# 論文 / 著書情報
# Article / Book Information

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| 論題(和文) | |
| Title(English) | Gold Nanoparticle-Doped Microspheres of Optical Cavity Structure |
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| 出典(和文) | , Vol. , No. , pp. O-14-015 |
| Citation(English) | XX International Congress on Glass, Kyoto, Japan, Vol. , No. , pp. O-14-015 |
| 発行日 / Pub. date | 2004, |

# GOLD NANOPARTICLES-DOPED MICROSPHERES OF OPTICAL CAVITY STRUCTURE

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The gold nanoparticles-doped microspheres of optical cavity structure have been fabricated. The Au ion-doped hybrid microspheres of $n_D$=1.72 were prepared by the vibrating orifice technique using titanium tetra-n-butoxide and diphenyldimethoxysilane. $HAuCl_4$ and n-(2-aminoethyl)-3-amino-propyltrimethoxysilane, were co-doped as Au ion sources and their stabilizer. Au nanoparticles precipitated in the hybrid microspheres at 120ºC heating. After subsequent heating at 600ºC, they were changed to $TiO_2$-$SiO_2$ oxides microspheres of $n_D$=2.6 with their amorphous state and good spherical shape keeping. Au nanoparticles in the microspheres also kept their narrow size distribution.
(Key words: Au nanoparticles-doped glass, high refractive index, sol-gel technique, spherical optical cavity structure)

## 1. Introduction

Metal nanoparticles-doped glasses have been attracted much attention because of their enhanced third-order nonlinear optical susceptibility, $\chi^{(3)}$ [1], and ultrafast response time applicable to optical switches [2]. The $\chi^{(3)}$, related with the plasma absorption of the glass caused by surface plasma resonance of metal nanoparticles, depends on the diameter of nanoparticles, therefore controllable precipitation of the metal nanoparticles are essential requirements in their application. Much work has been reported on fabricating and investigating of metal nanoparticles-doped glasses, and there are many techniques to prepare the metal nanoparticles-doped glasses; heat treatment precipitation from conventional melt-quenching glass, ion implantation technique and sol-gel technique for instance. We focused on the sol-gel technique because of having advantages of that; being easy to apply to coating process, having possibility to achieve the low processing temperature and to have wide choice of the both dopant and host matrix material. Furthermore, sol-gel technique has another attractive merit for us that can be applied the vibrating orifice technique, which we already developed for fabricating the micrometer-sized spherical optical cavity structure as described below. In our work, the mono-dispersed silver or gold nanoparticles-doped $SiO_2$ film from hybrid sol containing metal ions with stabilizer was fabricated on silica glass substrates by the sol-gel dip coating technique. High thermal- and photo-stability of Au nanoparticles and complicated changes of Ag nanoparticles by heating were observed [3].

Although the glass contained metal nanoparticles has many strong points and its $\chi^{(3)}$ has been improved to $10^{-7}$ esu order by the efforts of material scientists [4, 5], a higher $\chi^{(3)}$ is still required for practical applications. The incorporation of nanoparticles into a cavity structure is the way to obtain the high $\chi^{(3)}$, and the micrometer-sized spherical optical cavity structure is the most hopeful one for its high quality factor $Q$, which indicates the efficiency of the light encapsulation [6]. Since confinement of the optical field inside the sphere can lower the threshold of nonlinear effects, combining the optical spherical cavity with high $\chi^{(3)}$ of metal nanoparticles will lead to a new opt-opt switching devices. We already investigated to make silica spheres containing Ag nanoparticles using two sol-gel fabrication methods; a modified Stöber method and coating the microsphere with Ag nanoparticles-doped silica thin films [7]. In spite of the micrometer-sized silica spheres containing incorporated controllable Ag nanoparticles with good surface smoothness were achieved, we have been confronted with two big problems: one is the low relative refractive index $n_r$=($n_{sphere}$/$n_{medium}$) of silica microspheres, and another is the low stability of Ag nanoparticles. The quality factor $Q$ depends on the sphere's diameter and $n_r$=($n_{sphere}$/$n_{medium}$) [8], so high $n_r$ is inevitable to accomplish the spherical optical cavity structure in micrometer-sized particle. From a practical point of view, the

