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Room Temperature Preparation and Optical Properties of Titania and Silica Thin Films Embodying Polymer-Protected Ultrafine Metal Particles at High Concentrations

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Titania and silica glass thin films embodying Au and Pt ultrafine particles at the particle concentrations on the order of 10^{16} cm^{-3} are prepared thoroughly under ambient temperature and pressure by adding the liquid dispersion of the particles in the course of the sol-gel process. Changes in the reduction conditions vary the size of the Au particles giving the smallest mean diameter of 2.8 nm, and lead to the films showing the plasma absorption ranging from 530 to 620 nm and the absorption coefficients up to 1.0×10^{3} cm^{-1}.

Nano-scaled particles of metals and semiconductors exhibit several intriguing properties different from those of their bulk state. In particular, the third-order optical nonlinearity of the ultrafine particles is the most attractive today owing to its peculiar responses in sub-picosecond. Although there have been quite many reports on the optical nonlinearity of the ultrafine particles of semiconductors such as CdS and CuCl,[1,2] such studies on metals are scarce.[3,4] In preparation of such nano-scaled particles, sufficiently narrow size distribution, as well as the small sizes themselves, is crucial for detailed investigation. Most of the preparing procedures previously reported on glasses containing metal particles included the processes at elevated temperatures such as melting the glass components and the thermal diffusion of metal ions, and thereby the broadened size distributions were inevitable.[5] Moreover, the heat treatments often degraded the optical nonlinear responses. It has been reported that the reduction of metal ions in a solution with a soluble polymer yields a stable dispersion of ultrafine metal particles protected by the polymer which prevents aggregation and growth of the particles. In particular, photoreduction can form extremely small particles with narrow size distribution.[6] Sol-gel glasses of metal oxides are preferable as a matrix because of their high optical and mechanical quality, wide variety of the electric properties, and good applicability to microporous host materials. In the present study, we have combined the liquid phase preparation of the ultrafine metal particles with the sol-gel process to develop a new route to prepare the glasses containing the nano-scaled metal particles. The whole procedures were carried out under the ambient conditions, and thereby titania and silica glass thin films embodying gold and platinum ultrafine particles with appreciably narrow size distributions were obtained without aggregation even at high particle concentrations.

Ultrafine particles of gold and platinum were prepared by photoreduction[6] of $HAuCl_4$ and K_2PtCl_4, respectively, in the presence of a protective polymer, poly(*N*-vinyl-2-pyrrolidone) (PVP) or poly(methyl vinyl ether) (PMVE). The starting metal compound and the protective polymer were dissolved in an ethanol-water mixed solvent ([metal atom] = 1.0×10^{-3} or 5.0×10^{-3} mol dm^{-3} and [monomeric residue of the polymer]/[metal atom] = 20). The solution in a Pyrex vessel was degassed twice by the freeze-thaw cycles and was subsequently irradiated with a 500 W xenon lamp through a hard glass filter until the change in color of the solution was

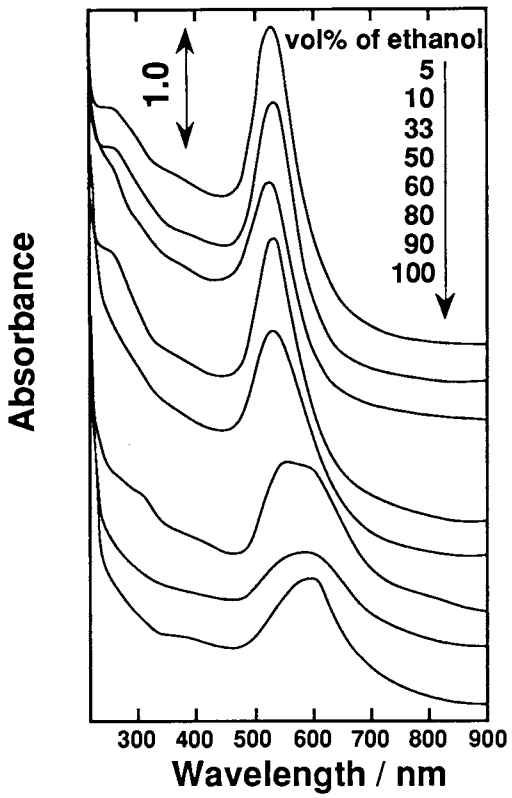

Fig. 1. UV-Vis absorption spectra of Au ultrafine particles prepared in ethanol-water mixed solvents at various compositions.

