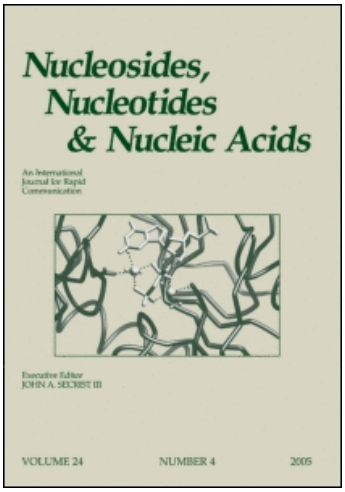

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Formation of Au(III)-DNA Coordinate Complex by Laser Ablation of Au Nanoparticles in Solution

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FORMATION OF Au(III)-DNA COORDINATE COMPLEX BY LASER ABLATION OF Au NANOPARTICLES IN SOLUTION

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▫ *We discovered that an Au(III)-DNA coordinate complex, Au(III)(DNA-base)$_2$(amine)$_L$, are formed by laser ablation of Au nanoparticles in an aqueous solution containing DNA molecules in the presence of amines and multi-valent cations, where L represents an unknown ligand (either amine or water). Optical absorption spectrum of the solution after laser ablation exhibited a 360 nm absorption peak assigned to ligand→Au(III) charge transfer (LMCT) band of the coordinate complex. The complex is considered to be formed as follows: 1) the DNA molecules are neutralized by binding the multi-valent cations to their negatively charged phosphate groups, and adsorbed on the surface of the Au nanoparticles by a hydrophobic interaction, 2) Au(III) ions are liberated from the Au nanoparticles by laser ablation, and 3) an Au(III) ion reacts with amine and two DNA bases of a DNA molecule into an Au(III)(DNA-base)$_2$(amine)$_L$.*

Keywords Au Nanoparticles, DNA Molecules, Laser Ablation, Au(III)-DNA Coordinate Complex

INTRODUCTION

Some of the d^8 square planar Au(III) coordinate complexes exert antitumor activities since the coordination of Au(III) with DNA base moieties affects activation of nucleotide- or poly nucleotide-dependent enzymes.[1] For instance, Au(III) complexes, $AuCl_2$(damp) and Au(acetato)$_2$(damp), exhibit cytotoxicity in vitro and in vivo antitumor activity against human carcinoma xenografts.[2] A bipyridyl Au(III) compound, $[Au(bipy)(OH)_2]^+(PF6)^-$, shows cytotoxic activities toward a

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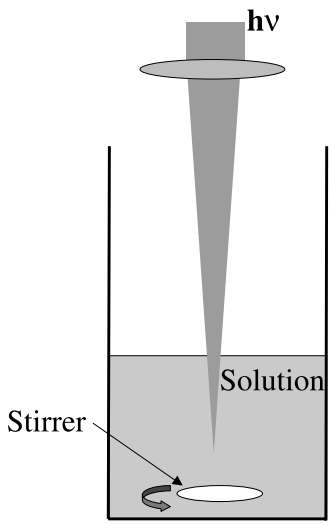

FIGURE 1 Schematic diagram of the experimental apparatus.

panel of human tumor cell lines.[3] These Au(III) coordinate complexes injected in a cell line as a precursor react with DNA of the cell into Au(III)-DNA coordinate complexes, which possess cytostatic activity. It is difficult to use Au(III) ions directly for the formation of Au(III)-DNA coordinate complexes instead of using a precursor for formation of the Au(III) coordinate complexes because Au(III) ions are instable in an aqueous solution without coordination of adequate ligands such as pyridine.[1]

Here, we report a novel formation method of an Au(III)-DNA coordinate complex without using such a precursor but with using Au(III) ions produced by the following laser technique. Namely, an Au(III)-DNA coordinate complex such as Au(III)(DNA-base)$_2$(amine)L was directly synthesized with Au(III) ions generated through laser ablation of Au nanoparticles in an aqueous solution containing DNA molecules, amines, and multi-valent cations (see Figure 1), where L represents an unknown ligand, which is considered to be amine or water. This method is the first example of using Au(III) ions produced from Au nanoparticles by laser ablation in the formation of the Au(III)-DNA coordinate complex. In the optical absorption spectra of the solution after the laser ablation, the characteristic peak was found to emerge at 360 nm and was assigned to the ligands→metal Au(III) charge transfer (LMCT) band of the Au(III)-DNA coordinate complex.