microspheres should be coated with clad materials of lower refractive index than those of particles. Supposing that we use available low-index materials for cladding (e.g. solvent or plastics of $n_{medium}$=1.3-1.4), $n_{sphere}$>2.0 is needed to satisfy the high index difference of nearly $n_r$>1.5, and the silica sphere couldn't realize such high $n_r$. This is the detail of first problem. The second problem is the heat-induced precipitation and light-induced degradation of Ag nanoparticles. Of course, this phenomenon is interesting from the scientific point of views, but it is not suitable for the practical applications. To meet the requirement of high $n_r$, we have been investigated the high-index microspheres. In our previous work, $Eu^{3+}$-doped $TiO_2$-$SiO_2$ microspheres of $n_D$>2.0 applicable to the practical use were fabricated and the resonant emission from them was confirmed by pumping with a laser light of 514.5nm wavelength of a CW-$Ar^+$ laser [9]. As concerns stability of metal-nanoparticles, we found that the Au nanoparticles have enough properties to apply the practical uses [3].

In this paper, we present the first trial to prepare the Au nanoparticles-doped microspheres of $n_D$>2.0 and investigate the precipitation condition, size distribution and thermal stability of Au nanoparticles in high refractive-index microspheres.

## 2. Experimental

Au nanoparticles-doped microspheres were prepared by the following steps: (1) preparing the starting sol solution, (2) fabricating the hybrid microspheres and (3) heating them at 120-600ºC to precipitate the Au nanoparticles and to realize the high refractive index of $n_D$>2.0. Starting sol solution of Au nanoparticles-doped hybrid microspheres was prepared from titanium tetra-n-butoxide (TTBu) and diphenyldimethoxysilane (DPhDMS) in the molar ratio of 80:20. The DPhDMS was dissolved in tetrahydrofuran and hydrolyzed in aqueous HCl solution of pH=2 at room temperature for 3 days.
After the reaction, the TTBu dissolved in isopropanol was titrated into the solution. Small amount of $H_2O$ diluted with isopropanol was subsequently titrated slowly into the solution to accelerate the hydrolysis of TTBu. In order to avoid inhomogeneity caused by high-rate chemical reaction, the solutions were held at 3ºC. The TTBu/$H_2O$ was chosen in the molar ratio 1:1, which was just half amount of $H_2O$ to complete the hydrolysis of TTBu. The resultant solution was stirred for 1 day at room temperature for aging. Then Hydrogen tetrachloroaurate (III) $HAuCl_4$ dissolved in ethanol with a stabilizer, n-(2-aminoethyl)-3-aminopropyltrimethoxysilane (APTS) was added to the solution and used as the starting sol. Typical $HAuCl_4$ and APTS concentration were $1x10^{-4}$ and $2x10^{-4}$ mol/g ($HAuCl_4$:APTS = 1:2 in molar ratio) respectively.

Hybrid microspheres were fabricated by the vibrating orifice technique followed by the similar manner in our previous work [10]. A cylindrical liquid jet passing through the orifice of 20μm in diameter broke up into equal-sized droplets by mechanical vibration. The droplets were carried by airflow through a pipe, and during the process, alcohol solvent of these droplets was evaporated. Subsequently, these droplets were trapped and solidified in 25wt% ammonium water. Surfactant dodecyl benzene sodium sulfonate was added into the ammonia water to avoid coagulation of particles.
The resultant microspheres were placed on a fused silica glass plate and dried at 30ºC for 30min, and heated at 120ºC for 15min. For increasing the refractive index, the microspheres were heated with a heating rate of 10ºC/h up to a certain temperature of 200-600ºC and kept 2hrs in an electric resistance furnace under oxygen atmosphere.

The shape of the microspheres was checked by an optical microscope and by a field-emission type scanning electron microscopy (FE-SEM; JEOL, Model JSM-6301). The diameters of the microspheres were measured by SEM photographs. The diameters of Au nanoparticles were measured by backscattered electron (BSE) image. Change in weight, structure and organic components of the microspheres during heating were measured by DTA-TG (Rikagaku Co., Thermo plus TG8210) and microscopic Raman-scattering spectroscopy (JASCO, Model NRS-2100).

