

# Size-Growth of Gold Nanospheres Induced by the Pulsed-laser Irradiation of Polycation - Gold Nanoparticle Aggregates

Takahiro Kawasaki<sup>1</sup>, Hironobu Takahashi<sup>1</sup>, Hideya Kawasaki<sup>2</sup>, Yasuro Niidome<sup>1,3</sup>  
and Sunao Yamada<sup>1,3\*</sup>

<sup>1</sup>Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

<sup>2</sup>Department of Chemistry, Graduate School of Science, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

<sup>3</sup>Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

Fax: +81-92-642-3579, e-mail: sunaotcm@mbox.nc.kyushu-u.ac.jp

Large and highly-spherical gold nanoparticles could be formed by pulsed-laser irradiation of polycation - gold nanoparticle complexes formed in an aqueous solution. The complex of negatively-charged gold nanoparticles (~10 nm diameter) and cationic poly(diallyldimethylammonium chloride) (PDDA) was formed by electrostatic interactions. Then, pulsed 532-nm laser light excited the gold nanoparticles having strong surface plasmon bands around 520 nm, which resulted in fusion of trapped gold nanoparticles into large and highly-spherical ones. Absorption, transmission electron microscopy, dynamic light scattering, and zeta-potential measurements verified the size growth mechanism.

Key words: gold nanoparticle, laser, fusion, size growth

## 1. INTRODUCTION

Noble metal nanoparticles such as gold nanoparticles exhibit unique optical properties depending on their sizes, shapes, and aligned structures, that are based on surface plasmon (SP) oscillation of free electrons present in the particles [1]. Thus, control of size and/or shape of gold nanoparticles is essentially important for successful applications of gold nanoparticles in various technological fields. As to the shape of gold nanoparticles, various types have recently been reported, such as nanorods [2-10], multipods [11], nanoprisms [12], and so on. Control of the particle size is also very important, and the seeding method by Jana et al [13] has been very useful for controlling the size of gold nanospheres from 5 to 40 nm. This method could be further applied for preparing over 100-nm gold particles [14]. In general, however, the chemical approaches for the preparation of larger particles lead to irregularly polygonal structures. Therefore, the useful methods for the preparation of well-spherical gold nanoparticles have not yet been established.

Recently, photoirradiation processes have been found to possess the potential to change the size of gold [1,15-19] or silver [20] nanoparticles. They include repeated cycles of laser-induced photofragmentation, aggregation, and fusion, and has also been successful for shape transformation of gold nanorods [21,22]. Especially, the use of near-infrared pulsed-laser (for example, 1064 nm) was effective for generating huge gold nanospheres [18]; however, it took very long time for the growth of gold nanoparticles beyond several hundreds of nanometers.

As to photoexcitation of gold nanoparticles, visible lasers are more useful, because they usually show strong

absorption bands in the visible region due to surface plasmon oscillation of free electrons. In addition, in order to avoid the diffusion of gold nanoparticles, that must be disadvantageous to fuse them into larger sizes, the formations of some aggregated structures of gold nanoparticles must be an key for causing fusion effectively. From these viewpoints, we have tried to confine gold nanoparticles inside polymer globules in order to fuse them effectively and quickly by pulsed 532-nm laser light. The size growth from ~8 to ~40 nm with the highly-spherical structure was achieved within several minutes.

## 2. EXPERIMENTAL SECTION

Negatively charged gold nanoparticles (AuNPs) were prepared from the chemical reduction of HAuCl<sub>4</sub> (0.5 mM in H<sub>2</sub>O) with sodium citrate as described previously [14]. We used poly(diallyldimethylammonium chloride) (PDDA: MW = 400,000~500,000, Aldrich), as a polycation. First, 3 ml of the as-prepared colloidal solution was pipetted into a glass vessel, and 50  $\mu$ l of aqueous PDDA solution (20 wt%) was added with stirring. By addition of PDDA, the color of colloidal solution quickly changed from red-wine to dark blue, suggesting the formation of some aggregates. However, no appreciable precipitates were formed under the present condition. Therefore the resultant aggregates are stably dispersed in the solution. The zeta( $\zeta$ )-potential and the average size from the dynamic light scattering (DLS) method were -36 mV and 8 $\pm$ 2 nm for the initial colloidal solution, but they changed into +40 mV and 260 $\pm$ 80 nm after addition of PDDA, as summarized in Table 1. These results show the formation of stable PDDA-AuNP complexes. Then, the pulsed 532-nm laser

light (Nd:YAG laser, 10 mJ/pulse, 10Hz), irradiated the colloidal solution from 0.5 to 5.0 minutes with stirring, and then absorption spectra, transmission electron micrograph (TEM) images, DLS spectra, and  $\zeta$ -potentials were measured and analyzed.

