FORMATION OF Au CLUSTER/ SILICA NANOCOMPOSITE GELS

Masao Watanabe[1], Sakae Tanemura[1], Yutaka Tai*[2], and Koji Tajiri[1, 2]

1. Nagoya Institute of Technology, Nagoya 466-8555, Japan
2. Chubu Research Base, National Institute of Advanced Industrial Science and Technology (AIST),
Nagoya 463-8560, Japan * Fax: 81-52-736-7288, e-mail: tai.y@aist.go.jp

A nanocomposite of dodecanethiol-passivated gold clusters (average diameter 2.6 nm) and a silica aerogel has been synthesized. It was found that the gold particles were efficiently adsorbed on a silica wet gel in toluene and the particles were not flushed out during supercritical CO_2 drying. The size distribution of the gold cores was not changed by the drying process. The nature of the adsorption interaction between the passivated clusters and silica gel is discussed in the light of adsorption rate measurements.
Keywords: Gold cluster, Silica, Adsorption, Supercritical drying, Aerogel

1.INTRODUCTION

Chemical and physical properties of small metal particles have been subjects of intensive research because of their scientific and technological importance. Small metallic particles are chemically reactive, and because of this property, some of them are used as catalysts for various purposes. Likewise, as proved from gas-phase studies, the smallest analogues, metal clusters (or nanoparticles), are reactive with gaseous molecules and, in some cases, the reactivity differs by orders of magnitude according to the cluster size [1-3]. The metal nanoparticles are also expected to have enhanced non-liner optical properties which are important in the development of ultrafast optical switching devices [4,5]. Thus, the production of a mono-dispersed cluster system with a specific cluster size would have a great impact on various technological fields. As for a nanoparticle support, silica aerogel is regarded as a material with unique potential advantages. Silica aerogel is a very porous material with a large surface area which is prepared by the polymerization of monomer or oligomer silicates followed by drying under supercritical conditions [6]. The pore size (1-100 nm) and porosity can be controlled by the preparation conditions such as the concentration of starting materials and the pH of reaction system [6]. A large surface area enables aerogel to retain nanoparticles at high number density, and a large pore size enables reactant molecules encounter the particles not only on the surface but inside the material, which is advantageous for catalytic uses. Moreover, silica aerogel is transparent in the visible region; thus, could be used for optical purposes as well. Incorporation of metal nanoparticles in silica aerogel has been attempted by several methods so far. Heinrichs et al. prepared silica aerogel and xerogel containing Pd nanoparticles inside the pores or the silica particles by changing synthetic procedures [7]. Their methods are based on sintering of metal particles from metal chelate ions bound to Si-O skeletons. Rolison and co-workers reported a method utilizing preformed colloidal particles in which the particles are added to an about-to-gel silica sol [8]. The key question for the nanocomposite formation is how to fix the nanoparticles firmly on the silica structure.

In this paper, we will show that thiol-passivated gold nanoparticles are efficiently adsorbed on the silica matrix in toluene solution. The gold particles were immobilized on the silica structure to the extent that they are not flushed out upon supercritical CO_2 (sc-CO_2: critical points, Tc=304.2 K, Pc=7.38 MPa, ρc=10.6 mol/dm^3) drying. Since the sc-CO_2 drying is carried out at temperatures only slightly higher than room temperature, diffusion and aggregation of the metallic cores can be suppressed. By the recent progresses in the surfactant-passivation methods, isolated nanoparticles of various elements, noble metals [9,10], transition metals [11,12], and metal oxides [13,14] etc. with minimum core size as small as 1nm have been synthesized [15]. Supporting these material in the silica xerogel and aerogel matrixes would open a way to introduce them into catalytic chemistry and optics or opto-electronics.

2.EXPERIMENTAL

Dodecanthiol-passivated gold nanoparticles (described as $Au_x(SC12)_y$ hereafter) were prepared according to the method of ref. [9]. Briefly, $AuCl_4^-$ ion was extracted from the water to the toluene phase by excess tetraoctylammonium bromide and reduced by sodium borohydride in the presence of dodecanethiol. The molar ratio of Au atom and dodencanethiol was 1:1. The reaction was performed at room temperature. The product was washed with ethanol and purified two times by recrystallization from the toluene/ethanol mixed solvent (1:40 in volume) at 255K.

Silica wet-gel was synthesized by the hydrolysis of tetramethoxysilane (TMOS) in methanol using ammonia catalyst: one mole of TMOS was dissolved in 10 mole of methanol and 6 mole of water containing 0.1 N NH_4OH was added to the solution. A jelly-like bulk solid was yielded by gelation within a few hours. The product was aged for one day and then kept in ethanol.