## 3. Results

Photographs of microspheres by an optical microscope are shown in Fig. 1. The samples after 120ºC and 600ºC heating are shown in (a) and (b) in the figure respectively. The color of the 120ºC-heated microspheres was pale-pink, and it changed to dark-violet after heating at 600ºC. Initial diameter of the microspheres was 7μm, and after 600ºC heating, their diameter shrank to 4.5μm. The change in the diameter of the microspheres plotted against the heating temperature is shown in Fig.2-(a). The

diameter decreased steeply at 250ºC, and finally, nearly 35% decrease was confirmed after 600ºC heating. It means that the volume of the microspheres was decreased to 30% of initial. Each microspheres possess good spherical shape and narrow size distribution despite its volume decreased drastically as shown in Fig.1. Figure 2-(b) shows the DTA-TG result. The sharp exothermic peak along with the weight loss more than 10%, slightly small weight loss continued up to 450-500ºC and broad exothermic peak around 450ºC were observed.

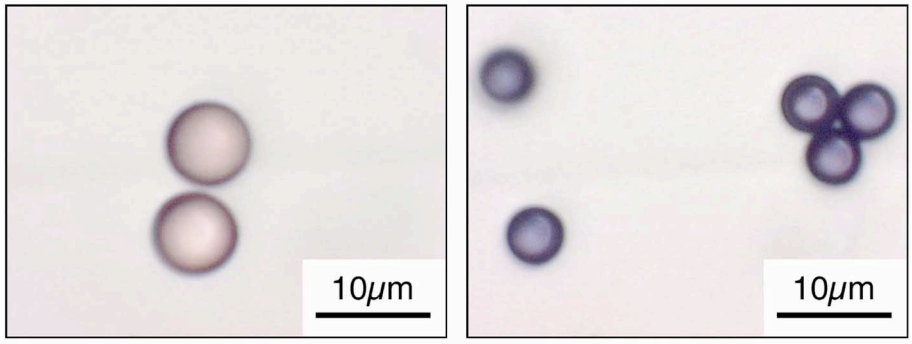


Fig. 1. Photographs of microspheres by an optical microscope. The microspheres heating at 120ºC and 600ºC are shown in (a) and (b). The diameter of the microspheres in (a) and (b) are 7.0μm and 4.5μm respectively.

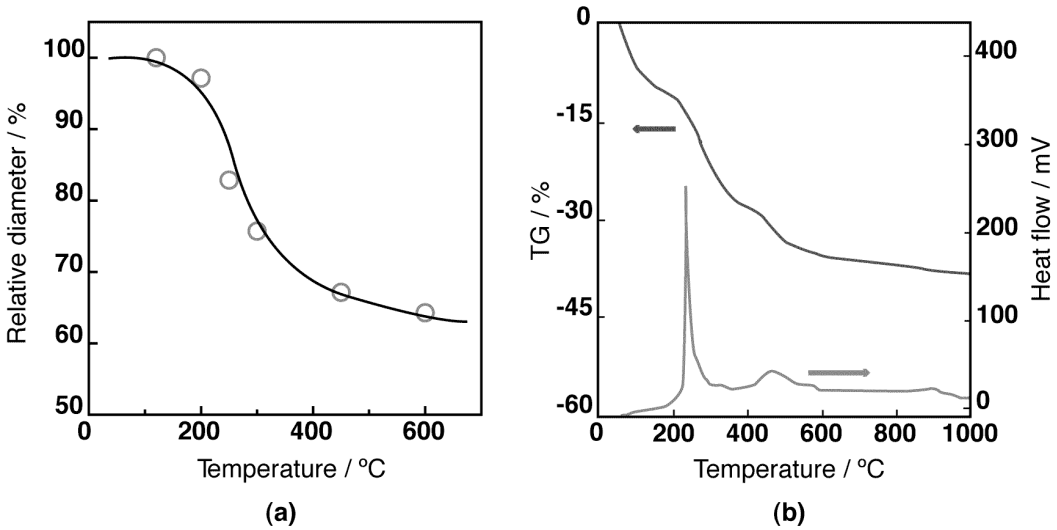


Fig. 2. (a) Change in relative diameter of the microspheres by heating. (b) DTA-TG traces of the 80TTBu-20DPhDMS sample. Heating rate was 2ºC/min.