RESULTS AND DISCUSSION

Figure 2 shows a typical optical absorption spectrum (solid line) of an aqueous solution consisting of $CaCl_2$ (10 mM), Tris (10 mM), lambda DNA (12.5 nM), and Au nanoparticles (1.3 nM) after laser ablation (532 nm, 17 mJ/pulse) and that

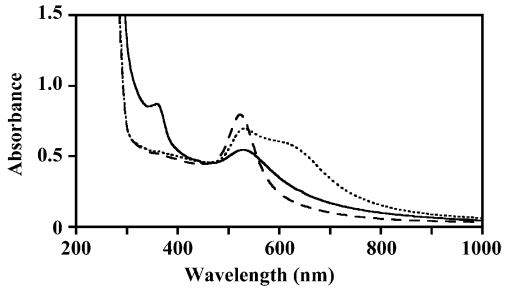

FIGURE 2 Optical absorption spectra of aqueous solutions containing Au nanoparticles (1.3 nM), lambda DNA (12.5 nM), Tris (10 mM), and $CaCl_2$ (10 mM) after laser ablation (solid line) and that before laser ablation (dotted line). A spectrum of an aqueous solution made by eliminating $CaCl_2$ from the solution mentioned above is also shown (broken line). A characteristic absorption band appears at 360 nm after the laser ablation, which was assigned to the $p \rightarrow d$ charge transfer band (LMCT) between a ligand and an Au(III) of an Au(III)(DNA-base)$_2$(amine)L coordinate complex. The absorption band shorter than 300 nm was assigned to the overlap of the band due to $n-\pi^*$ or $\pi-\pi^*$ transition of the DNA bases and the Au interband transition, and the absorption band at 530 nm was assigned to the surface plasmon band of the Au nanoparticles. The broad absorption band centering at 650 nm (dotted line) was assigned as the band due to Au nanoparticle-DNA entanglements.

(dotted line) before laser ablation. A spectrum (broken line) of an aqueous solution made by eliminating $CaCl_2$ from the solution mentioned above is also shown in Figure 2 in comparison. A characteristic absorption band appears at 360 nm after the laser ablation as shown in Figure 2. As described in the following, the band was assigned to the $p \rightarrow d$ charge transfer band (LMCT) between a ligand and an Au(III) in an Au(III)(DNA-base)$_2$(amine)L coordinate complex. Therefore, the intensity of the 360 nm absorption band is treated as the abundance of the Au(III)-DNA coordinate complex in the solution. An intensive investigation of the necessary factors for the formation of Au(III)-DNA coordinate complex leads us to conclude that 1) multivalent cations (Ca^{2+}, Mg^{2+}, etc.), 2) amine, 3) DNA molecules, and 4) Au nanoparticles are the necessary factors for the formation of the coordinate complex. However, anions such as (Cl^-, I^-, and CH_3COO^-) and monovalent cations such as (Na^+) did not contribute to the formation of the coordinate complex. The absorption band shorter than 300 nm was assigned to overlap of the band due to the $n-\pi^*$ or $\pi-\pi^*$ transition of the DNA bases and that due to the Au interband transition, and the absorption band at 530 nm was assigned to the surface plasmon band of the Au nanoparticles. The broad absorption band centering at 650 nm in the spectrum given by the dotted line originates from aggregation of the Au nanoparticles.[4]

Figure 3 shows the abundance of the Au(III)-DNA coordinate complex as a function of the concentration of Ca^{2+}. The abundance increases with the Ca^{2+} concentration especially when it exceeds $\sim 8 \times 10^{-3}$ M.

Figure 4 shows the optical absorption spectra of solutions of (a) nucleotide (ATP), (b) dimer (AC), and (c) tetramer (ATGC) after the laser ablation. The LMCT band is observed in the solution containing dimer or tetramer, whereas, no LMCT band is observed for the monomer. This result is consistent with the

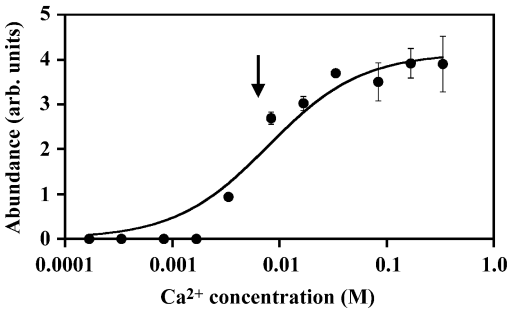

FIGURE 3 Abundance of an Au(III)-DNA coordinate complex as a function of the concentration of Ca^{2+}, where the intensity of the 360 nm absorption band is treated as the abundance. The solid line represents the theoretical curve (see text). The arrow indicates the Ca^{2+} concentration at the inflection point of the coordinate complex formation.

