

Laser-Induced Deposition of Gold Nanoparticles onto Glass Substrates in Cyclohexane

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ABSTRACT

Gold nanoparticles can be deposited on the glass surface using pulsed 532-nm laser irradiation of the dodecanethiol-passivated gold particles in cyclohexane. The size of the deposited particles depends on the irradiation condition.

Noble metal nanoparticles exhibit unique characteristics that are observed neither in molecules nor in bulk metals.^{1,2} The unique optical properties have materialized extended applications of the nanoparticles to photochemical catalysts,^{3,4} sensors,^{5,6} and nonlinear optical materials.⁷ The distinctive absorption band in the ultraviolet–visible region, which is known as the surface plasmon band, is a typical example of the characteristics that come from their small sizes and high surface/volume ratios.⁸ The fundamental photophysics of the nanoparticles followed by the photoexcitation of the plasmon band has been explored by fast laser spectroscopy.^{9–12} Photoirradiation of the colloidal gold nanoparticles induces coagulation in solution¹¹ and agglomeration on a gold surface.¹⁴ Pulsed laser excitation has also induced some morphological changes of the colloidal gold nanoparticles such as fusion and/or fragmentation of the nanoparticles,^{15–17} and transformation of nanorods to nanospheres.¹¹

Previously, we reported that the pulsed laser excitation (532 nm, ~10 ns) of the colloidal gold nanoparticle in cyclohexane resulted in the direct deposition of the spherical gold particles onto a glass surface.¹⁸ The deposition occurred only at the laser irradiated part of the glass substrate. Any surface modification to control the deposition area by some functional groups (–SH, –NH₂, –CN, and so on) having strong affinity to gold is not needed. In this paper, we have found some experimental conditions that affect the degree of deposition. The deposition mechanism will be also discussed.

Experimental. A glass substrate was first made hydrophilic by treating with the mixed solution (1:1) of aqueous

hydrogen peroxide (31%) and ammonia (28%) at its boiling temperature for a few minutes. The substrate was rinsed with deionized water and kept in it, and dried by blowing a stream of N₂ gas just before use. The surface of the glass substrate was also modified with two kinds of silane coupling agents; 3-mercaptopropyltrimethoxysilane (MPS) and dimethyloctadecylchlorosilane (DMOS). The hydrophilic glass substrate was immersed into a toluene solution of the silane coupling agent (5%) for 1 day, followed by rinsing with chloroform and water. Cyclohexane solutions of dodecanethiol (DT)-passivated gold nanoparticles were prepared according to the previous procedure.^{19,20} The second harmonic light from a Q-switched Nd:YAG laser (Continuum Surelite, 532 nm, 6–8 ns, 10 Hz) was used without focusing (spot size ~0.4 cm²). The cyclohexane solution of the DT-passivated gold nanoparticles was filled in a glass cell (1 × 2 × 3 cm).

In the case of laser irradiation experiments (See Figure 1), the substrate was immersed into the cyclohexane solution of DT-passivated gold particles. The glass substrate was fixed in contact with the inner wall of the front-side of the cell as to the laser path. With proceeding laser irradiation, the gold particles were deposited on the rear surface of the substrate. After ceasing laser irradiation, the substrate was removed from the cell, washed with cyclohexane, and dried in air. Scanning electron micrographs (SEMs) were obtained by a Hitachi S-5000 scanning electron microscope. Absorption spectra of the deposited particles were measured by using an optical fiber attached with a multichannel spectrophotometer (Ocean Optics D1024WR).

