

Preparation and Characterization of Gold-Titania Nanoparticles

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We prepared gold-titania composite nanoparticles by the gas condensation method, and evaluated their physical and optical characteristics. The structure of obtained particles mainly showed that the gold particles, whose diameter ranged from 10 to 60 nm, were covered with spherical titania particles which were composite phases of anatase and rutile. The effect on the crystal structure and shapes of titania was not clearly observed by compounding with gold.

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1. Introduction

The gas condensation method¹⁾ is one of the promising low emission manufacturing techniques, and is easy to get pure ultra fine metal particles. This method is also capable to make metal oxide particles in the inert gas containing oxygen. Though many investigations have been done about this technique, there are still unsolved problems, especially in composite metal oxides preparation. The combination of metal oxide particles with noble metal clusters²⁾ make it all the more efficient to dissolve the stinking materials, or to synthesize organic substances when it is used as catalysts. These catalysts are generally prepared by chemical syntheses, and few of them are done by the gas condensation method. If the gas condensation method is applied to these composite particles preparations, there are some possibilities to get unique characteristics, structures, optical properties, or catalyses. In this experiment, we selected the combination of gold and titania composite and analyzed its characteristics.

2. Experiment

We prepared gold-titania composite nanoparticles using PJ-930KK apparatus produced by Vacuum Metallurgical Co. Ltd. We used gold and titanium powders as source materials. The sizes of gold and titanium powders were under #100 and #350 mesh, and purity of them were 99.99% and 99.9%, respectively. We prepared the composite particles under three mixing conditions. The mixing ratios of gold to titanium were 0, 0.004, and 0.450 in weight (hereinafter referred to as TiO₂, TiO₂-Au-a, and TiO₂-Au-b). We mixed and averaged gold and titanium powders with an agate mortar for about 10 minutes, then put them into the water cooled copper hearth in the evaporation chamber. A direct arc discharge heating method was applied for the preparations, using a consuming carbon cathode and a water cooled copper hearth anode. The applied voltage and the current were 20 V and 40 A, respectively. The ambient gas was helium containing 10 vol% oxygen, and its purity was 99.99%. The pressure of the evaporation chamber was kept at 1.5×10^5 Pa during the evaporation. The condensed particles would adhere to the walls of the evaporation chamber. We collected the particles from them.

The collected particles were evaluated by TEM, XRD, dif-

fuse reflectance and Raman spectroscopy. TEM observation was done with JEOL JEM-2000FXII, with accelerated voltage of 200 kV. XRD analysis was carried out by using Rint1500 equipment, and the applied voltage and current were 40 kV and 100 mA, using a copper target. Samples for XRD were films fabricated on silicon(100) substrate. Diffuse reflectance was measured with Shimadzu UV-3100PC, using BaSO₄ standard reference. We prepared diffuse reflectance samples as follows. Powder samples were dispersed in ethanol, and ethanol with powders was dropped on quartz glass, and then dried up. Raman spectra were obtained with JRS-SYSTEM2000 using Ar⁺ laser of 514.5 nm.

3. Result and Discussion

3.1 Sizes and Structures of Nanoparticles

Figure 1 shows the TEM images of gold and titania composite nanoparticles, where (a), (b) and (c) is the image of TiO₂, TiO₂-Au-a, and TiO₂-Au-b, respectively. Figure 1(a) shows that the titania prepared by the gas condensation method is spherical and has the large particles size distribution, about from 10 to 50 nm. This large size distribution is characteristic of the particles prepared by the direct arc discharge heating technique. The point where the electric arc hits would evaporate the most. In accordance with the distance from the point, evaporation rate would decrease. The uneven evaporating amount, which varied in the places of the source material, would cause the large size distribution.

Figures 1(b) and (c) show that the composite particles have a core-shell structure: gold particles were covered with titania. Titania particles also have a large size distribution and a spherical shape. The gold particle size of TiO₂-Au-b is from 10 to 60 nm, whereas that of TiO₂-Au-a is from 10 to 20 nm. In accordance with the gold content, the gold particles have a large size distribution.

Figure 2 shows the lattice image of TiO₂-Au-a. In the centered particles, we can observe several titania crystallite with crystal faces of different orientations. This implies that the titania surrounding the gold particle is consisted of several crystallite.