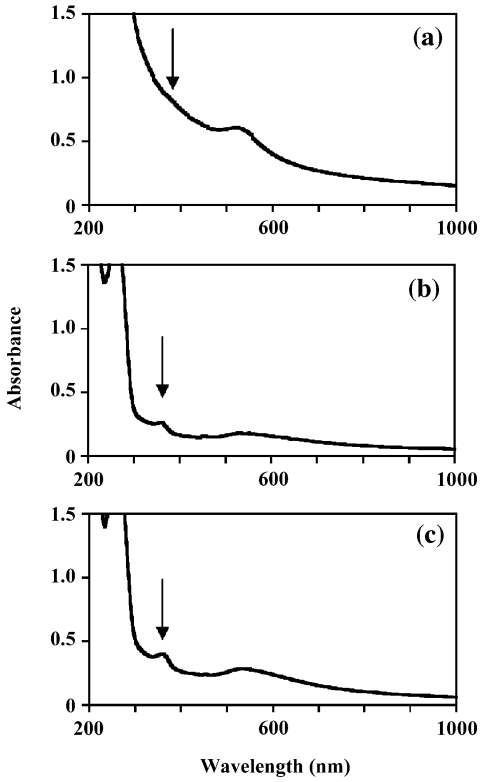

FIGURE 4 Optical absorption spectra of solutions of (a) nucleotide (ATP), (b) dimer (AC), (c) tetramer (ATGC) after laser ablation. The LMCT band is observed in the solution containing dimer or tetramer, whereas, no LMCT band is observed for the monomer. The arrows in all the panels indicate the position of the LMCT band at 360 nm.

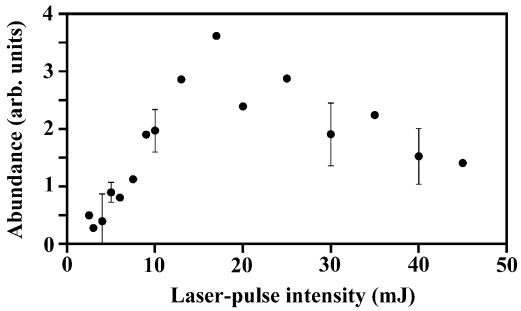

FIGURE 5 Abundance of the Au(III)-DNA coordinate complex plotted against the intensity of the ablation laser at 532 nm. The abundance of the Au(III)-DNA coordinate complex increases with the intensity up to 17 mJ/pulse and then decreases as the intensity is increased. The uncertainties of typical data points are shown by error bars.

plausible structure of the Au(III)-DNA coordinate complex, which contains two DNA bases in it.

Figure 5 shows the abundance of the Au(III)-DNA coordinate complex as a function of the intensity of a laser pulse (laser intensity) for the ablation. The abundance of the Au(III)-DNA coordinate complex increases with the laser intensity up to 17 mJ/pulse and then decreases as the laser intensity is increased.

Figure 6 shows the abundance of the Au(III)-DNA coordinate complex as a function of the time elapsed after the laser ablation. The abundance of the Au (III)-DNA coordinate complex decreases with the elapsed time probably because of hydrolysis of the coordinate complex.

Characterization of the Coordinate Complex by LMCT Band

As described in detail below, it is concluded that the Au(III)-DNA coordinate complex is given by Au(III)(DNA-base)$_2$(amine)L as illustrated in Figure 7, where L represents an unknown ligand, which is either amine or water. A amines coordinate complex of Au(III) shows a characteristic LMCT band at ~360 nm

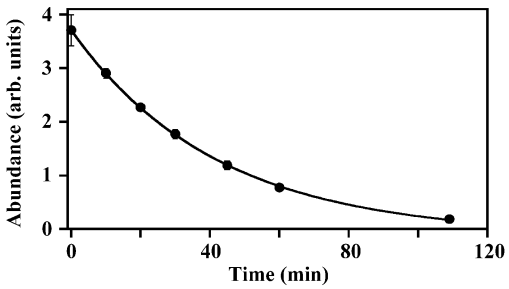

FIGURE 6 Abundance of the Au(III)-DNA coordinate complex as a function of the time elapsed after laser ablation. The abundance of the Au(III)-DNA coordinate complex decreases with the elapsed time probably because of hydrolysis of the coordinate complex.