Results and Discussion. A typical microscopic photograph of the irradiated region of the glass substrate is shown in Figure 2; in this case, laser irradiation was carried out through a photomask. Reddish rectangular patterns based on depos-

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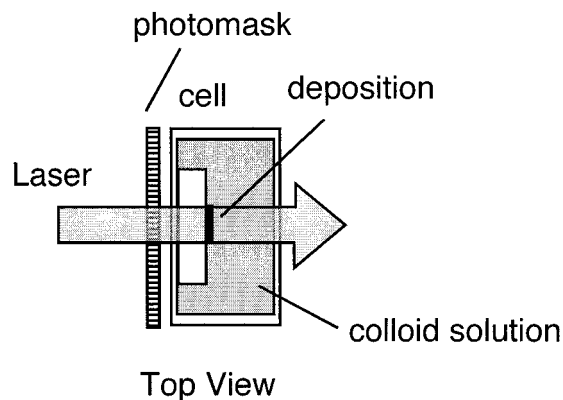


Figure 1. Experimental geometry.

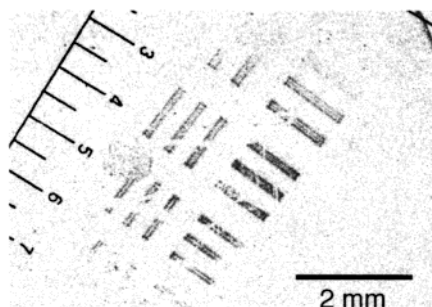


Figure 2. Microscopic photograph of the deposited gold particles on the hydrophilic glass substrate. Laser irradiation (532 nm, ca. $20 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, 2 min) was carried out through a photomask to the cyclohexane solution containing DT-passivated gold particles (initial gold particles: $7.3 \pm 6.2 \text{ nm}$, 0.2 mg/mL).

ited gold particles are clearly seen with the naked eye. The deposition of the gold particles occurs only at the laser-irradiated region of the substrate. No deposition was observed without laser irradiation. Thus, the deposition of the particles is induced by photoirradiation of the particles.

Figure 3 shows absorption spectra of the gold nanoparticles deposited on the substrates at different irradiation times in cyclohexane solutions. In this case, the laser irradiation was carried out without the photomask, so that the deposited region was identical to the spot of the laser beam. For 5 s of irradiation, the deposited region showed a weak and broad peak at around 570 nm, ascribing to the surface plasmon band of the gold particles. The plasmon band increased nonmonotonically with increasing the irradiation time up to 60 s, and shifted slightly. Further irradiation (120, 180 s) resulted in broadening and red shift of the plasmon band.

To investigate the size and the shape of the deposited particles, SEM observations were carried out at some selected irradiation times. Typical SEM photographs and size distributions of the particles from the SEM photographs are shown in Figure 4. For 5 s of irradiation, particles somewhat larger ($4.4 \pm 2.8 \text{ nm}$) than those of the initial particles in cyclohexane ($3.3 \pm 0.9 \text{ nm}$) were seen (a, b). It should be noted that the particles are not spherical. For 60 s of irradiation, most of the particles changed to roughly spherical (c), and the mean size of the particles increased to $7.6 \pm 5.4 \text{ nm}$ (d). The larger spherical particles must be formed by repeated cycles of coagulation and fusion of the par-

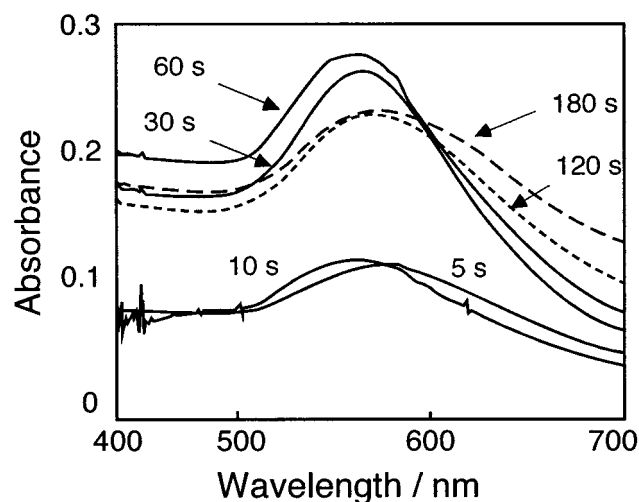


Figure 3. Absorption spectra of the gold particles deposited on hydrophilic glass substrates at different irradiation times of the 532-nm laser light (ca. $83 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$) in cyclohexane (initial gold particles: $3.2 \pm 0.95 \text{ nm}$, 8.0 mg/mL). Irradiation times are shown in the figure.