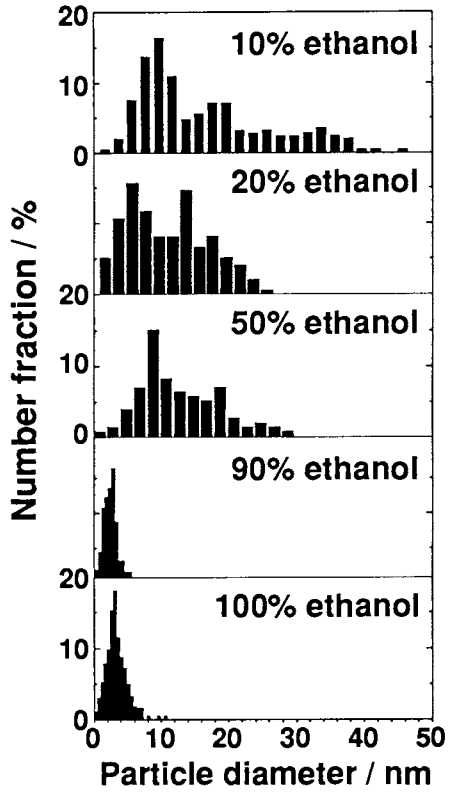

Fig. 2. Size distributions of Au ultrafine particles prepared in ethanol-water mixed solvents at various compositions.

completed. The resulting transparent dispersions of the polymer-protected ultrafine particles have intense colors such as dark brown for Pt, and deep red or deep blue for Au. Whereas the dispersions of both Pt and Au particles prepared with PVP were substantially stable, PMVE was incapable of preparing the stable Au dispersions.

The size and the optical absorption of the ultrafine particles changed with changing the conditions of the photoreduction, particularly for Au. Figure 1 represents the variation in the absorption spectra of the dispersions of the Au ultrafine particles yielded in the solvents with various ethanol content. The surface plasma resonance absorption of Au particles has been reported to have a distinct maximum typically around 520 nm.[7] The dispersions prepared in the solvents with less than 30% of ethanol have deep red colors, and show the sharp absorption peaks at around 520 nm. Over 200 metal particles were examined for each sample with a JEOL JEM-2000FX transmission electron microscope (TEM) of Research Laboratory of High Voltage Electron Microscope, Kyushu University. The mean diameter of the particles prepared in 10% ethanol is 17.5 nm with the standard deviation of 9.6 nm. However, with increasing ethanol content in the solvent the absorption peak shifted to longer wavelengths, and simultaneously, the mean particle diameter decreased with narrowing the size distribution as shown in Fig. 2. Band broadening with decreasing particle size as seen in Fig. 1 has been predicted theoretically.[8] In 90% ethanol the peak wavelength reached 560 nm with the smallest mean diameter of 2.8 nm and the standard deviation of 0.94 nm. Nevertheless, in 100% ethanol the mean particle size became slightly larger (3.4 nm), and a new absorption maximum appeared at 603 nm with a shoulder at around 560 nm. Since a similar tendency of the particle size variation was observed for other aliphatic alcohols, the changes in the particle size could be related to the extent of hydration of PVP molecules and/or gold nuclei. However, the size as well as the optical absorption of the Pt ultrafine particles was much less dependent on the conditions of the preparation, resulting in

the mean diameter of 1.8 nm in 50% ethanol. Figure 3 shows the transmission electron micrographs of the Au and Pt particles in the dispersions which the size distributions presented in Fig. 2 stand for.

