Synthesis of Polystyrene-based Nanocomposite Thin Films with Domain Structure Consisting of Au Nanoparticles

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Abstract. We have presented a very simple approach, the incorporation of metal complex into polymer matrix followed by thermal decomposition of complex, to the fabrication of metal nanoparticles/polymer composite thin films and have determined their domain structure. The approach involves the polymerization of monomer with metal complex into polymerized matrix, and annealing in vacuum condition. Here, the key is to use a gold (I) complex with phenyl groups that have strong interaction between metal complexes. This method allows us to synthesize Au nanoparticles dispersed in polystyrene-based polymer thin films with Au domain structures.

1. Introduction

Inorganic nanoparticles are emerging as very attractive nanomaterials for advanced applications in catalysis, transistors, and sensors.[1-3] In particular, metal nanoparticles, such as gold, silver, and copper, have been of great interest as nanomaterials for optics, because of their surface plasmon resonances (SPR).[4-6] Despite progress in synthesis of metal nanoparticles, controlling the SPR, which depends on size and shape of nanoparticles, distance between nanoparticles, remains challenging. Whereas a variety of methods have been developed to prepare the metal nanoparticles and are now accessible for controlling the size and shape of nanoparticles, controlling the distance between nanoparticles is now being actively explored. [7-12] Therefore, plasmonic engineering of nanoparticles is currently faced with the challenge of developing arrangement technology of metal nanoparticles for feature distance between nanoparticles.

Recently, great efforts have been focused on fabricating composite nanostructures consisting of inorganic nanoparticles and organic polymers.[13-15] These include efforts to improve their physical and chemical properties, and to introduce additional functionalities because such nanocomposite can be useful in the field of optics and electronics. On the other hand, they have been of great interest because they provide a good model system for studying experimentally interaction with inorganic and organic materials.[16,17] Thus, preparation of nanocomposite containing nanoparticles has become a significant research field. Various methods have been developed to prepare nanocomposites, including incorporation of inorganic nanoparticles into polymer matrices[18-23] and vacuum deposition on polymer substrate.[24] In these works, however, distribution of nanoparticles in polymer matrices...
relies on interaction between organic ligands or surface energy of nanoparticles, which makes it
difficult to control the interparticle distance in polymers. To resolve this problem, we have attempted
in-situ synthesis of metal nanoparticles into polymer matrices by hydrogen reduction using ion-doped
polymers.[25-27] This synthesis was demonstrated to be a highly efficient approach for formation of
metal nanoparticles uniformly dispersed in matrices because the doped-ions were homogeneously
distributed in the polymers. Although the preparation of nanocomposite containing Ag, Cu, Ni, and Pt
nanoparticles with a diameter of 2-10 nm can be achieved by using polymers bearing ion-exchange
sites such as carboxylic groups, the synthetic approach for synthesis of Au nanoparticles using ion-
doped polymer is still rare.

Here, we demonstrate a novel ion-doped route to the fabrication of nanocomposite thin films made
of polystyrene-based polymer as a matrix embedded with Au nanoparticles formed through thermal
decomposition of gold (I) complex. Incorporation of complex is achieved by using AuCl(PPh)₃
[Chlorotriphenyl-phosphine gold (I)]. The present process allows one to fabricate the nanocomposite
thin films with unique domain structure consisting of Au nanoparticles.

2. Method

Preparation of Gold(I) Complex: Gold (I) complex, Au(OCOCH₃)(PPh)₃ complex, was prepared by
ligand exchange reaction. Ag(OCOCH₃) crystals were added into a chloroform solution of AuCl(PPh)₃
at room temperature. After reaction for 1 h, the resulting solution was filtered through a 0.2 µm
membrane filter to separate white precipitates.