3.2 Crystal structures

Figure 3 shows the X-ray diffraction patterns of the samples. Figure 3(a) is of TiO₂, Figs. 3(b) and (c) are of

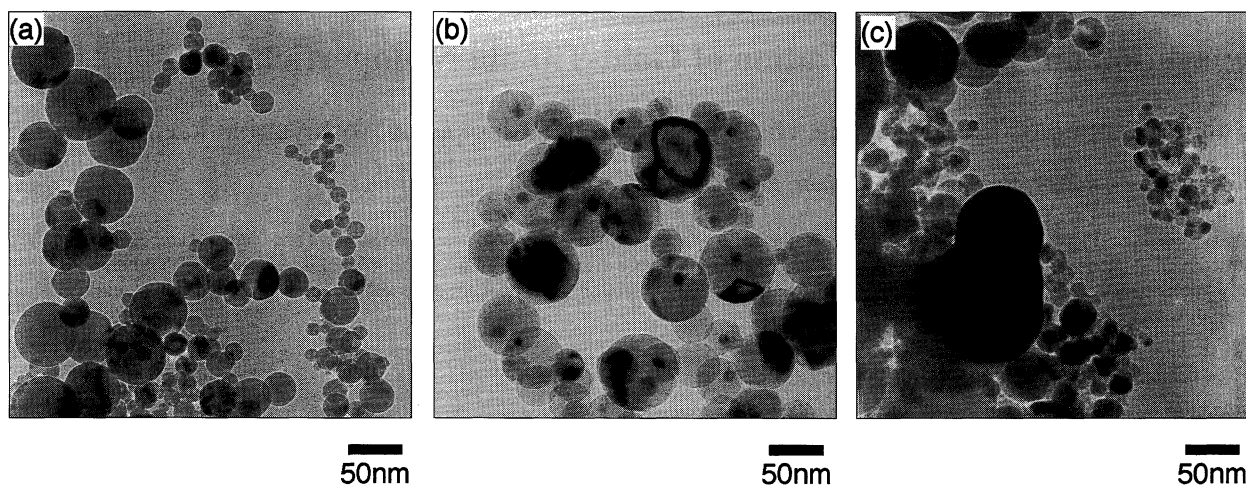


Fig. 1 TEM images of gold-titania composite nanoparticles; (a) TiO_2 (gold to titanium ratio is 0:1), (b) $\text{TiO}_2\text{-Au-a}$ (gold to titanium ratio is 0.004:1), and (c) $\text{TiO}_2\text{-Au-b}$ (gold to titanium ratio is 0.450 : 1).