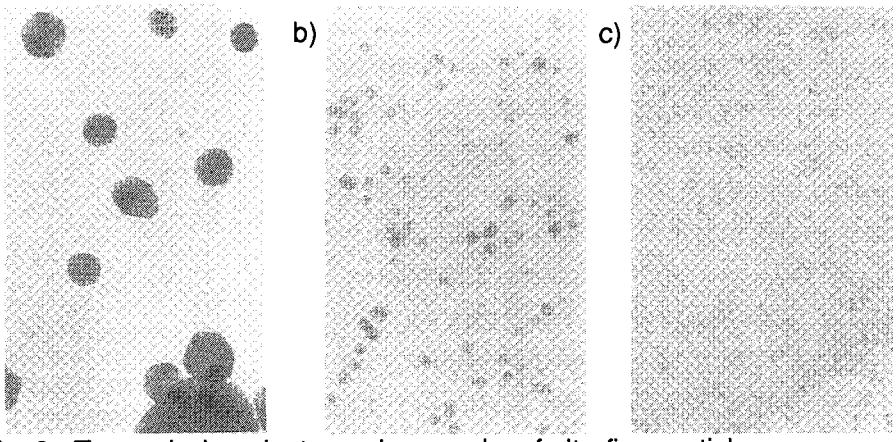

Fig. 3. Transmission electron micrographs of ultrafine particles prepared by liquid phase photoreduction in ethanol-water solvents. a), Au in 50% ethanol; b), Au in 90% ethanol; c), Pt in 50% ethanol.

In order to attain high optical density of the final products, the liquid dispersions with the initial metal concentration of 5.0×10^{-3} mol dm^{-3} were concentrated to 5 times with a rotary evaporator beforehand. A mixture of 10 cm^3 of the concentrated dispersion with 0.5 g of Triton X-100® (polyethylene glycol alkylphenyl ether, Rhom & Haas Co., USA) and 0.105 cm^3 of 9.6 mol dm^{-3} HCl was added dropwise to a solution of 1.0×10^{-2} mol of Ti(*i*-OC3H7)4 and 5.0×10^{-3} mol of acetylacetone as a chelating stabilizer[9] in 10 cm^3 of ethanol. All the mixing procedures were carried out under nitrogen. After 30 min of stirring the mixture was exposed to ambient moisture and then a homogeneous sol was obtained. A slide glass plate as a substrate was then immediately dipped into the sol. The dip-coating procedure was repeated if thicker films were required. For the preparation of the silica films, similar procedures using Si(OC2H5)4 were carried out thoroughly in air, without the addition of acetylacetone. Unfortunately, addition of PVP to the solution containing Si(OC2H5)4 resulted in formation of unfavorable precipitation, which implies a crosslinking reaction of the polymer. Similar precipitation with Si(OC2H5)4 was observed also for other protective polymers such as poly(vinyl alcohol) capable for the stable Au dispersions. The preparation of silica glass films embodying the Au ultrafine particles is hence unsuccessful at present.

The thin glass films successfully obtained were examined with a JEOL JSM-T330A scanning electron microscope (SEM) and their extremely flat and smooth surfaces were revealed. Since the dispersions of the Pt ultrafine particles have no absorption maximum within the region observed, both the titania and silica glass films embodying the Pt particles exhibit no marked spectroscopic features. Contrastingly, Figure 4 depicts the absorption spectra of the titania films embodying the Au ultrafine particles along with those of the corresponding starting dispersions prepared in 50% and 100% ethanol. When the Au particles were embedded into the titania glass matrix, the absorption band due to the particles shifted to longer wavelengths without significant change in the shape of the band. This would be ascribed to a difference in ε_m, the dielectric constant of the surrounding medium, between the ethanol-water solvents and titania, since an increase in ε_m should lead to an de-