FE-SEM photographs of the microspheres after 120ºC and 600ºC heating were shown in Fig. 3. Fig. 3-(a) and (b) are the photographs of 120ºC heated microsphere, and (c) and (d) are the microsphere after 600ºC heating. Precipitation of a large number of Au nanoparticles in every microsphere heated at 120-600ºC was confirmed by backscattered electron (BSE) images (Fig. 3(b) and (d)). From the photographs, we noticed that the Au nanoparticles are not so influenced by heating temperature. Particle size distributions of Au nanoparticles after 120ºC and 600ºC heating, estimated from the BSE images, are shown in Fig. 4. The both of average radiuses of Au nanoparticles after 120ºC and 600ºC heating were 8nm. The nanometer-sized surface irregularities were also observed at 120-450ºC heated microsphere as shown in Fig. 3(a). The size of the irregularities didn't change by heating under 450ºC. After heating at 600ºC however, the irregularities almost disappeared (Fig. 3(c)).

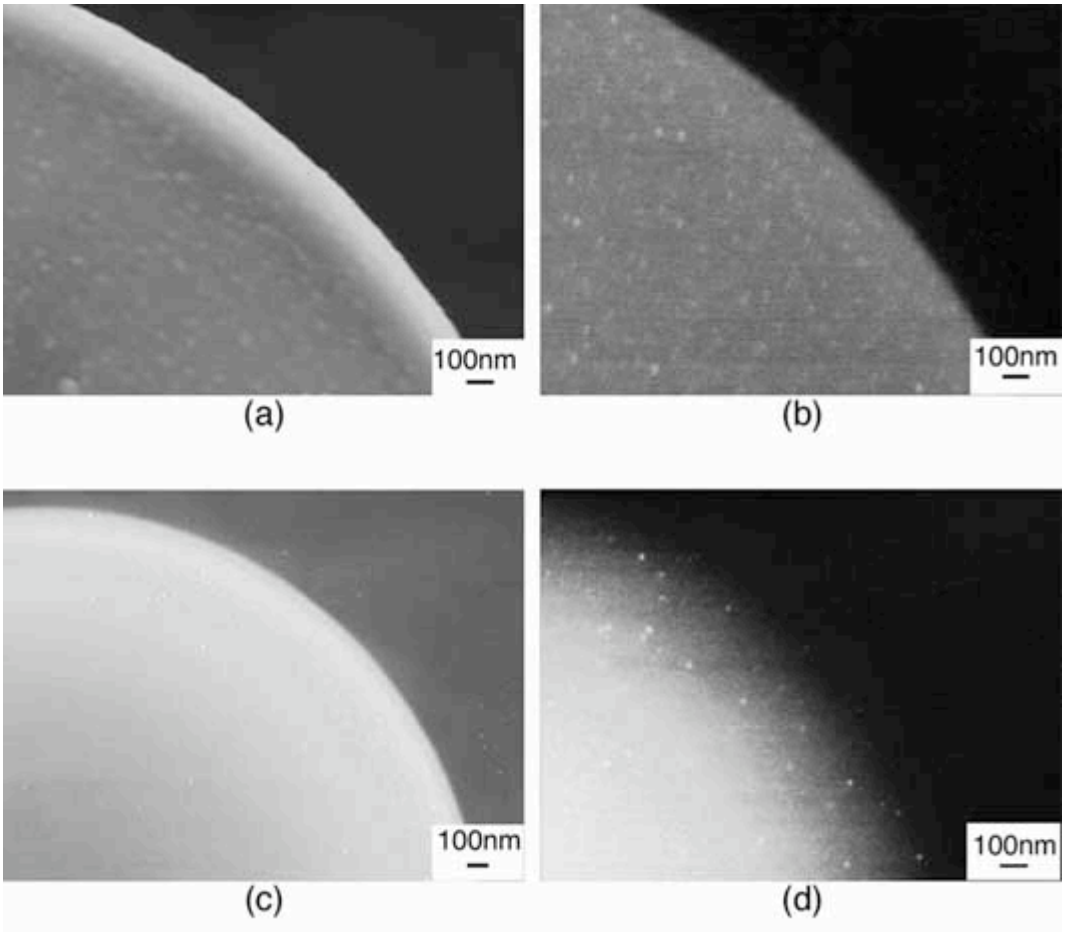


Fig. 3. (a) SEM photograph and (b) backscattered electron (BSE) images of 120ºC heated microsphere, and (c) SEM photograph and (d) BSE images of 600ºC heated microsphere. The bright dots in (b) and (d) are the Au nanoparticles.