Preparation of Au Nanoparticles/PS Composite: A chloroform solution of styrene, divinylbenzene,
and 2,2′-azobisobutyronitrile was heated at 60 °C for 12 h under Ar atmosphere to form cross-linked
polystyrene (PS)/chloroform solution. Au (I) complex/PS thin films were prepared by a spin-coating
using the mixture of chloroform containing cross-linked PS and Au(OCOCH₃)(PPh)₃ complexes. The
concentration of Au (I) complex was changed from 0.5 to 2.0 M. The thin films were annealed at 120-
200 °C for 30 min in vacuum.

Measurements: Fourier transform infrared (FT-IR) measurements was performed to confirm the
changes in chemical structure of the Au(I) complex by ligand exchange reaction. The FT-IR spectra
were obtained using FT/IR 670plus (Jasco) and were recorded at a resolution of 4 cm⁻¹ and 100
accumulations. X-ray powder diffraction (XRD) data were collected on a Rigaku RINT-2200 Right
System (Ultima IV) diffractometer with CuKα radiation. The microstructure of the composite films,
i.e., distribution in the films, mean size, and size distribution of Au nanoparticles was confirmed by
transmission electron microscopy (TEM, JEM-2000, JEOL) operating at 120 kV. The Optical
properties of the obtained films were characterized by a UV/VIS spectrophotometer (V-550, Jasco).

3. Results and Discussion

AuCl(PPh)₃ complex was soluble to chloroform, but the saturation solubility of complex against
chloroform is low. To improve the solubility of the complex, we conducted the ligand exchange
reaction with chloride anion to acetate anion using Ag(OCOCH₃) crystals. Figure 1 schematically
describes the procedure for the preparation of Au(OCOCH₃)(PPh)₃ complex. By mixing chloroform
solution of AuCl(PPh)₃ complex and Ag(OCOCH₃) crystal, the white precipitate was seen in the
solution. In order to confirm the chemical structure of complex, FT-IR spectroscopy was used for the
Au(I) complex before and after ligand exchange reaction. As shown in Figure 2, the FT-IR spectrum

![Figure 1. Schematic illustration of ligand exchange reaction for Au(I) complex.](image-url)
measured for AuCl(PPh)₃ complex showed two bands at 1480 and 1435 cm⁻¹ arising from benzene ring. After ligand exchange reaction, two typical bands at 1630 and 1370 cm⁻¹ arising from acetate ligand are newly observed, and there are no distinct changes in benzene ring bands. This result indicates that the ligand exchange reaction of Au(I) complexes can be achieved by mixing AuCl(PPh)₃ complexes with Ag(OCOCH₃) crystals. For further study of the ligand exchange process, the precipitate obtained by ligand exchange reaction was characterized by XRD measurement. The precipitates exhibited five well-resolved diffraction peaks in the 2θ=20-70° (2θ) that can be indexed as AgCl with cubic structure. This is expected because silver (I) cation can be readily reacted with chloride anion, leading to the ligand exchange with chloride anion of gold (I) complex and acetate anion of silver acetate.

Au nanoparticles/PS composite thin films were prepared by the spin-coating of mixture solution containing cross-linked PS and Au(OCOCH₃)(PPh)₃ complex followed by annealing in vacuum condition. In Figure 3, TEM images of the thin films after annealing show that there is indeed a unique domain structure, and spherical Au nanoparticles with a particle diameter ranging from 10 to 15 nm were formed in PS matrix. Interestingly, according to high-resolution TEM images, the domain structure were found to be constructed by Au nanoparticles with nearly closed-packing assemblies. Recently, there are many reports for preparation of inorganic nanoparticles/polymer thin film composites by mixing with as-prepared nanoparticles and polymer matrix.[18-23] These studies suggest that the microstructure of composite films is dependent on the rate of solvent evaporation and interaction between nanoparticle ligand and polymer matrix.[23] In our present study, during spin-coating for preparation of thin films, the rate of chloroform evaporation may be too fast to form uniformly dispersed Au(I) complexes in PS matrix. In addition, the complex ligands and matrix exhibit insufficient affinity, leading that the phase separation is induced by minimizing the interface surface energies.