Drying of the composite wet-gel by sc-CO_2 was performed as follows. The composite wet-gel was placed in an autoclave with pore-filling toluene solvent, and CO_2 was fed into the autoclave. To substitute the solvent to liquid CO_2, the pressure of CO_2 was then raised and kept for two hours at above 7 MPa using a high pressure pump, allowing a small amount of CO_2 flowing out of the autoclave with the toluene solute. This operation was

done for three times to complete the substitution. The temperature of the whole system was kept below 297 K during the procedure. CO_2 was then removed at supercritical conditions: the vessel temperature and pressure were above 313 K and 8 MPa, respectively.

Transmission electron microscopy (TEM) images were taken by the JOEL 2010 with LaB_6 filament operated at 200 kV. For the TEM observations, $Au_x(SC12)_y$ toluene solution and ethanol dispersion of ground nanocomposite aerogel were dried on copper grids.

UV-vis. spectra were recorded on JASCO V-570 spectrometer.

3.RESULTS AND DISCUSSION

Figure 1a shows the TEM image of the Au nanoparticles. The size of the metallic cores of the product ranged from 1-6 nm with the average diameter at 2.6 nm as shown in fig. 1(c).
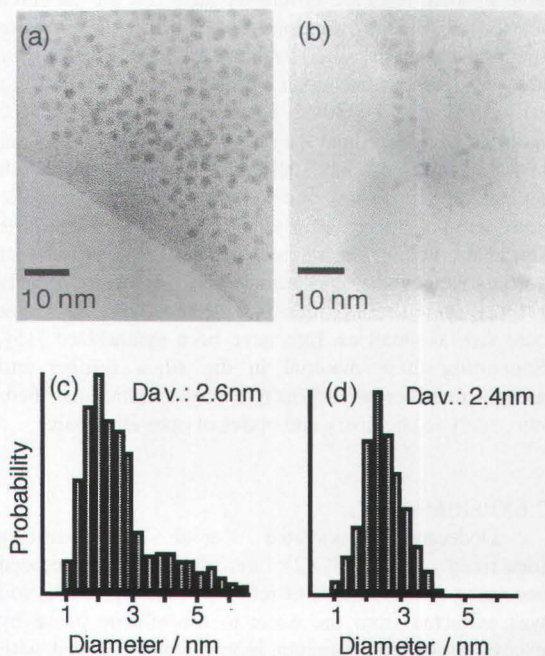

Figure 1. TEM images and corresponding core size distributions of the $Au_x(SC12)_y$ nanoparticle (a, c) and the $Au_x(SC12)_y$ /silica composite aerogel (b, d). The core size distributions were measured for 200 - 300 particles.

Addition of passivated gold particles was attempted by soaking the wet-gel in a toluene solution. It is well known that there are mesopores ($\approx$1-50 nm) in silica gel which can potentially be filled by the nanoparticles. The wet-gel prepared in the present conditions is considered to have pores larger than the nanoparticles. The structure of a wet-gel, to a large extent, can be evaluated from that of the corresponding aerogel formed under supercritical drying because in supercritical drying conditions, there are no liquid-vapor interfaces and thus capillary pressure, the driving force for shrinking, does not exist. The nitrogen adsorption-desorption isotherm results for an aerogel formed via sc-CO_2 drying of the wet-gel prepared in the present conditions gave a pore distribution maximum around 10 nm   [16].