Absorption spectra were recorded on a Shimadzu 2400 absorption spectrophotometer. Laser irradiation experiments were performed using Q-switched Nd:YAG laser (Continuum Surelite, 532 nm, 6-8 ns, 10 Hz). TEM observations were carried out with a Hitachi A-5000 microscope. DLS and  $\zeta$ -potential measurements were done with Otsuka Electronics DLS-7000 and ELS-8000 instruments, respectively, where the He-Ne lasers (632.8 nm) were used as light sources.

Table 1. Mean size and zeta-potentials of sample solutions.

Sample	size / nm		$\zeta$ -potential / mV
	TEM <sup>b</sup>	DLS	
AuNP	10±1	8±2	-36
PDDA-AuNP (0) <sup>a</sup>	10±1	260±80	+40
PDDA-AuNP (0.5)		150±50	+40
PDDA-AuNP (2.0)		120±40	+40
PDDA-AuNP (5.0)		90±20	+37

<sup>a</sup> Values in ( ) are irradiation times of 532-nm laser light.

<sup>b</sup> Size distributions of AuNPs after laser irradiation are too broad to obtain mean sizes.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the illustration of our basic strategy. Since AuNPs are prepared from the chemical reduction of  $\text{HAuCl}_4$  with sodium citrate, they are capped with citrate ions and thus negatively charged. On the other hand, we used PDDA as a polycation with relatively narrow distribution of molecular weight (400,000~500,000). First, we prepare PDDA-AuNP complexes by mixing the two solutions. Then, pulsed 532-nm laser irradiation is carried out to make fusion of trapped AuNPs leading larger and highly-spherical AuNPs.

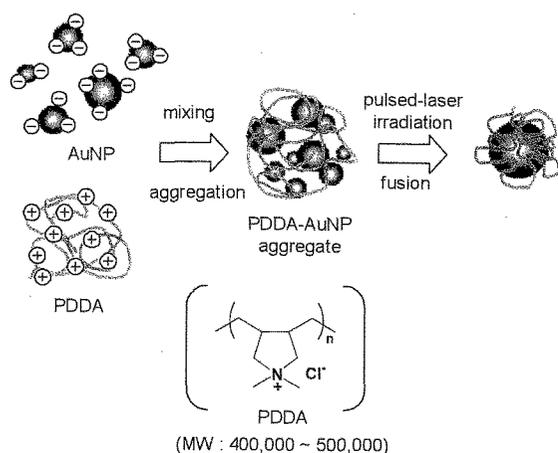


Figure 1. Schematic illustration of our strategy for aggregation-assisted fusion of AuNPs for obtaining larger and highly-spherical AuNPs.

Figure 2(a) shows the absorption spectrum of the colloidal solution of AuNPs before complex formation with PDDA. A sharp SP band is observed at 520 nm. From the TEM image (Figure 2(A)), the mean diameter is evaluated to be 10±1 nm. By mixing with the PDDA solution, the absorption band showed dramatic red-shift and broadening as shown in Figure 2(b), indicating the formation of PDDA-AuNP complexes. Broadening of SP band is due to interparticle plasmon coupling [1].

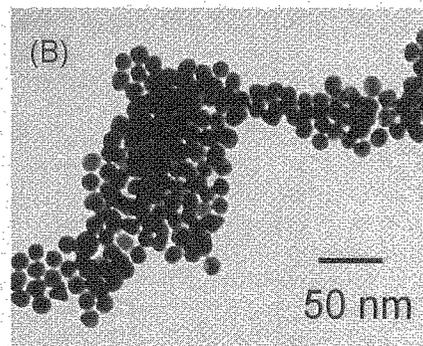
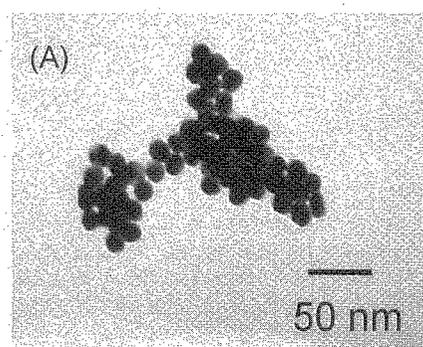
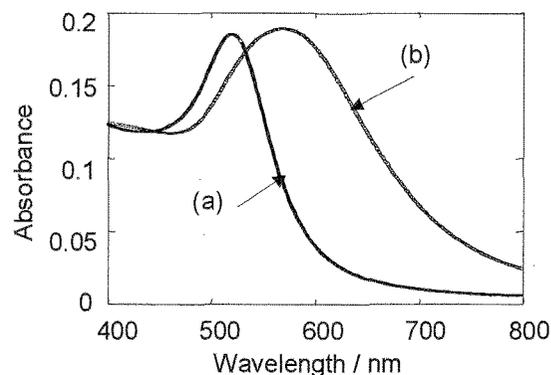


