— Communication —

A Facile Synthesis of AuAg Alloy Nanoparticles Using a Chemical Reaction Induced by Sputter Deposition of Metal onto Ionic Liquids

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Sputter deposition of silver (Ag) onto an ionic liquid (IL) produced Ag nanoparticles whose size was varied greatly dependent on the sputtering conditions. Change in discharge current from 10 to 40 mA increased Ag particle size from 5.7 to 11 nm, though prolongation of sputtering time simply caused a higher concentration of Ag nanoparticles in IL without change in their size. Sputter deposition of Ag onto IL solutions containing H₂AuCl₄ resulted in the appearance of a single surface plasmon resonance peak in the absorption spectra of the resulting solution, and their peak position was red-shifted with an increase in the concentration of H₂AuCl₄. The obtained results clearly indicated that Ag metal species sputter-deposited in IL can reduce H₂AuCl₄ to give AuAg alloy nanoparticles and that their chemical composition varies depending on the initial concentration of H₂AuCl₄.

Key Words : Ionic Liquids, Nanoparticles, Sputter Deposition, Alloy, Surface Plasmon Resonance

1 Introduction

Ionic liquids (ILs) have been promising solvents for various reactions such as organic^{1,2)} and inorganic^{3,4)} syntheses and electrochemical reactions.^{5,6)} Preparation of metal nanoparticles has attracted much attention because they could catalyze unique reactions in ILs that did not occur in conventional organic or aqueous solvents. Several strategies have been developed for the preparation of metal particles, such as Pt,⁷⁾ Rh,⁸⁾ Ir,⁸⁾ and Au,⁹⁾ uniformly dispersed in ILs. Recently, we have developed a clean method to prepare metal nanoparticles in ILs without any additives, such as reducing agents and/or stabilizing agents. The extremely low vapor pressure of ILs enabled sputter deposition of metal species onto ILs under vacuum, resulting in the formation of highly dispersed metal nanoparticles, such as Au, Ag and AuAg, having sizes of 2~5 nm.^{10,11)} Furthermore, it has been reported that injection of low-energy electrons into ILs induced the reduction of metal ions, such as Ag⁺,^{12,13)} and AuCl₄⁻,¹⁴⁾ to produce corresponding metal particles. If metal nanoparticles having an oxidation potential were sputter-deposited in ILs containing another metal ions having more positive reduction potential, the latter metal ions could be reduced to form nanoparticles. However, such an attempt has never been made.

In this study, we prepared Ag nanoparticles having various sizes by sputter-deposition onto an IL with different conditions. Furthermore, Ag-sputtering was made onto IL solutions containing H₂AuCl₄ to produce AuAg alloy particles.

2 Experimental

An IL of 1-butyl-3-methylimidazolium hexafluorophos-

Fig. 1 Absorption spectra of BMI-PF₆ taken after Ag sputter deposition (a, c) and the dependence of average size (open circles) and concentration (solid circles) of the thus-obtained Ag nanoparticles on sputtering conditions (b, d). The discharge current of 10 mA was used for Ag sputtering (a, b), or the sputtering time was fixed to 5 min (c, d). The optical length of a quartz cuvette used was 1.0 mm. The numbers in figures represent the sputtering time (a) or the discharge current (c). The error bars in figure b and d indicate the size distribution.

phate (BMI-PF₆) was purchased from Kanto Chemical Co., Inc. A portion of H₂AuCl₄ ethanol solution was added to BMI-PF₆, followed by drying for 3 h at 378 K under vacuum. A 0.60 cm³ portion of thus-obtained solution was

Fig. 2 Absorption spectra of BMI-PF₆ solutions containing 0 (a), 50 (b), 65 (c), and 100 $\mu\text{mol dm}^{-3}$ (d) HAuCl₄ taken after sputter deposition of Ag. The optical length of a quartz cuvette used was 1.0 mm. The SPR peak wavelengths are plotted as a function of the initial concentration of HAuCl₄ (inset). Sputter deposition of Ag onto ILs was carried out for 5 min with a discharge current of 10 mA.