Before immersing the wet-gel, the solvent of the gel, ethanol originally, was exchanged to toluene via ethanol/toluene (1:1 in volume): the gel was soaked in the ethanol/toluene solvent for one day, then neat toluene for one day two times, and finally kept in toluene. Figure 2(a-c) show the photographs of the wet-gel in the $Au_x(SC12)_y$ solution in which 3.0 mg of $Au_x(SC12)_y$ was dissolved in 50 cc of toluene. The diameter and the height of the gel were 40 and 10 mm, respectively. The color of the gel, transparent originally (fig. 2(a)), became as dark as the solution after 5 hours (fig. 2(b)), and surprisingly, after   57 hours, the solution in turn became transparent, indicating all the gold particles were adsorbed on the gel (fig. 2(c)). The gold nanoparticles adhered to the silica structure firmly enough not to be flushed out by sonication in toluene, using a standard ultrasound washing equipment, in a condition that the bulk wet-gel was torn into small pieces. By cutting the gel, it was seen that the gold particles are located mainly in the peripheral part of the gel. For comparison, silica wet-gel was immersed in the toluene solution of C_{60}. In this case, the solution penetrated into the gel, however the C_{60} molecules were not adsorbed on the silica structure.
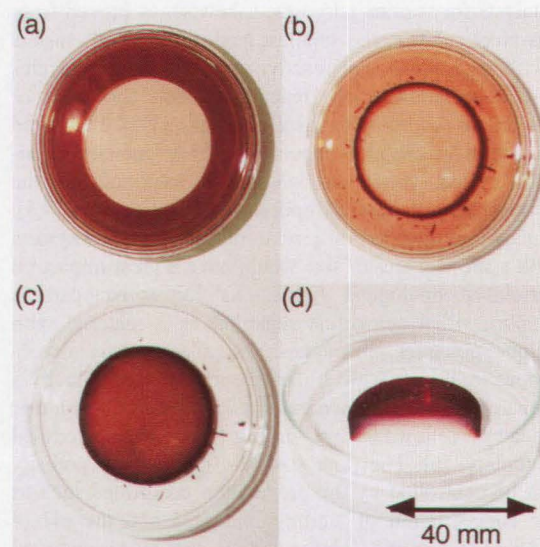

Figure 2. Photographic images of silica wet-gel in the $Au_x(SC12)_y$ toluene solution at (a) 0, (b) 5, and (c) 57 hours after immersion. (d) photographic image of the $Au_x(SC12)_y$/silica composite aerogel. The product aerogel was cut into two by a razor to show the spatial distribution of the nanoparticles.

It is considered that there are two possible interactions to cause nanoparticle adsorption on silica. One is an electrostatic interaction. Generally, on the silica surface, uncondensed hydroxyl groups remain to confer upon the gel its polar properties [17]. Thus, polar molecules are captured on the silica surface by electrostatic interaction (and hydrogen bonding interaction specifically for water). In the Au nanoparticles, surrounding thiol molecules probably form dipole-layers (R^+-S^-) which are analogous to those in the self-assembled thiol monolayers on gold surfaces

[18]. Thus, the dipole-dipole interaction possibly anchors the particles on the surface in low dielectric constant solvents like toluene. The other is affinity between the alkyl chains of the thiol group and residual methoxy or ethoxy groups on the silica surface. Ethoxy groups can be formed by the alcohlysis reaction of OH groups in ethanol, initial pore filling solvent.

To clarify the nature of the adsorption interaction, adsorption rate was evaluated in solvents with different polarity. Figure 3 shows an example of the experiment. The inset in fig.3(a) shows a sketch of the UV-vis. absorbance measurement. A cylindrical gel (ϕ7.8 x length 8.0 mm) with pores filled with neat toluene was put in the toluene solution of $Au_x(SC12)_y$ in a quartz cell with a screw cap. The particle concentration in the solution was 0.083 g/L (the absorbance at 500 nm was 0.7). At this concentration, the number of the adsorption site is far beyond the particle number in the solution. The time dependence of the absorption spectrum was investigated for light beam passed more than $\approx$1mm over the gel. The UV-vis. spectrum showed a broad absorption (plasmon band) around 515nm superimposed on that of transitions from 5d to 6sp bands [10]. Fig. 3(a) shows a series of the absorption spectra. Absorbance of the solution gradually decreased with time. Fig. 3(b) shows the time dependent absorbance at 300, 500, and 600 nm. The absorbances exhibited exponential decay with time except for a few hours after the immersion.
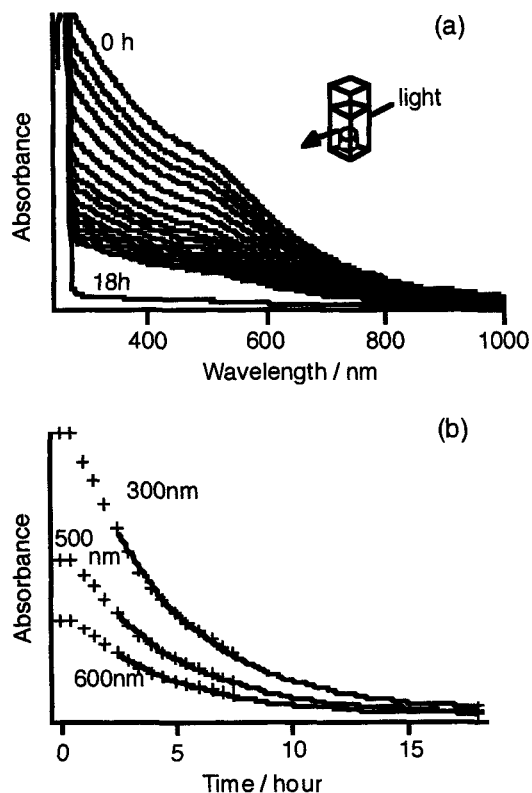

