Supporting Information

Remarkable Photothermal Effect of Interband Excitation on Nanosecond Laser-induced Reshaping and Size Reduction of Pseudo-spherical Gold Nanoparticles in Aqueous Solution

Daniel Werner†, Shuichi Hashimoto‡*, Takayuki Uwada‡

† Department of Ecosystem Engineering, The University of Tokushima, Tokushima 770-8506, Japan.
‡ Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan
* corresponding author, E-mail: hashi@eco.tokushima-u.ac.jp

Contents
A. Extinction spectra, TEM images and size distribution of gold particles employed in this study
   Fig. S1, Fig. S2
B. Remark on the estimation of absorbed laser energy by Au NP
C. Simulated spectra of continuous size reduction based on the Mie theory
   Fig. S3
D. In situ spectra for original 55 nm gold particles in aqueous solution
   Fig. S4
E. Remark on thermionic emission and photoelectric effect
   Fig. S5
F. Method for estimating \(Q_{\text{melt}}\) and \(Q_{\text{evap}}\) to calculate the specific heat capacity of Au NPs
   Fig. S6
G. Remarks on in situ spectral measurement for initial 20 nm Au NPs in aqueous solution
   Fig. S7
H. TEM and extinction spectroscopic observations of laser-induced size reduction for 20 nm Au NPs
   Fig. S8, Fig. S9
I. Contribution of inter- and intraband components to the absorption spectra of 60 nm and 20 nm Au NPs and the Fermi distribution for bulk gold
   Fig. S10, Fig. S11
J. \(\Delta A\) vs. laser fluence (mJ·cm\(^{-2}\)) representation for the experimental data given in Fig. 2
   Fig. S12
A. Extinction spectra, TEM images and size distribution of gold particles employed in this study

1) 55 nm Au particles (BBI, EMGC60)

**Fig. S1 (a)** Experimental and simulated UV-Vis-NIR extinction spectra for 55 nm gold particles in aqueous solution. The solid curve shows the experimental spectrum and the red dotted curve shows that of simulation based on Mie theory including the intrinsic size effect of the dielectric function for 55 nm spherical gold particles in water with a particle concentration of $3.1 \times 10^{10}$ ml$^{-1}$. Concentration given by BBI is $2.6 \times 10^{10}$ ml$^{-1}$, in good agreement with the simulation.

**Fig. S1 (b)** TEM image of 55 nm gold particles (BBI, EMGC60).
Fig. S1 (c) Histogram of particle diameter distribution constructed from TEM images for 250 particles. The mean diameter of 54 nm with a standard deviation of 7 nm was estimated by the Gaussian fitting.

2) 20 nm Au particles (BBI, EMGC20)

Fig. S2 (a) Experimental and simulated UV-Vis-NIR extinction spectra of 20 nm (BBI, EMGC20) gold particles in aqueous solution. The solid curve shows the experimental spectrum and the red dotted curve, the extinction spectrum of $6.8 \times 10^{11} \text{ml}^{-1}$, 20 nm spherical gold particles in water calculated based on Mie Theory including the intrinsic size effect of the dielectric function. Particle concentration given by BBI is $7 \times 10^{10} \text{ml}^{-1}$.
Fig. S2 (b) TEM image of 20 nm gold particles (BBI, EMGC20).

Fig. S2 (c) Size distribution for 350 particles. The mean diameter of 19 nm with a standard deviation of 3 nm was obtained by the Gaussian fitting.
B. Remark on the estimation of absorbed laser energy by Au NP

Previously, Inasawa\textsuperscript{15} estimated the absorbed energy differently based upon the Lambert-Beer’s law given by:

\[
E_{\text{abs}} = \frac{I(1-10^{-A})}{c_A \ell_0}
\]