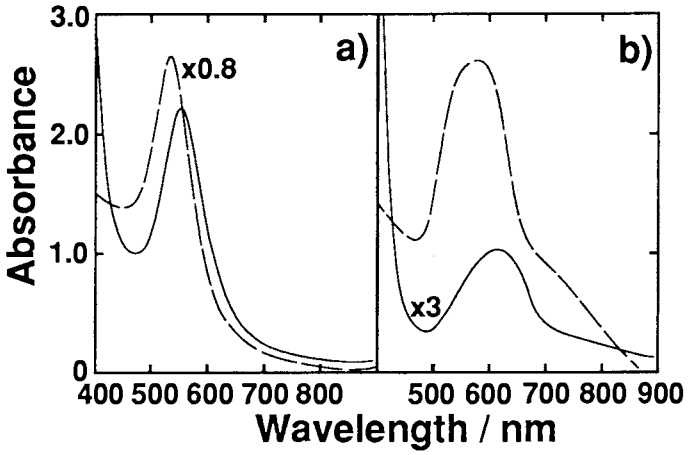

Fig. 4. UV-Vis absorption spectra of titania glass thin films embodying Au ultrafine particles prepared in a) 50% and b) 100% ethanol. The spectra of the starting dispersions are also shown as the broken lines.

crease in the surface plasma resonance frequency of the embedded particle.[10] It has been pointed out by several authors that the optical absorption spectrum of small metal particles will be changed dramatically if the particles are aggregated.[8] In particular, the shape of the aggregates strongly influences the peak wavelength. However, the TEM observation of the embedded particles reproduced in Fig. 5 confirmed that the particles remained intact and that the distribution of the particles in the glasses were appreciably uniform, since there was neither any change in the particle size nor any aggregation of the particles even in such close vicinity each other as seen on TEM. These results infer that the absorption peaks of the titania thin films widely ranging from 530 to 620 nm are direct reflection of the plasma resonance absorption of the Au particles in the starting dispersions. The cross-sectional SEM observation revealed that the thickness of the triply coated films is typically 6-10 μm. The thickness and the maximum absorbance deduce the absorption coefficients of the films embodying the Au particles prepared in 50% and 100% ethanol as large as 1.0×10^3 and 270 cm^{-1}, respectively. The average number of the metal atoms in one particle calculated from the mean particle volume enables rough estimation of the particle concentration as ca. 3×10^{16} particles per cm^3 for the glass of Fig. 4b), assuming the same absorption coefficient per unit particle concentration both in the liquid dispersion and in the titania glass.

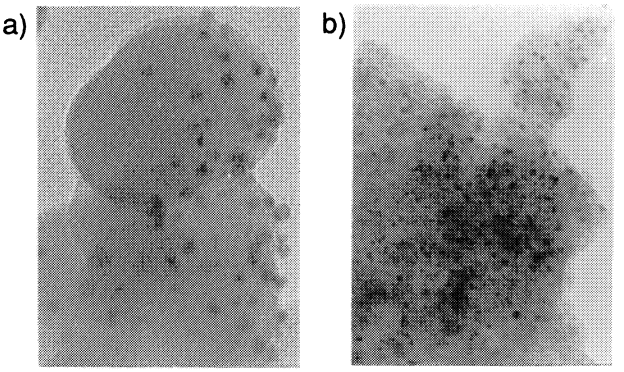

Fig. 5. Transmission electron micrographs of titania glass thin films embodying ultrafine particles of a) Au prepared in 100% ethanol and b) Pt prepared in 50% ethanol.

In conclusion, the liquid phase photoreduction of $HAuCl_4$ and K_2PtCl_4 followed by the sol-gel process of alkoxides have yielded the glass thin films embodying the well size-controlled ultrafine metal particles with no aggregation even at high concentrations thoroughly at room temperature. Since the preparing procedures of the particles and the films are essentially independent each other, this technique can give a versatile way to prepare thin films which embody nano-scaled particles or clusters keeping them intact. In addition, the sol-gel glass thin films exhibiting a variety of the plasma resonance frequency of metals would be valuable not only for the studies on the optical nonlinearity of the ultrafine metal particles but also for those on the resonant interactions between the particles and other dopant molecules under the intense electromagnetic fields.

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