Fig.3 Time dependence of UV-Vis. absorption spectra (a) and absorbance at three different wavelength (b) of $Au_x(SC12)y$ / toluene solution in the presence of silica wet-gel. The inset in (a) shows a sketch of the absorbance measurement.
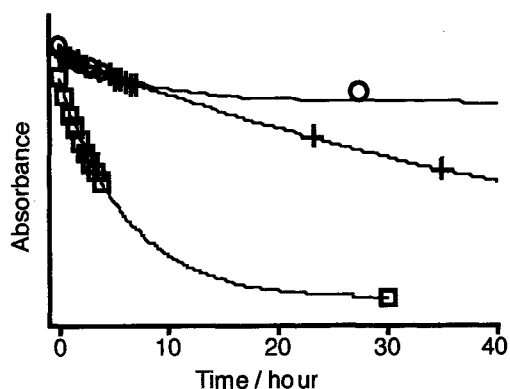

Fig.4 Time dependence of absorbance at 500 nm in toluene (square), THF (circle), and toluene/ THF (9:1 v/v) (cross) solvents. Solid lines are eye guides.

Figure 4 compares the time dependence of abosorbance at 500nm in toluene, tetrahydrofuran (THF) and the toluene/ THF (9:1 v/v) mixed solvent. As shown in the figure, doping 10% THF to toluene drastically decreased the adsorption rate of $Au_x(SC12)_y$ to silica wet-gel: the decay rate was smaller by about an order of magnitude than that in neat toluene. Since a THF molecule has much higher polarity than a toluene molecule, which is reflected in the large difference in dielectric constants of these solvents (toluene: 2.38, THF: 7.6 at 298K), it is expected that THF molecules aggregate at polar groups on silica, and this would hinder the adsorption of Au nanoparticles if the origin of the $Au_x(SC12)_y$ adsorption is electrostatic interaction between the silica surface and thiol chains. The result that THF doping greatly suppresses the adsorption rate is consistent with this assumption. In the neat THF solvent, absorbance did not decrease to zero. This is probably because of the increased amount of the THF molecules in the system which causes adsorption equilibrium to shift to a state in which some adsorption sites are occupied by THF molecules.

The wet-gel incorporating gold particles was dried in air and in sc-CO_2. Drying in air gave rise to a considerable shrinkage of the wet-gel, yielding a composite xerogel ($\approx$1/4 of the original volume). The UV-vis. spectrum was very similar to that of the $Au_x(SC12)_y$ solution. The spectral shapes for both central and peripheral parts of this composite did not show much difference.

Figure 2(d) shows the photograph of the product composite aerogel. The density of the composite was $\approx$0.2 g/cm^3. As described above, the gold particles were distributed mainly in the peripheral part of the gel, as seen in the photograph. The particle size distribution shown in fig. 1(d) largely overlaps that of $Au_x(SC12)_y$, but the average diameter was smaller (2.4 nm). However, it is not clear whether the difference in the average core diameters really exist since the distributions were obtained from the measurements for a limited number of particles. We want to emphasize that the size of the metal cores did not exhibit significant difference before and after the sc-CO_2 drying. Drying by sc-CO_2 can be performed at temperatures slightly above room temperature: in the present case, the temperature in the autoclave did not rise above 343 K. This temperature is

well below the temperature at which the thiol chain desorbs from the metallic core [19]. Moreover, it is expected that the adsorbed $Au_x(SC12)_y$ particles are not very mobile at such temperature in silica gel, since visually the spatial distributions of the nanoparticles in the wet-gel and the aerogel were not different.

4.SUMMARY

A nanocomposite of dodecanethiol-passivated gold clusters (average diameter 2.6 nm) and a silica aerogel has been synthesized. It was found that the gold particles were efficiently adsorbed on a silica wet gel in toluene and the particles were not flushed out during sc-CO_2 drying. For the particle adsorption, electrostatic interaction between the silica surface and the nanoparticles is proved to be important. The size distribution of the gold cores was not changed by the supercritical drying process. The spontaneous composite formation from the preformed nanoparticles and silica gel, and the formation of composite aerogel without changing the particle sizes can lead to a very simple and efficient way to the production of devices with high non-linear optical property or high catalytic activity.

ACKNOWLEDGEMENT

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