The effect of precursor concentration in the mixture solution on the size of nanoparticles and domain was investigated by TEM analysis. In Figure 3, the domain size consisting of Au nanoparticles increased with increasing the concentration of Au(OCOCH₃)(PPh)₃ complex in the PS precursor films, although the size of Au nanoparticles was almost constant at 10-15 nm. This effect may be explained in terms of interaction between Au surface and protective molecules. The resulting nanoparticles are stabilized by triphenylphosphine molecules, which show strong affinity against Au nanoparticles because phosphine molecules are often used as particle stabilizer.[28-30] The strong affinity inhibits the growth of Au nanoparticles, resulting in increasing the domain size of nanoparticles in PS matrix.

The changes in domain structure of composite films are clearly related to the changes in optical properties of Au nanoparticles. Before annealing in vacuum condition, the PS thin film containing

![Figure 2. Transmittance FT-IR spectra of (A) AuCl(PPh)₃ and (B) Au(OCOCH₃)(PPh)₃ complexes.](image-url)
Au(OCOCH$_3$)(PPh)$_3$ complex is a transparent and colorless. The color of nanocomposite films after heat treatment changed to red and this change is caused by SPR of Au nanoparticles. The tuning of plasmonic properties of nanocomposites can be readily controlled by the amount of doped Au(OCOCH$_3$)(PPh)$_3$ complex and annealing temperature. A small amount of complex (the concentration of complex for chloroform solution: 0.5M) led to the formation of nanocomposite thin films with pale red. Doubling the concentration of complex for the spin-coating solution was found to produce nanocomposite thin films with beautiful color of wine red. More concentrated solution above 1.5 M was used to evaluate the effect of amount of Au(OCOCH$_3$)(PPh)$_3$ complex on SPR properties of nanoparticles. The color of films gradually changed from purple to indigo blue by increasing the concentration to 2.0 M, which indicate that a coupling of SPR signals of Au nanoparticles strongly appeared because the domain size increased with increasing the concentration of complex (as shown in Figure 3).[27]

To clarify the effect of complex concentration on optical properties of nanocomposites, we conducted the UV-vis measurement of the resulting samples. Figure 4 shows UV-vis spectra of the nanocomposite films prepared by different concentration of complex. These spectra indicate that the peak wavelength of SPR depends on the concentration of complex and shift from 550 to 569 nm as the concentration of complex increases from 0.5 to 1.5 M. On the basis of TEM observation, the observed shift of SPR peaks may be attributed to the increasing the size of domain structure including Au nanoparticles. In addition, note that increase in the annealing temperature resulted in increasing in the intensity of SPR although the absorption peaks were almost constant. After annealing at 120 °C, Au nanoparticles with a diameter of ca. 5 nm were observed and the domain of nanoparticles were not dense. This result suggests that the doped-Au ions were not completely reduced below 120 °C. On the other hand, the annealing above 150 °C resulted in the formation of domain structure consisting of

![Figure 3. TEM images of PS composite films including Au nanoparticles obtained by using different casting solution containing (A,B) 0.5, (C,D) 1.0, and (E,F) 1.5 M of Au complex.](image-url)
closely packed Au nanoparticles with a diameter of ca. 10 nm (Figure 5). These experiments provide evidence for SPR properties of Au nanoparticles in polymer thin films depending on the size and packing density of nanoparticles.

4. Conclusion
We have reported that Au nanoparticles/PS composite thin films with an unique domain structure can be prepared by using Au(I) complexes. The domain structure of nanocomposites consists of Au nanoparticles assemblies. The optical properties of the composite films can be readily controlled by changing the concentration of gold (I) complex and annealing temperature, which may be caused by the coupling between nanoparticles and increasing the size of nanoparticles. The present synthetic approach allows one to control the SPR properties of Au nanoparticles, the ability of which is expected to be useful for the fabrication of optical devices.

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