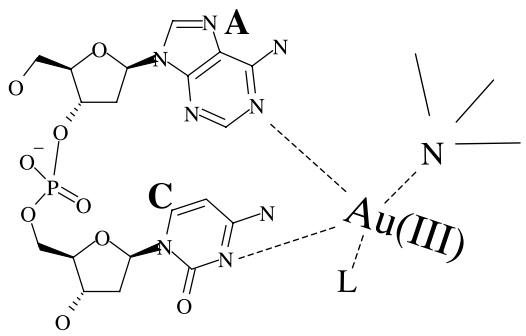

FIGURE 7 Plausible structure of the A Au(III)(DNA-base)$_2$(amine)L coordinate complex. Two nucleotides (AC in this figure) in a single DNA molecule, amine, and an unknown ligand form coordinate bonds with Au(III).

according to the study of Baddley et al.[5] For example, an Au(III) macrocyclic polyamine complex with cyclam (1,4,8,11-tetraazacyclotetradecane) exhibits an absorption band at 360 nm due to a LMCT transition.[6,7] In comparison with these reported results, it is concluded that the 360 nm absorption band in the optical absorption spectrum of the solution after the laser ablation originates from the $p \rightarrow d$ charge transfer band (LMCT) between the ligand and Au(III) in the Au(III)(DNA-base)$_2$(amine)L coordinate complex.

In addition, the 360-nm absorption band appears (at a pH of the solution higher than ~8.0) and disappears (at a pH lower than ~6.0) reversibly. This finding indicates that the lone pairs of the ligand is formed by its deprotonation in the alkaline solution with a pH higher than ~8.0 and charge transfer between the centered Au(III) and the deprotonated ligand gives the LMCT band at 360 nm. It is not likely that DNA bases in the complex are not involved in the charge transfer, because the DNA bases, which behave as aromatic N-donors in the complex, do not posses any lone pair.

Note that Au(III) ligated with cyclam tends to decompose slowly by hydrolysis into Au precipitates in its aqueous solution.[6] The hydrolysis of the coordinate complex formed in the present study also occurs in its aqueous solution as shown in Figure 6.

Formation Scheme of Au(III)-DNA Coordinate Complex

The abundance of the Au(III)-DNA coordinate complex increases with increase in the concentration of Ca^{2+} (generally multivalent cations) (see Figure 3) and the intensity of the ablation laser pulse (see Figure 5). These findings are explained in such a scheme that 1) DNA molecules are neutralized by binding Ca^{2+} to their negatively charged phosphate groups, so that the neutralized DNA molecules[8,9] and Au nanoparticles are mutually attracted by a hydrophobic interaction into Au nanoparticle-DNA entanglements, 2) Au(III) ions are produced from the Au nanoparticle-DNA entanglement by laser ablation and remain alive

within a distance of several nm around the Au nanoparticles, and 3) an Au(III) ion reacts to form an Au(III)(DNA-base)$_2$(amine)L coordinate complex with two amines and two DNA bases of a single DNA molecule in the vicinity of an Au nanoparticle in the entanglements from which the Au(III) ion is produced and defuses out. The validity of each postulation given in the formation scheme is argued separately in the following subsections.