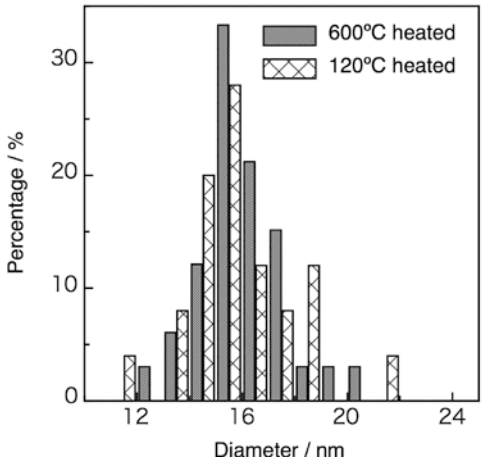


Fig. 4. Size distributions of Au nanoparticles in 120ºC- and 600ºC-heated microspheres.

## 4. Discussions

Au nanoparticles were not affected by heating while the matrix of microsphere was completely changed. It is not so surprise that the Au nanoparticles didn't change because of its high thermal and chemical stability. In additions, the same thermal stability in $SiO_2$ matrix was already reported [3]. Therefore, we discuss the changes of the microsphere's matrix while it was heated, and the effect to plasma absorption of Au nanoparticles of the heat treatment.

The diameter change of the microspheres by heating can be explains from the results of DTA-TG shown in Fig.2-(b). The diameter decrease at 250ºC corresponds to exothermic peak due to firing the solvents and the organic groups (phenyl group for instance) from hybrid matrix. Subsequently decrease in diameter in 250-600ºC, corresponds to a small amount of weight loss continued up to 600ºC, is the resultant of elimination and evaporation of organic groups as carbon dioxide. The hybrid microsphere changed to $80TiO_2$-$20SiO_2$ oxides after 400-600ºC heating, which was confirmed from the disappearance of the band due to phenyl group (600, 1000, 1600$cm^{-1}$) by Raman scattering measurement (not shown here). They kept its amorphous state after heating at 600ºC, which was checked by the XRD pattern (not shown here), in spite of $TiO_2$ nano-crystals (anatase structure), detected by Raman scattering spectra, were precipitated when the microspheres were heated above 450ºC.

Comparing the SEM photographs (Fig. 3(a)) and BSE images (Fig. 3(b)), we noticed that *all* Au nanoparticles are located in the nanometer-sized irregularities on the surface of microspheres. Au nanoparticles-doped $SiO_2$ thin film, non-doped and Eu ion-doped microsphere did not include these defects. Note that there are many irregularities without Au nanoparticles, thus Au nanoparticle was not the direct reason of formation of it. Moreover, apparent difference in composition around the Au nanoparticles didn't confirm from BSE images. Taking account of these facts, the irregularities were not compositional inhomogeneities and were possibly formed by the local hydrolysis and condensation of alkoxides around Au ion and APTS, acted as basic catalyst, antedating the spherical shaped formation. Hence, controlling the rapid reaction in sol solution by modifying the synthesis process and/or changing the quantity of APTS and $HAuCl_4$ probably prevent the generation of irregularities.

Plasma absorption spectra caused by Au nanoparticles in the microsphere after 120ºC and 600ºC heating calculated according to the Mie theory [11] were shown in Fig. 5. Both radii of Au nanoparticles used for the calculation were 8nm from the result of Fig. 4, and refractive indices $n_D$ of the microsphere were 1.72 for 120ºC and 2.6 for 600ºC sample. The indices of the microspheres were estimated in our previous work [9] from the approximately correlation between the mode spacing and microsphere's refractive index as described in the Ref. 8. The plasma absorption bands increased with increasing temperature (increasing refractive index) and shifted from 570nm to 690nm in wavelengths. The peak shift of plasma absorption and increase in number of Au nanoparticles per unit volume, due to the microspheres' shrinkage, caused microspheres' color change from pale pink to dark violet as shown in Fig. 1. The fact of that plasma absorption band of Au nanoparticles in high-index microsphere is around 700nm in wavelength suggests that conventional semiconductor laser can be used as the light source of the control signal. We also tried to measure the absorbance spectrum of the microspheres dispersed in matching oil using the conventional ultraviolet-visible spectrometer to confirm the plasma absorption of Au nanoparticles in microsphere directly, but we haven't be able to measure it because there is no suitable matching oil satisfied with the requirement of high refractive index (nD≈2.0) and density (d>4).