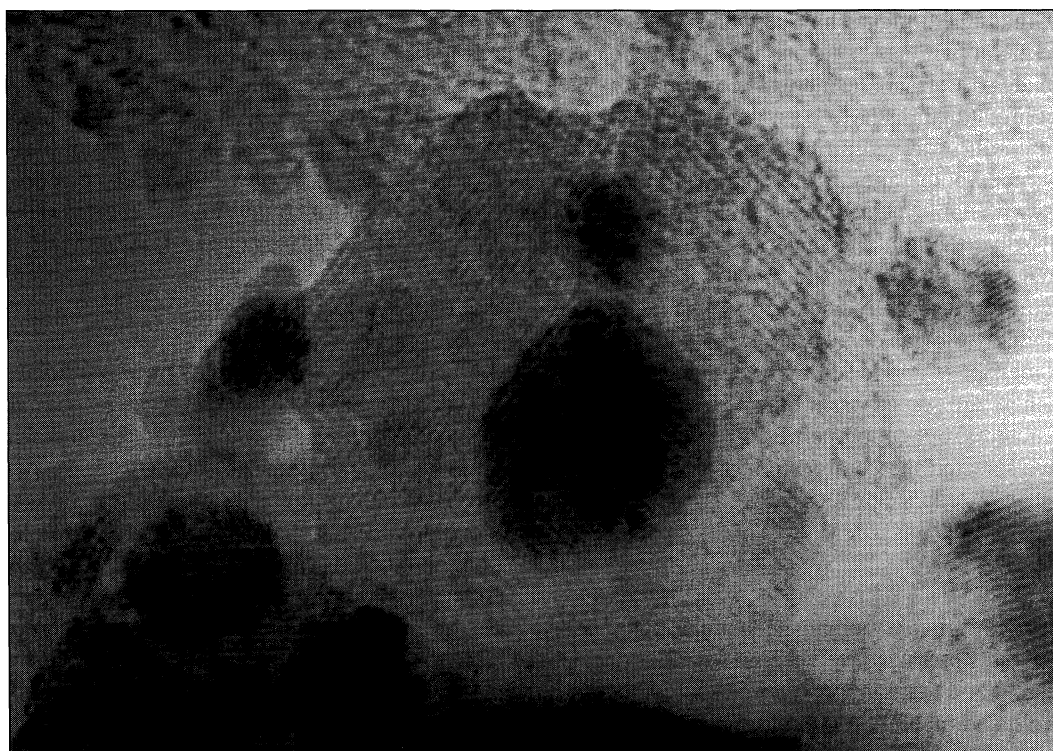


Fig. 2 Lattice image of gold-titania composite ultra fine particles; $\text{TiO}_2\text{-Au-a}$ (gold to titanium ratio is 0.004 : 1).

$\text{TiO}_2\text{-Au-a}$ and $\text{TiO}_2\text{-Au-b}$, respectively. Figure 3(a) shows that the crystal structure of obtained TiO_2 particles has composite phases of anatase and rutile. Anatase phase is dominant and its content is estimated to be 89.7% from the peak intensities.³⁾ This result is common in gas phase synthesis techniques such as the hydrolysis of titanium tetrachloride.⁴⁾ There are still some unidentified diffraction peaks in Fig. 3(a). These peaks are presumed to belong to non-stoichiometric compounds of TiO_x ($x < 2$). This fact implies that 10 vol% oxygen is not enough to oxidize titanium completely. Figures 3(b) and (c) show that the anatase contents are also dominant in composite particles; their anatase contents are 81.2%

and 80.1% for $\text{TiO}_2\text{-Au-a}$ and $\text{TiO}_2\text{-Au-b}$. And unidentified diffraction peaks are also observed. These results show that the combination of gold has no effect on the titania crystal structure. A strong peak observed at 33.1° is identified as silicon pieces from the substrate.

We roughly estimated the gold particle size by Scherrer method, using $\{111\}$ diffraction peak in Fig. 2(c), then got 18 nm. As Scherrer method is effective when particle sizes are equal, this value is presumed to be the maximum likelihood value of a gold particle size.

Figure 4 shows the Raman spectra of the prepared samples and of the vacuum deposition gold film (Au-film). From