Formation of Au(III)-DNA Coordinate Complex in Au Nanoparticle-DNA Entanglements

The abundance increase of the Au(III)-DNA coordinate complex with the Ca^{2+} concentration (see Figure 3) supports the formation scheme that the coordinate complex is produced in the Au nanoparticle-DNA entanglements since the entanglements are formed at an increasing extent with the increase of the Ca^{2+} concentration. The role of the Ca^{2+} (generally multivalent cations) in the formation of the Au nanoparticles-DNA entanglements is well recognized in the field of the DNA technologies,[10] and actually in the present study the finding of the formation of the entanglements is proved by the broad absorption band at 650 nm in the optical absorption spectrum of the solution before the laser ablation (see dotted line in Figure 2). Note that the entanglements having the optical absorption at 650 nm are not formed in the solution when Ca^{2+} is not dissolved in it (see broken line in Figure 2). This band is observed neither in the spectrum of the solution after the laser ablation (see solid line in Figure 2) because of disruption of the Au nanoparticles-DNA entanglements by the laser ablation. This mechanism is rationalized as follows: Let us assume that the life time for recombination of Au(III) ions with solvated electrons ejected by the laser ablation is in the order of magnitude of $\sim$ps by consulting the life time of solvated electrons produced by laser irradiation on Ag nanoparticles.[11] It is further assumed that water molecules in the vicinity of the Au nanoparticles do not hold rigid hydrogen bonding networks and an Au(III) ion have a kinetic temperature of $\sim 10^4$ K.[12] On these assumptions, a volume of the solution surrounding an Au nanoparticle, in which Au(III) ions are populated densely, is calculated to be $\sim 10^{-24}$ m^3. In the present system, the volume containing Au(III) ions is $\sim 10^{-6}$ times as large as the total volume of the solution since the concentration of the Au nanoparticles is 1.3 nM. If the DNA molecules and the Au nanoparticles are dispersed randomly in the solution, the collision probability of a DNA base with an Au(III) ion is less than $\sim 10^{-6}$. This estimation of the collision probability leads us to conclude that the DNA molecules should be adsorbed by the Au nanoparticles into the Au nanoparticle-DNA entanglements for efficient formation of the Au(III)-DNA coordinate complex. It is also plausible that DNA molecules are enriched on Au nanoparticles by a salt precipitation effect of Ca^{2+}. This mechanism should be ruled out because addition of NaCl does not enhance the formation rate of the Au(III)-DNA coordinate complex.

In the framework of the formation scheme of the Au(III)-DNA coordinate complex, the reaction processes for the formation of the Au(III)-DNA coordinate complex are written as follows:

$$\text{DNA p.g.} + \text{Ca}^{2+} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{DNA p.g.} - \text{Ca}^{2+} \tag{1}$$

$$\text{DNA p.g.} - \text{Ca}^{2+} + \text{Au n.p.} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \text{DNA p.g.} - \text{Ca}^{2+} - \text{Au n.p.} \tag{2}$$

$$\text{DNA p.g.} - \text{Ca}^{2+} - \text{Au n.p.} \xrightarrow{\text{laser ablation}} \text{Au(III)} - \text{DNA c.c.} \tag{3}$$

where DNA p.g., Au n.p., and Au(III)-DNA c.c. represent a DNA phosphate group, an Au nanoparticle, and an Au(III)-DNA coordinate complex, respectively, and X-Y (Au(III)-DNA c.c. for instance) represents a complex of X and Y. The concentration of the DNA p.g. and the Au n.p. are considered to be unchanged during the reaction. Accordingly, one obtains the relation Eq. 4 from Eqs. 1, 2, and 3 on the assumption that Au(III) ions are in excess through the reaction and hence [Au(III)-DNA c.c.] is proportional to [DNA p.g.-Ca^{2+}-Au n.p.] as follows:

$$[\text{Au(III)} - \text{DNA c.c.}] = \frac{A[\text{Ca}^{2+}]}{K + [\text{Ca}^{2+}]} \tag{4}$$

where A and K represent a constant independent of the Ca^{2+} concentration and k_1k_3/k_2k_4, respectively. In Figure 3, the theoretical prediction given by Eq. 4 is shown as a solid curve on the data points, where the uncertainties of the data points are typically 7% of the abundance. An arrow indicated in Figure 3 corresponds to the inflection point with the concentration of 8×10^{-3} M. As the Ca^{2+} concentration increase, the Au nanoparticles entangle with the neutralized DNA molecules at an increasing extent above the inflection point, and hence the formation rate of the Au(III)-DNA coordinate complex increases. The concentration of the EDTA in the solution ($\sim 10^{-4}$ M) used in the present study is much lower than that of Ca^{2+}. EDTA in it does not influence on determining the concentration of Ca^{2+} necessary for the complex formation.