ticles.^{8,18} Further irradiation (180 s) induced no remarkable changes in the size distribution, but small agglomerates increased (shown by circles in Figure 4e). Broadening and red-shift of the plasmon band (see Figure 3) should be mainly caused by these agglomerates.^{13,14}

Previously, we reported that the size growth of the DT-passivated gold particles induced by the pulsed 1064-nm laser excitation in cyclohexane was substantially suppressed in the presence of DT.¹⁷ Thus, the effect of DT on the degree of deposition was also investigated. Figure 5a shows absorption spectra of the irradiated region of the hydrophilic glass substrates after 30 s of irradiation in the colloidal cyclohexane solution at different concentrations of DT. The plasmon band due to the deposition is clearly seen in the absence of DT (A). In the presence of DT, on the other hand, no appreciable plasmon peaks are seen (B, C, D). This shows that DT molecules certainly suppress the deposition of the gold particles onto the glass substrate. In the presence of a small amount of DT (1 mM); however, the deposition could be seen when the solution had already been exposed to the laser light before the deposition experiment. As shown in Figure 5b, the deposition did not occur in the presence of DT (E = B) at first. Subsequent deposition experiments (30 s) were carried out by using the new hydrophilic glass substrate in the same solution. It is clear that the plasmon band appeared and increased with increasing exposure time (30 (F), 60 (G), and 90 (H) seconds). These results show that the deposition strongly depends on photoreactions (such as dissociation of DT, fragmentation, and fusion) of the particles in the solution.

Figure 6 shows SEM photographs and size distributions of the deposited particles on the hydrophilic glass plates when the initial size ($7.5 \pm 5.0 \text{ nm}$) of the gold particles and laser pulse energy ($163 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$) were considerably larger as compared with the case of Figure 4. The deposition occurred in much shorter times. After $\sim 1 \text{ s}$ (11 pulses) of irradiation, the deposition had already been observed and the deposited particles had a mean size ($8.7 \pm 2.9 \text{ nm}$) similar