in which \(I\): laser energy (mJ\cdot cm\(^{-2}\)), \(A\): absorbance at the excitation wavelength, \(c_A\): atomic concentration of Au NPs in aqueous solution (mol\cdot cm\(^{-3}\)) using an extinction coefficient at 520 nm: 2700-4200 M\(^{-1}\)\cdot cm\(^{-2}\), \(\ell_0\): optical pass length (1.00 cm). Typically, \(I=14\) mJ\cdot cm\(^{-2}\), \(A=0.035\), \(c_A=2 \times 10^{-8}\) mol\cdot cm\(^{-3}\), \(\ell_0=1.00\) cm gave \(E_{\text{abs}}=5.4 \times 10^{-8}\) J\cdot mol\(^{-1}\) for average 25 nm Au NPs. \(E_{\text{abs}}\) contains a large contribution of light scattering besides light absorption especially for Au particles greater than 20 nm diameter. Besides that, Mie theory dictates that the extinction coefficient is particle size dependent as opposed to the above equation. Therefore we employed eq. 1 instead of the equation given by Inasawa in the present study. Other studies\textsuperscript{16, 31} used equations similar to eq. 1 to estimate the absorbed energy.

C. Simulated spectra of continuous size reduction based on the Mie theory

![Simulated spectral changes of gradual size reduction of initial 60 nm gold NPs in aqueous solution based on the Mie theory. The dielectric constant of the surrounding medium is set to \(\varepsilon_m = (1.33)^2\) and the fill factor, which is defined as the product of particle volume and particle density (V \times N) to 2.3 \times 10^{-6}. The simulation clearly shows that the reduction in the intensity of the plasmon band is accompanied by the increased contribution in the red region.](image-url)

\textbf{Fig. S3} Simulated spectral changes of gradual size reduction of initial 60 nm gold NPs in aqueous solution based on the Mie theory. The dielectric constant of the surrounding medium is set to \(\varepsilon_m = (1.33)^2\) and the fill factor, which is defined as the product of particle volume and particle density (V \times N) to 2.3 \times 10^{-6}. The simulation clearly shows that the reduction in the intensity of the plasmon band is accompanied by the increased contribution in the red region.
D. In situ spectra for original 55 nm gold particles in aqueous solution
Fig. S4  In situ spectra of 55 nm gold particles in aqueous solution on exposure to laser light with wavelengths at (a) 266 nm, (b) 355 nm and (c) 532 nm. The arrows show the spectral changes with increasing irradiation time. Each graph corresponds to the TEM images in Fig. 3 and to the data points in Fig. 2.
E. Remark on thermionic emission and photoelectric effect

Thermionic emission
The electron flux $J_n (s^{-1})$ generated by thermionic emission is defined by the Richardson–Dushman Equation:\(^4\):

$$J_n = \lambda_B (1 - \lambda_R) \frac{k_B T}{\pi \hbar} W e^{-\frac{W}{k_B T}}$$

Here $\lambda_B$ and $\lambda_R$ denote correction factors, which take the band structure of the metal and the reflection of electrons at the particle surface into consideration. $T$, $W$, and $k_B$ are temperature, work function of gold, and the Boltzmann constant. Fig. S5 shows the electron flux per second for the work function of gold of 5.1 eV in vacuum (a) and the reduced work function to 4.3 eV considering an electron affinity of the surrounding water molecules of $-0.8$ eV (b).\(^*\) Note that at temperature range below the boiling point of gold (3129 K) postulated for our experiment, water cavities or bubbles are presumably formed around the particles. $W$ is then assumed to be between 4.3 (surrounded by water) and 5.1 eV (in vacuum). Then, the correction factors, $\lambda_B$ and $\lambda_R$, were set to 1 and 0.5. Thermoionic electron emission starts to take place at temperatures higher than 1500 K, which is higher than the melting point of bulk gold (1337 K). The maximum number of electrons emitted at the boiling point of bulk gold (3129 K) is about $8 \times 10^6$ s$^{-1}$ (Fig. S5 b). In our experiment, high temperatures inside the particle can only last $\sim$5 ns, which gives rise to an average electron flux of 0.04 per pulse at the boiling point. This means that thermionic electron emission is negligible at temperatures near the boiling point. The threshold temperature for the emission of $\sim$1 electron-pulse$^{-1}$ calculated by the Richardson–Dushman equation is 5000 K that is much higher than the maximum temperature expected for our experiment. Note that during the pulse duration of 5 ns the electron temperature $T_e$ and the lattice temperature $T_l$ establish equilibrium.


