metal salt and protective agent. In this work, we have successfully produced the gold nanoparticles-polymer composite from only PEO-NH_2 and $HAuCl_4$ *via* a new simple operation. The gold nanoparticle-polymer composite remains stable dispersed in PEO-NH_2 for more than several years. It is suggested that PEO-NH_2 has a three fold function as a solvent, a reducing agent and a protective agent.

4 Conclusion

The gold nanoparticle-polymer composite was prepared using only a gold salt and a melted polymer with a simple operation. The composite, which is in the wax state at room temperature, is highly soluble in water and lower alcohols, moreover the composite melts at about 50 °C.

The composite is suitable for industrial use because the production method is simple, low in cost and free from impurities.

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