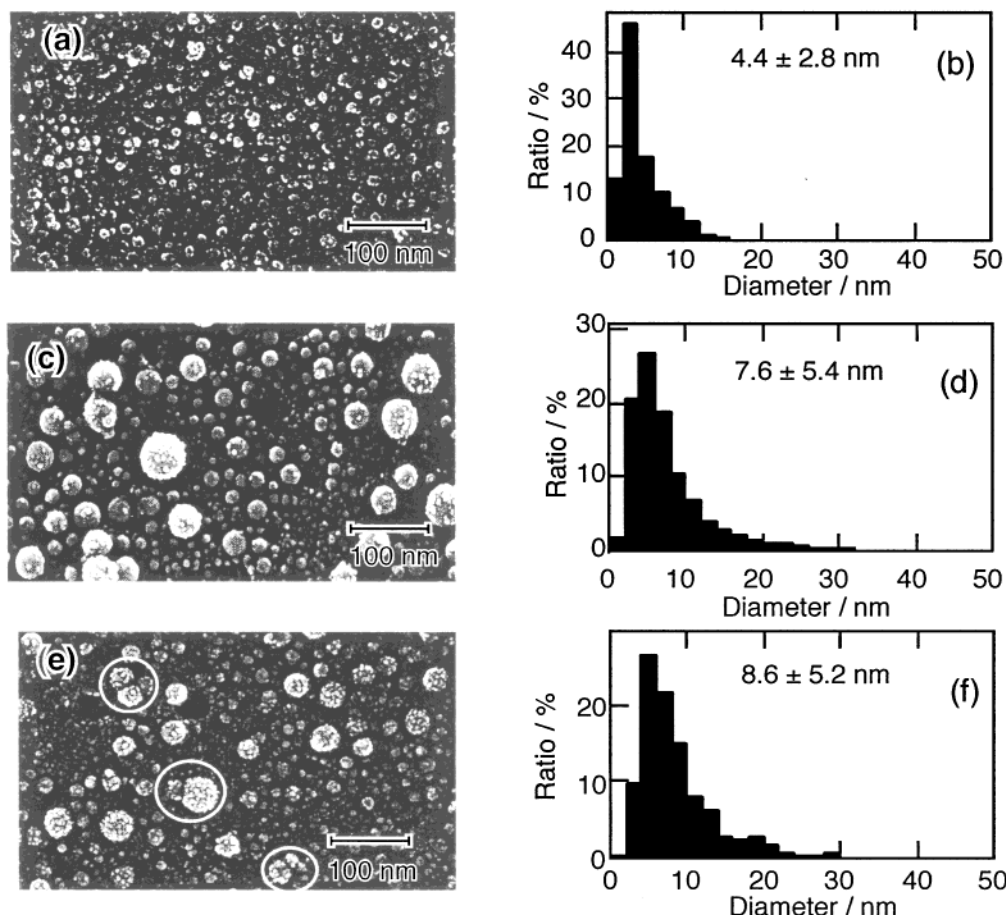


Figure 4. SEM photographs (left) and size distributions (right) of the deposited gold particles on the hydrophilic glass substrates caused by laser irradiation in the cyclohexane solution (initial gold particles: 3.2 ± 0.95 nm, 8 mg/mL). Irradiation time of the 532-nm laser light (ca. $83 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$): (a, b) 5 s, (c, d) 60 s, and (e, f) 180 s. Mean sizes and standard deviations of the particles are shown in (b), (d), and (f).

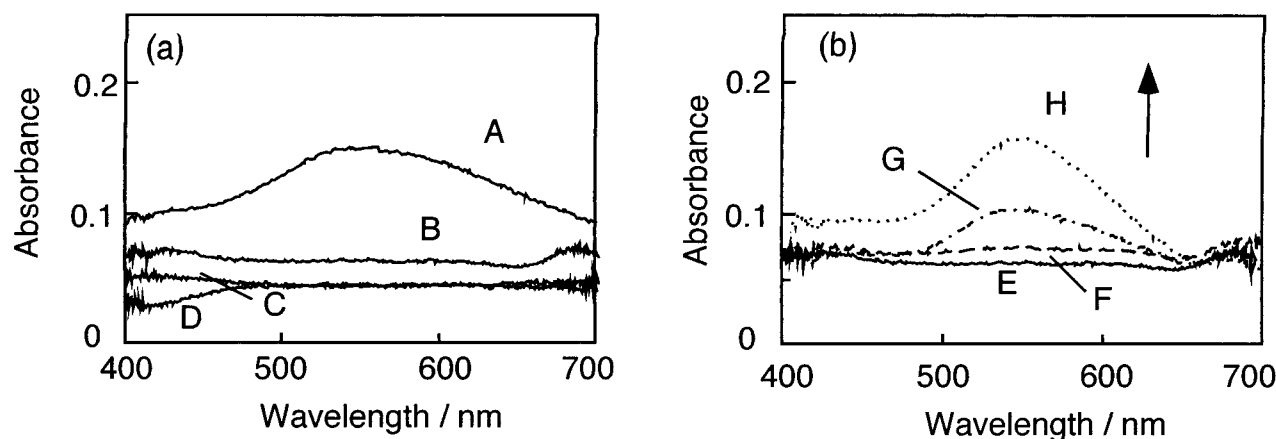


Figure 5. Effect of DT on the deposition of gold nanoparticles onto the hydrophilic glass substrate. (a) Laser irradiation was carried out for 30 s in the colloidal cyclohexane solution in the presence or absence of DT: [DT] = 0 (A), 1 (B), 10 (c), 100 mM (D). (b) Laser irradiation was carried out in the colloidal cyclohexane solution containing DT (1 mM), by replacing the new substrate after each 30 seconds of laser irradiation. Thus, the deposition time is 30 s for each substrate, while the solution was exposed to the laser light for 0 (E), 30 (F), 60 (G), and 90 (H) seconds. Therefore, the spectra of B (a) and E (b) are essentially identical. Laser: 532 nm, $83 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$.