**Fig. S5** Electron flux $J_n$ in s$^{-1}$ from a gold surface calculated for (a) $W = 5.1$ eV in vacuum and (b) 4.3 eV in water.
Photoelectric effect
It seems likely that the electron ejection takes place from the 6sp band when excited at 266 nm due to the high photon energy of 4.66 eV. We calculated the intraband excitation (absorption) probability at 266 nm for a 55 nm gold sphere (Fig. S10a) by separating the interband contribution from the plasmon band absorption (6sp band). The blue area shows the absorption cross section of the free electron gas in the conduction band. At 266 nm the contribution of blue area compared to that of the interband absorption from 5d to 6sp, red area, is very small. Thus, the intraband excitation is negligible. However, for much smaller gold spheres, the intraband excitation probability at 266 nm increases because of the effect of electron confinement within the particle. For instance, Fig. S10-b represents the absorption cross sections as a function of wavelength for a 20 nm gold sphere. In this case, the intraband excitation probability increases to 50 % of the interband excitation probability. Thus, for the 20 nm Au particles, the photoelectric effect on excitation at 266 nm should be taken into account. Nevertheless, our results of the excitation at 355 nm (3.55 eV) for the 55 nm gold particles gave similar thresholds for both melting and evaporation to those of the excitation at 266 nm. The photon energy of 3.55 eV is too small for the photoelectric effect to take place. Thus, we assume that the electron ejection process contributing to the reduced electron concentration of the free electron gas can be neglected in our model.
F. Method for estimating $Q_{\text{melt}}$ and $Q_{\text{evap}}$ to calculate the specific heat capacity of NPs

**Fig. S6 (a)** Temperature vs. $Q$ curve for a 55 nm aqueous Au NP constructed from an experimental $\Delta A$ vs. $Q$ curve on excitation by a single shot of 532 nm laser light. The values of $Q_{\text{melt}}$ (melting threshold energy = 200 J·g$^{-1}$) and $Q_{\text{evap}}$ (evaporation threshold energy = 560 J·g$^{-1}$) were determined experimentally by the onsets of two stepwise transitions observed in $\Delta A$ vs. $Q$ curve. To construct the $T$ vs. $Q$ curve, $T_0=298$ K was assumed with the phase transition temperature values of $T_{\text{melt}}=1337$ K and $T_{\text{evap}}=3129$ K for bulk gold.

**Fig. S6 (b)** Temperature vs. $Q$ curves for a 55 nm aqueous Au NP on excitation by 266 nm laser light drawn based upon an experimental $\Delta A$ vs. $Q$ curve. The experimentally determined values of $Q_{\text{melt}}$ (50 J·g$^{-1}$) and $Q_{\text{evap}}$ (223 J·g$^{-1}$) are significantly smaller than those determined for the excitation at 532 nm (Fig. S5 (a)).
G. Remarks on in situ spectral measurement for initial 20 nm Au NPs in aqueous solution

Figure S7 depicts the decrease in the extinction peak intensity of the plasmon band $\Delta A$, versus the absorbed energy $Q$, due to continuous laser irradiation. For 20 nm gold particles, we found that much higher $Q$ values are necessary to initiate the melting and evaporation of the particles compared with those for 55 nm particles (see Fig. 2 for comparison). For the excitation wavelength of 266 nm, for instance, the first and second threshold energies, $Q_{\text{melt}}$ and $Q_{\text{evap}}$, are located approximately at 200 J⋅g$^{-1}$⋅pulse$^{-1}$ and 500 J⋅g$^{-1}$⋅pulse$^{-1}$, which are 2–3 times greater than those observed for the 55 nm particles. At the same time, a $\Delta A$ vs. $Q$ curve for excitation at 266 nm was markedly different from that for excitation at 355 nm, which was not observed for 55 nm particles (Fig. 2). Thus, up to the absorbed energy of 500 J⋅g$^{-1}$⋅pulse$^{-1}$, no spectral changes and thus no shape and size changes of the particles could be observed for irradiation by 355 nm and 532 nm laser lights. The difference observed for 55 and 20 nm particles can be explained by a particle size-dependent cooling time, which was unravelled experimentally by Hartland$^{38}$ and Plech$^{39}$. According to their results, the time constant of heat dissipation to the surrounding medium for 55 nm gold particles is about 510 ps whereas only 75 ps for 20 nm particles. Accordingly, greater energy fluences are needed to heat up smaller NPs because of ~7 times faster cooling time due to the heat losses. No attempts were made presently to estimate the values of the heat capacity for 20 nm particles because of the serious heat losses that makes the correct evaluation of absorbed energies such as those for melting and evaporation difficult.