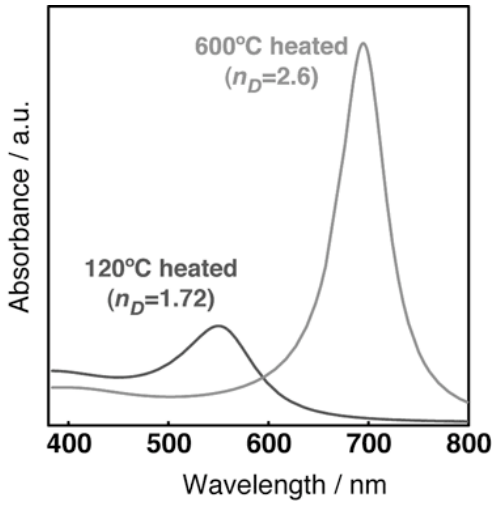


Fig. 5. Calculated absorption spectra of Au nanoparticles. Refractive indices $n_D$ of the matrix were 1.72 for 120ºC-heated and 2.6 for 600ºC-heated microsphere. Both radii of Au nanoparticles used for calculation were 8nm from the result of Fig. 4.

## 5. Conclusion

In conclusion, Au nanoparticles-doped 80TTBu-20DPhDMS microspheres of $n_D$=1.72 were prepared by vibrating orifice technique, and Au nanoparticles-doped $80TiO_2$-$20SiO_2$ microspheres of $n_D$=2.6 were successfully fabricated by subsequently heating at 600ºC. We confirmed the precipitation of mono-dispersed Au nanoparticles in every microsphere heated at 120-600ºC. The average radius of Au nanoparticles was 8nm and it wasn't affected by heating temperature. These results are considered the first steps of realizing the practical opt-switching device using the microspheres of optical cavity structure. Measurement of the optical effects of Au nanoparticles in the spherical optical cavity structure and perform the resonant emission from the Au nanoparticles-doped microsphere are in progress.

## 6. References


[1] F. Hache, D. Ricard, C. Flytzanis and U. Kreibig, *J. Opt. Soc. Am.*, **B3**, 1647 (1986).
[2] D. Ricard, P. Roussignol and C. Flytzanis, *Opt. Lett.*, **10**, 511 (1985).
[3] S. Shibata, K. Miyajima, Y. Kimura and T. Yano, *Proc. of the XII International Workshop on Sol-Gel Science and Technology*, Sydney, Australia (2003).
[4] K. Uchida, S. Kaneko, S. Omi, C. Hata, H. Tanji, Y. Asahara, A. J. Ikushima, T. Tokizaki and A. Nakamura, *J. Opt. Soc. Am.* B **11**, 1236 (1994).
[5] N. Kitazawa, T. Yano, S. Shibata and M. Yamane, *Jpn. J. Appl. Phys.*, **35**, 2228 (1996).
[6] M. Gorodetsky, A. A. Savchenkov and V. Ilchenko, *Opt. Lett.* **21**, 453 (1996).
[7] S. Shibata, K. Aoki, T. Yano and M. Yamane, *J. Sol-Gel Sci. Tech.*, **11**, 279 (1998).
[8] S. C. Hill and R. E. Benner, in *Optical Effects Associated with Small Particles*, edited by P. W. Barber and R. K. Chang (World Scientific, Singapore, 1988), pp.4-61.
[9] Y. Arai, T. Yano and S. Shibata, *Proc. of the XII International Workshop on Sol-Gel Science and Technology*, Sydney, Australia (2003).
[10] S. Shibata, A. Tomizawa, H. Yoshikawa, T. Yano, and M. Yamane, *Proc. SPIE* **3943**, 112 (2000).
[11] G. Mie, *Ann. Physik*, **25**, 377 (1908).