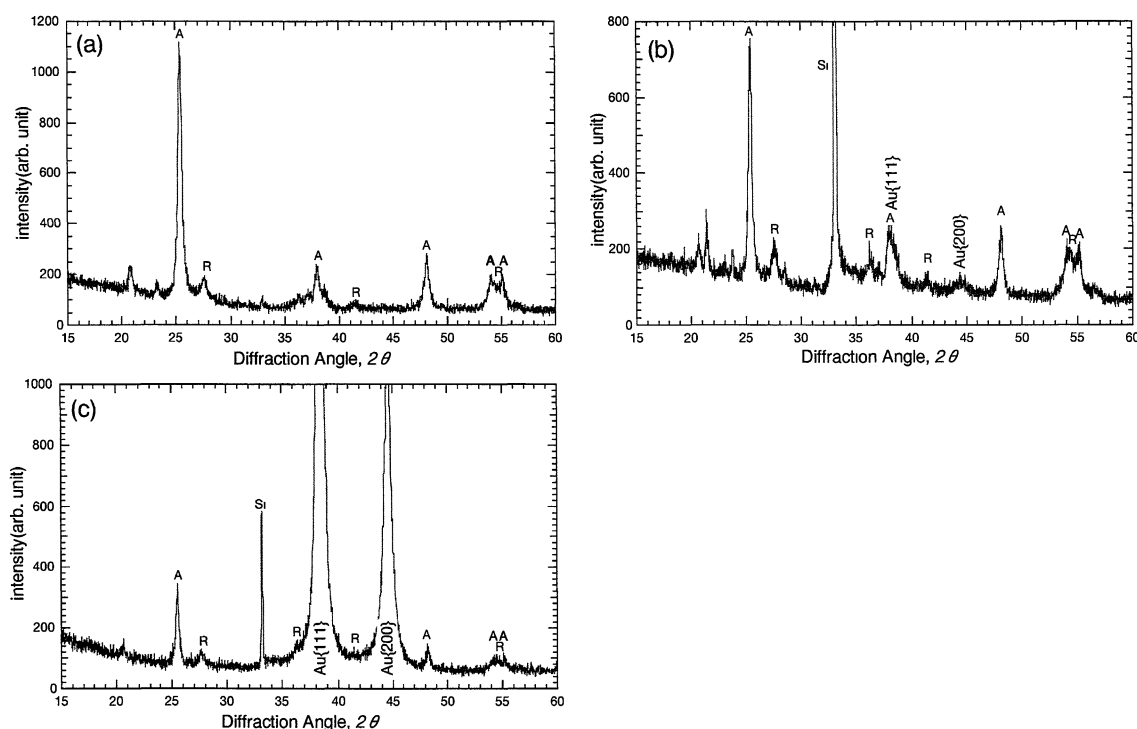


Fig. 3 X-ray diffraction patterns of gold-titania composite nanoparticles; (a) TiO₂ (gold to titanium ratio is 0 : 1), (b) TiO₂-Au-a (gold to titanium ratio is 0.004 : 1), and (c) TiO₂-Au-b (gold to titanium ratio is 0.450 : 1). Annotations A and R indicate the diffraction peaks of anatase and rutile, respectively.

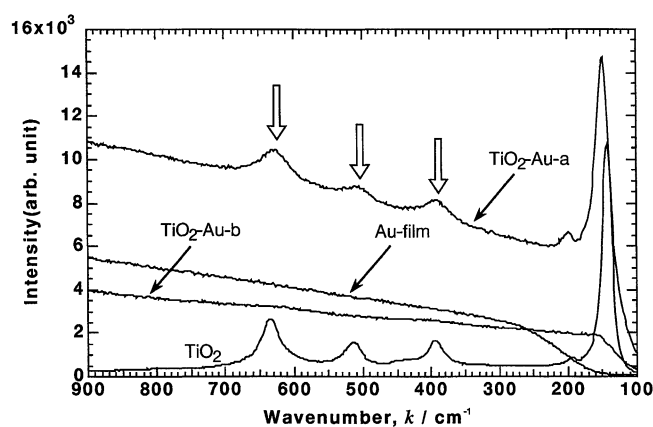


Fig. 4 Raman spectra of gold-titania composite nanoparticles; arrows show the Raman peaks of anatase.

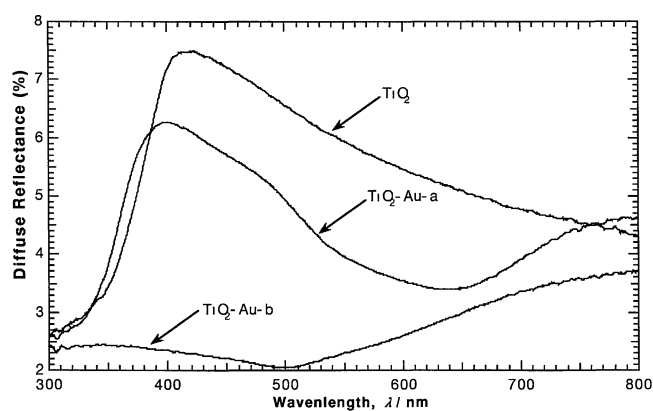


Fig. 5 Diffuse reflectance of gold-titania composite nanoparticles.

the spectrum of TiO₂, Raman peaks corresponding to anatase structure are clearly observed. In accordance with increase of gold content, the Raman peaks become to be broadened. The baselines of TiO₂-Au-a and TiO₂-Au-b spectra increase almost proportion to wavenumber. This increase of the baselines is caused by fluorescence of specimen, which is a kind of noise. As the Raman spectrum of Au-film shows the same tendency, the fluorescence is presumed to arise from Au nanoparticles and to have little relation with the defects, or dislocations of titania. And the peak broadening is caused by the decline of signal-to-noise ratio.