to the initial particles (7.5 ± 5.0 nm). Much larger particles were found for 2 s of irradiation (Figure 6c, d). After 30 s of irradiation, most of the deposited particles were spherical and large with broad size distribution (Figure 6f). From TEM

observations, larger particles were also found in this experimental colloidal solution. The larger particles in the colloidal solution are certainly formed after repeated melting-fusion (coagulation) cycles.^{16,17} In general, larger particles are not

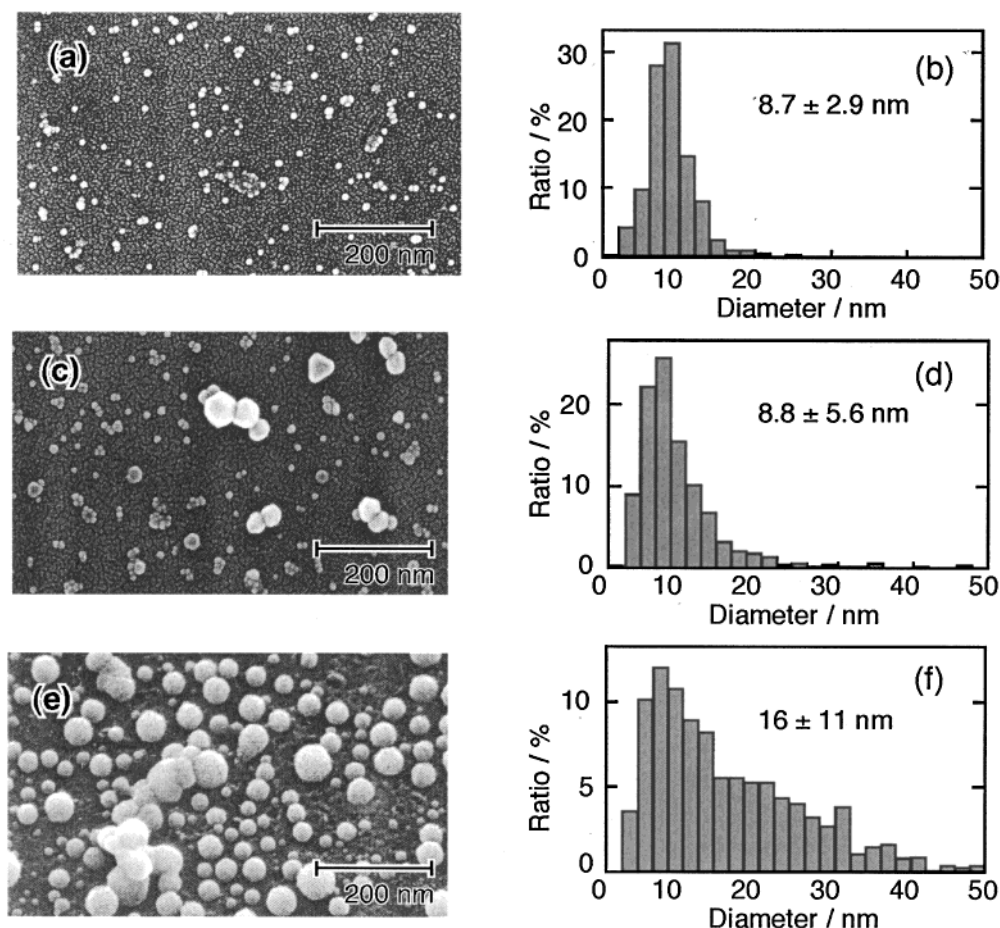


Figure 6. SEM photographs (left) and size distributions (right) of the deposited gold particles on the hydrophilic glass substrates caused by laser irradiation in the cyclohexane solution (initial gold particles: 7.5 ± 5.0 nm, 16 mg/mL). Irradiation time of the 532-nm laser light (ca. $163 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$): (a, b) 1.1 s, (c, d) 2 s, and (e, f) 30 s. Mean sizes and standard deviations of the particles are shown in (b), (d), and (f).