Oxidization State of Au Ions in Au(III)-DNA Coordinate Complex

It has been reported that Au ions, namely Au(I) and Au(III) ions are produced from Au nanoparticles dispersed in water by laser ablation.[13,14] As shown in Figure 4, the Au(III)-DNA coordinate complex synthesized by the present method is proved to accompany with two DNA bases of a single DNA molecule. In other words, the two Au ion coordination-sites are occupied with two DNA bases. Moreover, amines are required for the formation of the coordinate complex. In the

hard-soft-acid-base context of Pearson R.G., nitrogen ligands should prefer to bind a harder Au(III) ion oxidation state, in contrast to a soft ligands that form a very stable coordinate complex with a softer Au(I) ion. It follows that the Au(III) ion participates in the formation of the coordinate complex with amine and two DNA bases, because the Au(III) ion is stabilized by coordination to the nitrogen ligands in the present coordinate complex. Actually, it is generally accepted in coordination chemistry that coordination number of Au(III) is regarded to be four, whereas, that of Au(I) is rarely larger than two, and hence, the Au in the complex should be in a form of Au(III). In our different experiment, we have also observes similar LMCT band of Pt(II) coordinate complex in the vicinity of the wavelength of 360 nm when nanoparticles of Pt are employed instead those of of Au.[15] This finding is consistent with the fact that Au(III), which is isoelectronic to Pt(II) is involve in the complex.

In addition, it has been reported that a nucleotide with only nitrogen donors can bind only weakly to Au(I) ion, whereas Au(III) ion binds strongly to nitrogen donors and a number of Au(III) interacting with nucleotides have been reported.[1] This facts also supports that Au(III) ions participate in the Au(III)-DNA coordinate complex in the present system as mentioned above.

Small Abundance of Coordinate Complex at Higher Intensity of Ablation Laser

Figure 5 shows the abundance of the Au(III)-DNA coordinate complex as a function of the intensity of the ablation laser at 532 nm. The abundance increases with the laser power up to 17 mJ/pulse and then decreases. The decrease is explained as follows: 1) solvated electrons from An nanoparticles reduce DNA bases, 2) multi-photon absorption of the DNA-bases generates two unpaired electrons in an excited state of the DNA bases, which causes the DNA molecules to decompose, and 3) a local temperature jump due to an energy flow from heated Au nanoparticles by the intense laser causes the DNA molecules to degrade.

CONCLUSIONS

We developed a novel method to prepare an Au(III)(DNA-base)$_2$(amine)$_L$ coordinate complex in a aqueous solution containing Au nanoparticles, DNA molecules, amines and multi-valent cations under irradiation of an intense laser at the wavelength of 532 nm. The essence of this method is that short lifetimed Au(III) ions are produced by laser ablation of Au nanoparticles and allowed to react instantaneously with amines and DNA molecules adsorbed on the Au nanoparticles by Ca^{2+} neutralization. The reaction rate is controllable by changing the laser focusing, since the reaction is confined in a small volume as large as $\sim 10^{-24}$ m^3 around an Au nanoparticle.

EXPERIMENTAL SECTION

Chemicals

Oligonucleotides (dimer and tetramer) used in the present experiments were chemically synthesized, while a commercially available lambda DNA solution (TOYOBO. Co., Ltd.) and other chemicals were used without further purification.

Tris and EDTA were added in the lambda DNA solution as the buffer salt and as making chelate compounds, respectively. A lambda DNA solution free from any other additives than lambda DNA was prepared by dialysis, in order to search requisite components for forming an Au(III)-DNA coordinate complex in the solution.

Preparation of Au Nanoparticles in Pure Water

Au nanoparticles were produced by laser ablation of a Au metal plate in pure water.[16–18] The Au metal plate was placed in the bottom of a glass vessel filled with 10 mL of pure water and was irradiated with an output of the fundamental of Quanta-Ray GCR1-170 Nd:YAG laser operating a 10 Hz. The spot size of the laser beam focused by a lens (focus length of 250 mm) was ~1 mm in diameter on the Au metal plate surface.

Formation of Coordinate Complex by Laser Ablation of Au Nanoparticles

A solution containing Au nanoparticles (1.3 nM, 14 nm in diameter), DNA molecules, amines, and multi-valent cations was placed in an optical cell equipped with a stirrer on the bottom of it. As shown in Figure 1, the output of the second harmonic of Quanta Ray GCR 170 Nd:YAG laser was focused to a volume as large as 1 mm^3 in the solution from the gape of the cell by a lens having the focal length of 250 mm. A Scientech AC2501 power meter was used to monitor the laser power. The optical absorption spectrum of the solution was measured by a Shimadzu UV-1200 spectrometer.

