Preparation of Colloidal Au by a Femtosecond Laser

Chongjun Zhao,* Shiliang Qu, Jianrong Qiu, Congshan Zhu, and Kazuyuki Hirao†
Photon Craft Project, Shanghai Institute of Optics & Fine Mechanics, Chinese Academy of Sciences and Japan Science and Technology Corporation, Shanghai, 201800, P. R. China
†*Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501*

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Au colloid was photoinduced by a focused infrared femtosecond laser at 800 nm. The Au colloid was characterized by absorption spectra, X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM). A mechanism for the formation of Au nanoparticles was proposed.

Metal nanoparticles have been used in catalysis, nonlinear optics, material sciences and other fields.[1–3] Among these metals, Au nanoparticles have been studied because of their optical nonlinearity. Highly dispersed Au nanoparticles have been prepared by a wide variety of fabrication methods: radiolysis, ultraviolet photochemical and chemical reduction.[4–6] However, there is no report of photoinduced formation by an infrared laser as far as we know, though the laser has been used in the size and shape change of Au particles.[7–10] The use of near-IR laser for precipitate of Au nanoparticles, it will not only exploit a new method to prepare colloidal Au, but also have a high potential use in "photo-writing" Au microscopic structure. When the laser beam is focused inside of a transparent materials doped with gold ion, a 3-D "space selective" Au pattern will be produced inside of a transparent material while leaving the surface unaffected.[11] This is the unique merit for a near-IR irradiation, although it is usually less focused than UV. In this study, colloidal Au was prepared by irradiation with a pulsed 800 nm femtosecond laser.

Gold ion solution was prepared by dissolving $HAuCl_4$ in a previously fabricated TiO_2 solution prepared as the previous method.[5] Gold ion concentration was 5 mM.

In laser-irradiation experiment, 2 mL of the solution was introduced in a rectangular quartz vessel of $0.5 \times 1 \times 4\,\text{cm}^3$ and irradiated by the fundamental light (800 nm) from a regeneratively amplified femtosecond Ti: sapphire laser (Spectra-Physics) at room temperature. The typical pulse width, repetition rate, maximum pulse energy were 120 fs, 1 KHz, and 0.5 mJ, respectively. The laser light was focused into solution through a lens with 20-cm focal length in air.

X-ray diffraction (XRD) measurements were carried out to examine the crystallinity, and the sample was prepared by evaporating drops of the sample solution on a glass substrate. The absorption spectra were recorded on a Jasco V-570 Spectrophotometer. Transmission electron microscopy (TEM) observations were performed on a JEM-2010 electron microscope (JEOL). The sample was prepared by evaporating a drop of the sample solution on a copper grid coated with a carbon film.

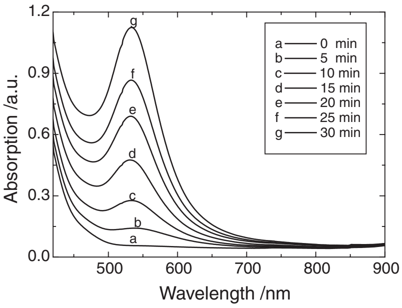

Figure 1. Absorption spectra for $HAuCl_4$ solution after irradiation of a focused near-IR femstosecond laser for 0 min (a), 5 min (b), 10 min (c), 15 min (d), 20 min (e), 25 min (f), and 30 min (g). (0.36 mJ/pulse)

Figure 1 shows the absorption spectra of the sample solution with laser irradiation time. After the solution was irradiated, surface plasma resonance absorption band appeared around 530 nm resulting from the coherent oscillation of the free 6 s electrons in the conduction band, which was characterization of Au nanoparticles.[4–6] Along with the irradiation time, the absorption peaks increased monotonously.

On the other hand, the color of $HAuCl_4$ solution also changed with proceeding laser irradiation. The color of $HAuCl_4$ solution under focused laser light irradiation changes in the order of yellow → orange → wine-red.

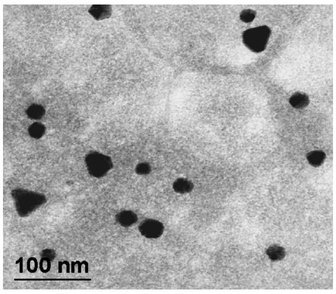

Figure 2. TEM photograph of $HAuCl_4$ solution after irradiation by a focused near-IR femtosecond laser with 0.36 mJ/pulse for 0.5 h.