stable in the colloidal solution and tend to agglomerate and precipitate. These results suggest that the larger particles formed in the solution lose stability and tend to deposit onto the glass surface. Because the DT molecules suppress the formation of the larger particles, longer irradiation times are needed to the deposition in the presence of DT. At the same time, melting-fusion (coagulation) processes of the particles on the surface may also be taken into account if the deposited particles are larger and/or the irradiation time is long enough to deposit the agglomerates as shown in Figure 6f.

To investigate interactions between the gold particles and the substrate surface, the surfaces of the substrate were modified with MPS or DMOS. Figure 7 shows the absorption spectra of the irradiated regions of the modified substrates after 30 s of laser irradiations together with the results of the hydrophilic glass substrate. It is clear that the plasmon band is largest in the MPS-modified substrate (a), because the terminal thiol group of MPS facilitates immobilization of the gold particles by Au–S bonding. In the case of DMOS-modified substrate (c), on the other hand, the plasmon band became smaller. Thus, the hydrophobic substituent suppresses the deposition. It has been reported that some DT molecules were removed from the gold particles by pulsed laser irradiation.¹² The larger particles formed by the

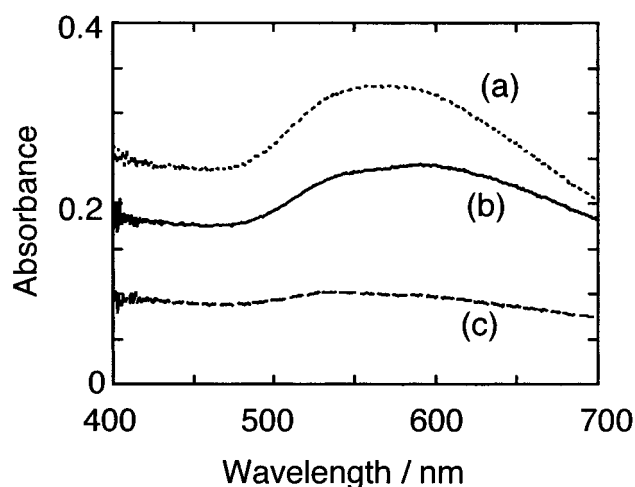


Figure 7. Absorption spectra of modified glasses after deposition experiments. Reagents for surface modification: (a) MPS, (b) none (hydrophilic), (c) DMOS. Deposition condition, initial gold particles: 4.0 ± 1.7 nm, 0.5 mg/mL. Laser irradiation: 532 nm, $83 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, 30 s.

laser irradiation must lose at least some extent of DT molecules during the size growth.²¹ These results and considerations suggest that the deposition is mainly due to

the van der Waals interaction between the larger gold particles and the hydrophilic glass surface.

In conclusion, the use of pulsed 532-nm laser light was effective for the facile and direct deposition of spherical gold particles on the hydrophilic glass substrate. Size, shape, and density of the deposited particles depended on the laser irradiation condition, initial particle size, and surface property of the substrate.

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- (21) FT-IR measurements of the deposited gold particles were carried out using a CaF₂ substrate instead of the glass plate. Three bands were clearly seen at 2954, 2922, and 2850 cm⁻¹ that were assignable to C-H stretching bands of methyl and methylene groups. They were quite similar to those of DT molecules casted on the CaF₂ plate. Thus, some of the DT molecules are still retained on the gold particles even after the deposition onto the CaF₂ plate.

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