REFERENCES

1. Sadler, P.J.; Sue, R.E. The chemistry of gold drugs. Met.-Based Drug. **1994**, *1*, 107–144.
2. Buckley, R.G.; Elsome, A.M.; Fricker, S.P.; Henderson, G.R.; Theobald, B.R.C.; Parish, R.V.; Howe, B.P.; Kelland, L.R. Antitumor properties of some 2-[(dimethylamino)methyl]phenylgold(III) complexes. J. Med. Chem. **1996**, *39*, 5208–5214.
3. Marcon, G.; Carotti, S.; Coronnello, M.; Messori, L.; Mini, E.; Orioli, P.; Mazzei, T.; Cinellu, M.A.; Minghetti, G. Gold(III) complexes with bipyridyl ligands: solution chemistry, cytotoxicity, and DNA binding properties. J. Med. Chem. **2002**, *45*, 1672–1677.
4. Boal, A.K.; Ilhan, F.; Derouchey, J.E.; Thum-Albrecht, T.; Russell, T.P.; Rotello, V.M. Self-assembly of nanoparticles into structured spherical and network aggregates. Nature **2000**, *404*, 746–748.
5. Baddley, W.H.; Basolo, F.; Gray, H.B.; Nölting, C.; Pöe, A.J. Acidodiethylenetriaminegold(III) complexes: preparation, solution chemistry, and electronic structure. Inorg. Chem. **1963**, *2*, 921–928.

6. Kimura, E.; Kurogi, Y.; Takahashi, T. The first gold(III) macrocyclic polyamine complexes and application to selective gold(III) uptake. Inorg. Chem. **1991**, *30*, 4117–4121.
7. Rossignoli, M.; Bernhardt, P.V.; Lawrance, G.A.; Maeder, M. Gold(III) template synthesis of a pendant-arm macrocycle. J. Chem. Soc. Dalton Trans. **1997**, *3*, 323–328.
8. Ahmad, R.; Arakawa, H.; Tajmir-Riahi, H.A. A comparative study of DNA complexation with Mg(II) and Ca(II) in aqueous solution: major and minor grooves bindings. Biophys. J. **2003**, *84*, 2460–2466.
9. Iwata, K.; Sawadaishi, T.; Nishimura, S.; Tokura, S.; Nishi, N. Utilization of DNA as functional materials: preparation of filters containing DNA insolubilized with alginic acid gel. Int. J. Biol. Macromol. **1996**, *18*, 149–150.
10. Sanford, J.C.; Klein, T.M.; Wolf, E.D.; Allen, N. Delivery of substances into cells and tissues using a particle bombardment process. Part. Sci. Technol. **1987**, *5*, 27–37.
11. Roberti, T.W.; Smith, B.A.; Zhang, J.Z. Ultrafast electron dynamics at the liquid-metal interface: femtosecond studies using surface plasmons in aqueous silver colloid. J. Chem. Phys. **1995**, *102*, 3860–3866.
12. Takami, A.; Kurita, H.; Koda, S. Laser-induced size reduction of noble metal particles. J. Phys. Chem., B **1999**, *103*, 1226–1232.
13. McGrath, T.E.; Beveridge, A.C.; Diebold, G.J. Laser-induced "regeneration" of colloidal particles: the effects of thermal inertia on the chemical reactivity of laser-heated particles. Angew. Chem., Int. Ed. **1999**, *38*, 3353–3356.
14. Takeda, Y.; Mufané, F.; Kondow, T. Abstract in the 11th CHEMINAS **2005**, *41*.
15. Takeda, Y.; Mafuné, F.; Kondow, T. Formation of metal-DNA complex by laser ablation of gold and platinum nanoparticles. Abstract in the 47th Houshasenkagaku Touronkai **2004**, 77–78.
16. Mafuné, F.; Kohno, J.; Takeda, Y.; Kondow, T. Full-physical preparation of size-selected gold nanoparticles in solution: laser ablation and laser-induced size control. J. Phys. Chem., B **2002**, *106*, 7575–7577.
17. Mafuné, F.; Kohno, J.; Takeda, Y.; Kondow, T.; Sawabe, H. Formation of gold nanoparticles by laser ablation in aqueous solution of surfactant. J. Phys. Chem., B **2001**, *105*, 5114–5120.
18. Mafuné, F.; Kondow, T. Formation of small gold clusters in solution by laser excitation of interband transition. Chem. Phys. Lett. **2003**, *372*, 199–204.