Figure 2. Absorption spectra of the colloidal solution of AuNPs before (a) and after (b) addition of PDDA. The corresponding TEM images before and after addition of PDDA are shown as (A) and (B), respectively.

Figure 2(B) shows the TEM image of PDDA-AuNP complexes. Though the size of AuNPs is not different from the initial particles, substantially larger complexes are found in the TEM image, as compared with the initial state (Figure 2(A)). The  $\zeta$ -potential of the initial colloidal solution showed a negative value of -36 mV, but was changed into the positive value of 40 mV, after complexing with PDDA. DLS measurements were also carried out before and after complexation with PDDA, and the predominant values were obtained to be 8±2 and

260±80 nm, respectively. These results are summarized in Table 1, and show the formation of stable PDDA-AuNP complexes.

As shown in Figures 3(a)–(d), absorption bands of the PDDA-AuNP solutions showed blue-shift and band narrowing with proceeding laser irradiation from 0 to 5 minutes. This results show the decrease in the interparticle plasmon coupling among the trapped AuNPs with proceeding laser irradiation. TEM images of the laser-irradiated solutions (Figures 3(B)–(D)) clearly show the formation of larger and highly-spherical AuNPs with proceeding irradiation times.

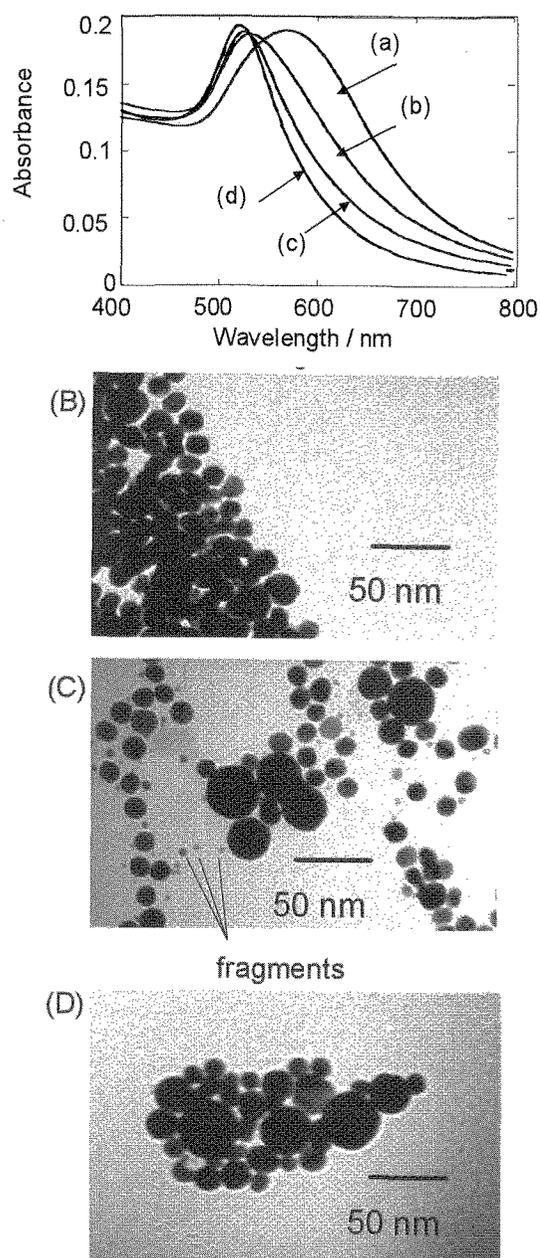


Figure 3. Absorption spectra of the colloidal solution of PDDA-AuNP before (a) and after 0.5(b), 2.0(c), and 5.0(d) minutes of 532-nm irradiation. TEM images of the sample solutions after corresponding irradiation times are also shown as (B), (C), and (D), respectively.