spread on a glass plate (10 cm²) that was horizontally set in a DC sputtering apparatus (Sanyu Electron Co., Ltd, SC-701HMCII). It was located at a distance of 85 mm from the silver (99.99% in purity) foil target. Sputter deposition of Ag in ILs was carried out under an argon pressure (5 Pa) at room temperature. The concentration of Ag deposited in IL was determined by using X-ray fluorescence spectrometer (XRF; Rigaku EDXL300). A 0.2 cm³ portion of Ag particle IL solution was mixed with 1.0 cm³ methanol solution containing 1,6-hexanedithiol (0.05 cm³), followed by the centrifugation. Thus-obtained precipitates of Ag particles were dissolved in a HNO₃ aqueous solution and then subjected to the XRF analysis.

For the preparation of TEM and XPS samples, metal nanoparticles dispersed in ILs were isolated by precipitation with addition of a small amount of acetonitrile to BMI-PF₆ solution, washed with acetonitrile several times, and dispersed in acetonitrile. The structure and size distribution of nanoparticles were examined using a HITACHI H-7650 transmission electron microscope (TEM) with an acceleration voltage of 100 kV. TEM samples were prepared by dropping the resulting suspension onto a copper TEM grid with amorphous carbon overlayers, followed by removal of the excess amount of solution with a filter paper. Elemental composition of isolated AuAg alloy particles was examined with X-ray photoelectron spectroscopy (XPS; JEOL JPS-9000MC), by considering peak areas of each band in XPS spectra and their corresponding relative sensitivity factor.

3 Results and Discussion

Figure 1 (a) shows changes in the absorption spectra of BMI-PF₆ by sputter deposition of Ag with various sputtering times. A sharp absorption peak at ca. 420 nm that developed with elapse of sputtering time was assigned to the surface plasmon resonance (SPR) peak of Ag nanoparticles. The concentration of Ag linearly increased from 0.26 to 2.4 mmol dm⁻³ with sputtering time from 5 to 45 min (Fig. 1 (b)). TEM observation revealed that the spherical Ag nanoparticles with a size of ca. 5.7 nm were formed regardless of sputtering time. Similar behavior was observed for Au sputter deposition

Fig. 3 TEM images of Ag nanoparticles sputter-deposited in pure BMI-PF₆ (a) and AuAg nanoparticles prepared in BMI-PF₆ containing 65 (b) and 100 (c) $\mu\text{mol dm}^{-3}$ HAuCl₄. Size distributions are also shown on the right side of the corresponding TEM images.

in our previous study.¹¹⁾ On the other hand, as shown in Fig. 1 (c), the SPR peak intensity of Ag particles increased with an increase in discharge current from 10 to 40 mA, resulting in an increase in the concentration of Ag from 0.26 to 1.4 mmol dm⁻³. The size of nanoparticles formed also increased from 5.7 to 11 nm with an increase in discharge current from 10 to 40 mA. In sputter deposition, bombardment of energetic gaseous ions on the Ag foil surface causes physical ejection of surface atoms and/or clusters, which are injected into the IL solution. The density of these Ag species at the solution surface became high enough to coalesce with each other, the degree being remarkable with high discharge current. The coalescence of sputtered species proceeds until Ag nanoparticles have been stabilized by the adsorption of ions of the IL.

Figure 2 shows absorption spectra of BMI-PF₆ containing HAuCl₄ after sputter deposition of Ag. A single SPR peak is observed in each spectrum. The peak shape became broad and then the peak wavelength (λ_{SPR}) was red-shifted with an increase in HAuCl₄ concentration (inset of Fig. 2). It has been reported by Xia and co-workers that AuCl₄⁻ ions in aqueous solutions were reduced by oxidative dissolution of Ag metal, according to eq. 1, resulting in AuAg alloy formation of particles or hollow shells.^{15,16)}

In this case also, it seems reasonable that AuAg alloy particles in BMI-PF₆ were formed by the reduction of HAuCl₄ with sputter-deposited Ag species because it has been reported that AuAg alloy nanoparticles exhibited a single SPR peak in absorption spectra whose wavelength

was linearly red-shifted with an increase in the fraction of Au atoms in the particles.¹⁷⁾ It was confirmed by TEM and XPS that the chemical composition of AuAg alloy nanoparticles was changed by changing the concentration of HAuCl₄ in BMI-PF₆.