Direct observation of Au nanoparticles was carried out on a transmission electron microscopy, as shown in Figure 2. In the figure, well-separated black particles are seen clearly. These particles should be metallic Au, because they were not seen in the TiO_2 solution or TiO_2 solution containing gold ion untreated by laser. It is interesting that triangular particles are observed, as seen in a silica gel.[12]

Figure 3 shows the XRD patterns of a film of the $HAuCl_4$ sample solution after 30 min irradiation. According to the

JCPDS reference (01-1172), the peaks $2\theta = 38.3^\circ$ and $2\theta = 44.3^\circ$ are, respectively, assigned as (111) and (200) reflection lines of cubic Au, indicating the formation of metallic Au. The size of Au particles was determined using Scherrer's equation:

$$d = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

Where, λ is the wavelength of the X-ray source and β (radians) the full width at half maximum of the X-ray diffraction peak at the diffraction angle θ. The diameter of Au nanoparticles was calculated using the line broadening of the diffraction band at $2\theta = 38.3^\circ$ to be ca. 22 nm.

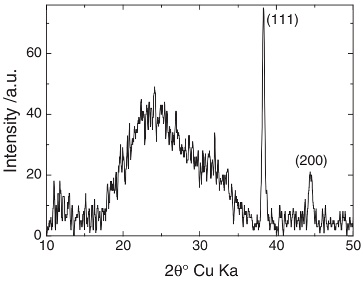

Figure 3. X-ray diffraction (XRD) pattern of a film of $HAuCl_4$ solution after 30 min irradiation by laser.

The effects of the experimental conditions were studied.

Effect of the TiO_2: The fact that Au nanoparticles were also efficiently prepared in the absence of TiO_2 indicates that TiO_2 was unnecessary for Au colloid formation. On the other hand, colloidal Au prepared with TiO_2 can be stable for more than one month, compared with one week for that without TiO_2. This was attributed to the electrostatic interaction between Au ion and positively-charged TiO_2 surface.[5] Colloidal SiO_2 and TiO_2 were also used for photoreduction of silver ion or gold ion, the quantum yield increased several times by using SiO_2 as protective agent.[13,14]

Effect of the laser pulse energy and laser focus position: Laser pulse energy and focus position affected both the particles size and the number of Au nanoparticles. When the focus position approached the solution surface or the laser pulse energy increased, the peak position blue shifted and peak intensity increased distinctly, suggesting that the particle size decreased and particle number increased.

Since the $HAuCl_4$ solution was transparent for an unfocused laser light at 800 nm, we suggested that a multiphoton process was involved in the formation of the Au nanoparticles when the sample solution was irradiated by a focused femtosecond laser pulse.[15] While the femtosecond laser pulse was tightly focused inside of solution a power density up to $3 \times 10^{13}\ \mathrm{W{\cdot}cm^{-2}}$ was obtained at the focus spot. The power density was so high as to cause multiphoton absorption process, i.e., gold ion was photoreduced by near-IR multiphoton instead of a UV photon.

On the other hand, microsized and high-temperature plasma would be created.[14] According to Mazur et al. the temperature of hot plasma could be roughly estimated.[16] Absorption of 30% of the energy 0.36 mJ pulse would produce a temperature of 3,600 K, which was much higher than the decomposition temperature of $AuCl_4^-$ to Au.[17]

So, referring to the literatures,[4,13,17] formation of Au particles can be demonstrated briefly as follows,

$$AuCl_4^- \xrightarrow{nh\nu} AuCl_3^- + {}^{\bullet}Cl \quad (n \geq 2) \qquad (2)$$

$$2AuCl_3^- \longrightarrow AuCl_4^- + AuCl_2^- \qquad (3)$$

$$AuCl_2^- \xrightarrow{nh\nu} Au^0 + {}^{\bullet}Cl + Cl^- \quad (n \geq 2) \qquad (4)$$

or

$$AuCl_4^- \xrightarrow{Q} Au^0 + 3Cl + Cl^- \qquad (5)$$

$$m\ Au^0 \longrightarrow (Au^0)_m \qquad (6)$$

Where n is the number of the photon involved in multiphoton process, m the number of Au atoms congregating into Au nanoparticles. In addition, Q is the caloric coming from the transient hot plasma.

In conclusion, Au nanoparticles with size of ca. 20 nm were photoinduced from $HAuCl_4$ dissolved in a previously prepared TiO_2 solution. The formation of Au nanoparticles was attributed to electron and hot plasma caused by multiphoton process of the femtosecond laser. TiO_2 played an important role in keeping the stability of the Au colloid.

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