At the same time, very small particles are seen in Figure 3(C) as a typical example, which indicates the concomitant occurrence of laser-induced fragmentation at some extent. The  $\zeta$ -potentials of the laser-irradiated sample solutions (40–37 mV, see Table 1) did not change substantially, in spite of proceeding the laser irradiation. This suggests the existence of PDDA-AuNP complexes even after growth of trapped AuNPs into larger ones by fusion, that is, larger particles are still incorporated in the PDDA globules. On the other hand, DLS measurements of the laser-irradiated sample solutions suggested the decreases in the size of PDDA-AuNP complexes as summarized in Table 1.

As a control experiment, we have carried out laser irradiation of the colloidal solution of AuNPs in the absence of PDDA. Thus, the AuNPs were homogeneously distributed in the solution. In this case, the absorption spectrum after 5 minutes of 532-nm irradiation showed only slight change, as shown in Figure 4(b). Slight blue-shift and band narrowing may be attributed to the results of some laser-induced fragmentation, though fragmented particles were not detectable from the TEM image (Figure 4(B)).

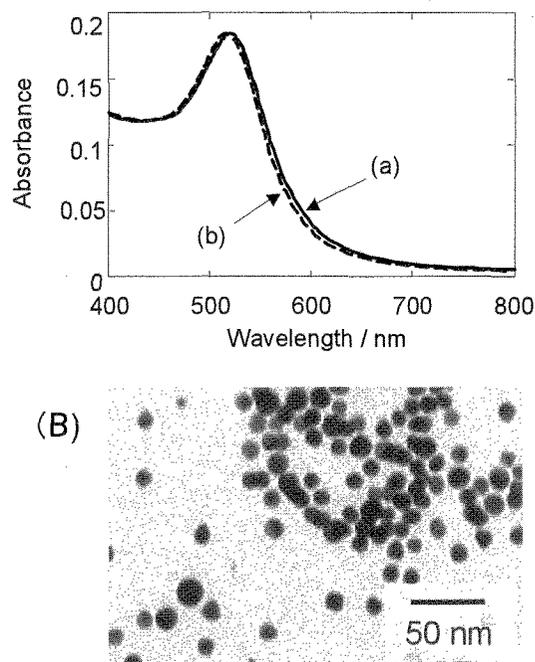


Figure 4. Absorption spectra of the colloidal solution of AuNPs in the absence of PDDA: (a) before irradiation, (b) after 5 minutes irradiation. (B) TEM image of the colloidal solution after 5 minutes of laser irradiation.

These observations clearly show that the size growth is achieved only from the complex formation of AuNPs with PDDA. From Table 1, it is suggested that the size of PDDA-AuNP complexes decrease with increasing the irradiation times, yet the AuNPs are growing, as schematically shown in Figure 5. Before the formation of PDDA-AuNP complexes, the mean size of AuNPs is very small (8–10 nm), because all AuNPs are randomly distributed in the solution. The formation of PDDA-AuNP complexes gives the large value of size in the DLS method, and is verified from absorption and

TEM measurements. With proceeding subsequent laser irradiation, DLS results indicate the size decrease of the PDDA-AuNP complexes, because the number of trapped AuNPs are decreasing with proceeding fusion. In fact, TEM images certainly show the formation of large and highly-spherical particles.

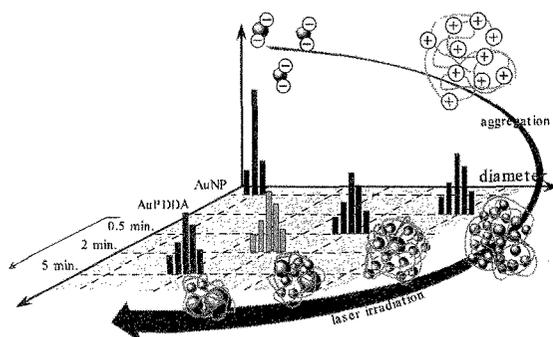


Figure 5. Schematic illustration of the size growth of AuNPs by the complexation with PDDA, and subsequent irradiation of pulsed 532-nm laser light for fusing the trapped AuNPs in the PDDA scrambles.

Accordingly, we have shown the novel method of preparing larger and highly-spherical AuNPs, by electrostatic trapping AuNPs with PDDA. In this method, the distribution of the chain length of polymer should be as narrow as possible in order to strictly control the size of AuNPs. At the same time, the use of a flow system of the solution may be better to avoid possible photofragmentation of grown particles that can absorb photons more effectively than the smaller particles. The work is in progress along the large-scale synthesis of large and highly-spherical AuNPs.

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