3.3 Optical properties

Obtained powders presented characteristic colors corre-

sponding to the content of the gold. TiO₂, TiO₂-Au-a, and TiO₂-Au-b, showed yellowish white, Nile green, and dark purplish red. These colors reflect gold particle sizes. Figure 5 shows that the diffuse reflectance of the samples. The diffuse reflectance of TiO₂ is decreasing at longer wavelength more than 450 nm. This reason is assumed that the volume of TiO₂ powders on quartz glass is too little to get sufficient reflectivity. Two other samples were under the same condition as TiO₂. When we compare the diffuse reflectance among these samples, we have to take this effect into consideration. TiO₂-Au-b shows the apparent absorption around 500 nm, and this absorption is supposed to be caused by the surface plasma resonance of gold nanoparticles. This result confirms the color of TiO₂-Au-b. As for TiO₂-Au-a,

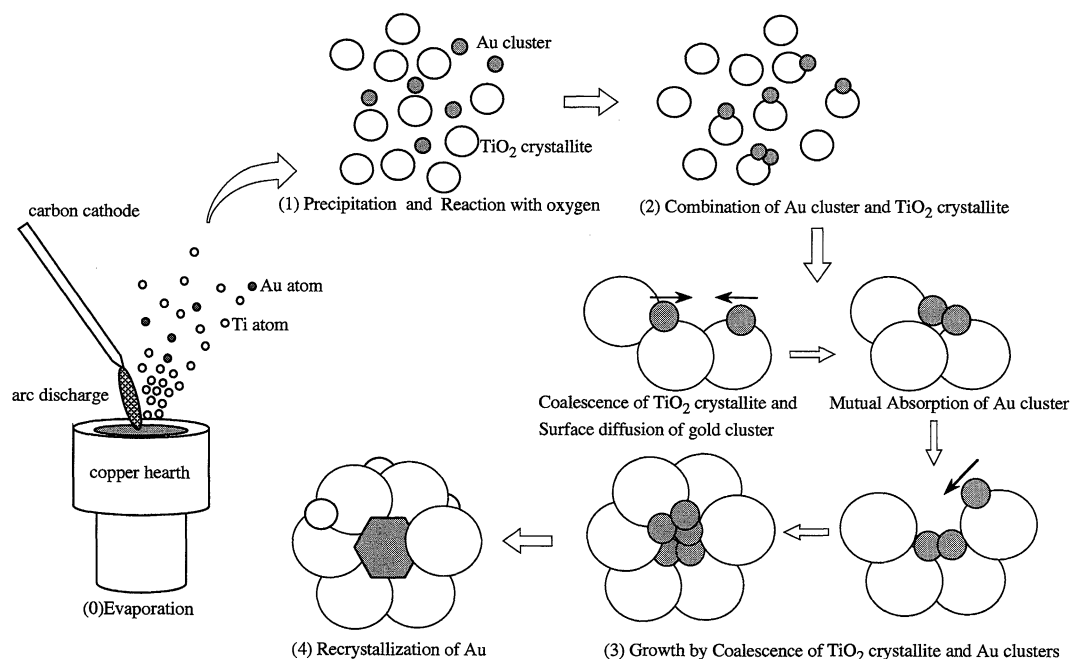


Fig. 6 Schematic image of the formation process of core-shell structure.

this surface plasma resonance absorption is observed around 550 nm and causes the Nile green color. Though the relationship between wavelength of surface plasma resonance absorption and the particle sizes varies according to the experimental conditions,⁵⁾ reducing particle sizes will generally bring about blueshift in absorption spectra. This result may explain that the major gold particle size of TiO₂-Au-b is presumed to be 18 nm estimated by Scherrer method.

3.4 Composite particle formation process

Figure 6 shows a presumed formation process of the core-shell structure. (1) Gold clusters were condensed, and titania crystallite was precipitated in oxidizing atmosphere at the temperature of the boiling point of gold, or the decomposition point of titania. (2) Then gold clusters and titania crystallite combined, but gold clusters were still melting and could move on the surface of titania crystallite. (3) During the growth process by absorbing gas phase atoms, plural titania crystallite with melting gold would collide and associate. A melting gold cluster on a titania crystallite would diffuse and absorb other gold clusters. This process was repeated, and the gold cluster would grow to be a particle. (4) In this process,

gold particles were centered and recrystallized under melting point of gold. The boundaries of titania crystallite would be filled by grain growth process.

4. Summary

We prepared gold-titania composite nanoparticles by the gas condensation method. The composite particles had core-shell structures. Crystal structures of prepared titania had mixed phases of anatase and rutile, and had no relation to the gold content. Diffuse reflectance measurements showed the surface plasma resonance absorption around 550 and 500 nm for TiO₂-Au-a and TiO₂-Au-b, respectively.

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