Alloy particles were isolated by the addition of acetonitrile to IL solutions. TEM observation of these particles revealed that solid spherical nanoparticles were formed in BMI-PF₆ solutions by sputter deposition of Ag, regardless of the concentration of HAuCl₄, as shown in Fig. 3. The size determined from TEM measurements increased slightly with an increase in the initial concentration of HAuCl₄: the Ag nanoparticles sputter-deposited in pure BMI-PF₆ had an average diameter (d_{av}) of 5.7 nm with a standard deviation (σ) of 1.8 nm, while sputter deposition onto solutions containing 65 and 100 $\mu\text{mol dm}^{-3}$ HAuCl₄ produced particles having d_{av} (σ) of 6.4 (2.6) and 6.9 (2.9) nm, respectively. A little larger values of d_{av} and σ for AuAg alloy nanoparticles than those for Ag nanoparticles is due probably to progress of some aggregation during Ag oxidation and Au deposition reactions. However, the prepared AuAg nanoparticles were stable for several days without change in their absorption spectra.

XPS spectra of AuAg particles isolated from BMI-PF₆ containing 65 $\mu\text{mol dm}^{-3}$ HAuCl₄ showed that the binding energies of Au 4f_{7/2} and Au 4f_{5/2} appeared at 83.1 and 86.8 eV and those of Ag 3d_{5/2} and Ag 3d_{3/2} appeared at 367.3 and 373.3 eV, respectively. The energies for gold and silver were in good agreement with the literature values reported for AuAg alloy particles.¹⁸⁾ Since no signals assigned to Cl atoms were detected, AgCl particles were not contained in the particles isolated from IL solutions. These facts suggest that AgCl particles are extremely small even if they are formed according to eq. 1, and then the simple addition of acetonitrile to IL solutions can not cause the precipitation of AgCl under the conditions used in the present study. The present sputtering conditions must give 260 $\mu\text{mol dm}^{-3}$ Ag concentration in the BMI-PF₆ solutions. Therefore, according to eq. 1, alloy nanoparticles formed in solutions containing HAuCl₄ of 65 and 100 $\mu\text{mol dm}^{-3}$ are expected to form AuAg alloy with Au/Ag ratios of 0.50/0.50 and 1.00/0, respectively. However, XPS analyses revealed the ratios of 0.34/0.66 and 0.90/0.10, respectively. These facts suggest that all sputtered Ag atoms did not react with HAuCl₄ in the solutions. It is likely that the formation of Au-rich alloy shells retards the oxidative dissolution of Ag nanoparticle cores.

4 Conclusion

The size of Ag nanoparticles prepared by sputter-deposition of Ag onto BMI-PF₆ and their concentration varied depending on sputtering conditions, such as magnitude of discharge current. Sputtered Ag species caused reduction of HAuCl₄ in the IL, resulting in the formation of AuAg alloy nanoparticles. The chemical composition and optical property of the alloy nanoparticles were easily controlled by changing the concentration of HAuCl₄. Although only AuAg alloy was prepared

in the present study, various metal and alloy nanoparticles can be prepared in ILs by appropriately selecting the metal to be sputter-deposited on ionic liquids to reduce different metal ions. Furthermore, since highly reactive metals, such as Zn and Li, are in principle vacuum-deposited onto ILs to form nanoparticles, this technique will be useful for the development of novel chemical reactions in ILs under vacuum using ultrafine metal nanoparticles as reagents.

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