![Fig. S7](image-url)

**Fig. S7** Difference peak extinction value ($\Delta A$) of the plasmon band vs. absorbed energy for initial 20 nm gold particles in aqueous solution on exposure to the laser light with wavelengths 266 nm, 355 nm and 532 nm. The data points represent the values for the irradiation period of 60 minutes (10 Hz, 36000 laser shots). The dotted line (M) on the far left represents the absorbed energy corresponding to the melting point of bulk gold calculated by eq. 2a and the second dotted line (G) shows the energy at which the melting enthalpy ($\Delta H_{\text{melt}} = 62.8$ J⋅g$^{-1}$) is consumed. The dashed-dotted line (B) on the far right shows the energy where the boiling point of bulk gold calculated with equation (2b) is reached. The circled and labelled data points represent those at which TEM images are given in Fig. S8 and extinction spectra are given in S9 under each irradiation condition.
H. TEM and extinction spectroscopic observations of laser-induced size reduction for 20 nm Au NPs

**Fig. S8** TEM images of the initial 20 nm gold particles after 60 minutes of pulsed-laser irradiation at 266 nm (10 Hz). The notations of the graphs are related to Fig. S7. Fig. S8 a3-1 and a3-2 are obtained from the same sample at different locations.
Fig. S9 In situ spectra of the 20 nm gold particles in aqueous solution on laser irradiation at 266 nm (a) and 355 nm (b). The arrows show the spectral changes with increasing irradiation periods. The notations of the graphs are the same as the TEM images given in Fig. S8 and the data points in Fig. S7. TEM image for Fig. S9 (b1) was not measured.
I. Contribution of inter- and intraband components to the absorption spectra of 60 nm and 20 nm Au NPs and the Fermi distribution for bulk gold

Fig. S10 (a) Simulated interband (red) and intraband (blue) absorption spectra for a 60 nm gold sphere dispersed in aqueous solution representing the separated contributions of the two transitions. The interband threshold is 2.4 eV (518 nm) with a tail at 1.8 eV (689 nm) at room temperature.

Fig. S10 (b) Simulated spectra of interband (red) and intraband (blue) absorption probabilities for a 20 nm gold sphere. The interband threshold is 2.4 eV (518 nm) with a tail at 1.8 eV (689 nm) at room temperature.
Fig. S11 Energy dependence of the Fermi distribution for bulk gold with a Fermi energy of 5.5 eV. The black solid line represents the Fermi distribution at 0 K, where a sharp Fermi edge is clearly seen. The red solid line gives the Fermi distribution at 3129 K (boiling point of gold), in which the Fermi edge is smeared out. Here, electrons contributed to an energy of $2k_B T_e = 0.54$ eV are excited to energy levels above the Fermi level.
Fig. S12 (a) A plot of the decrease of the peak extinction value ($\Delta A$) of the plasmon band vs. laser fluence for the 55 nm gold particles in aqueous solution at various excitation laser wavelengths. All data points are for the irradiation period of 60 minutes (10 Hz, 36000 laser shots). This figure shows that the excitation at 266 nm or 355 nm is more efficient than that at 532 nm for melting and size reduction of Au NPs even by plotting against laser fluence as abscissa by ignoring $C_{\text{abs}}$.

Fig. S12 (b) A plot of the decrease of the peak extinction value ($\Delta A$) of the plasmon band vs. laser fluence for the 20 nm gold particles in aqueous solution excited at 266 nm, 355 nm and 532 nm. All the points are for the irradiation period of 60 minutes (10 Hz, 36000 shots). This figure also shows that the excitation at 266 nm is more efficient than that at 532 nm for melting and size reduction of Au NPs even by plotting against laser fluence as abscissa by ignoring $C_{\text{abs}}$. However, a difference was observed between the excitation at 266 nm and that at 355 nm presumably because of various contribution of inter- and intraband transitions dependent on the excitation wavelengths for the small particles (see Fig. S10-b).