Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

CW-Laser-Induced Morphological Changes of a Single Gold Nanoparticle on Glass: Observation of Surface Evaporation

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S1. Particle image acquired by TEM and the corresponding size distribution.

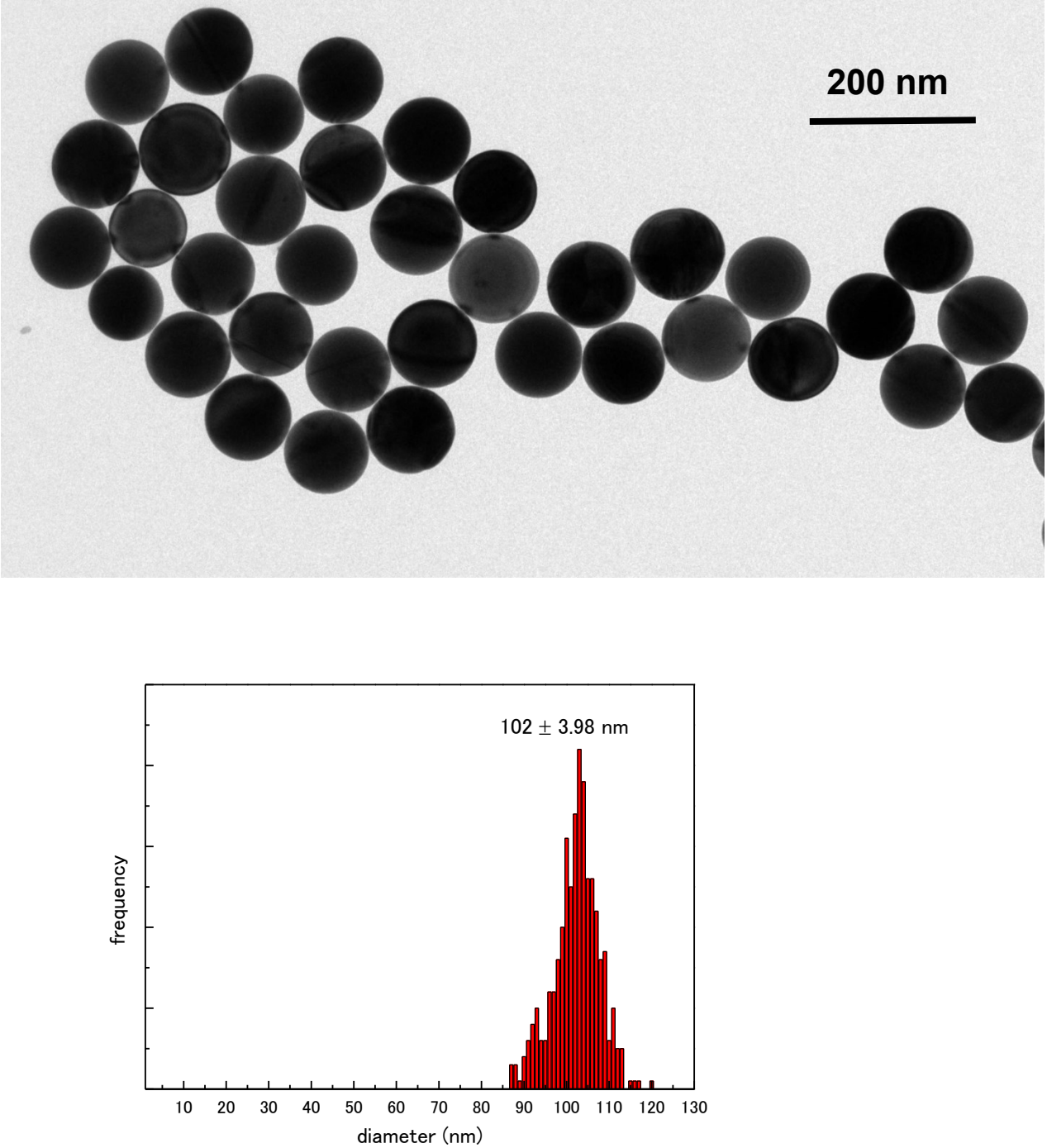

Fig. S1. TEM image and the corresponding size distribution of Au NPs (BBI EMGC 100) after reshaping by irradiating 532-nm, 5-ns pulsed lasers (10 Hz, 3 h, ~10 mJ cm^{-2}).

S2. Experimental Setup and darkfield images of 100-nm diameter Au NPs.

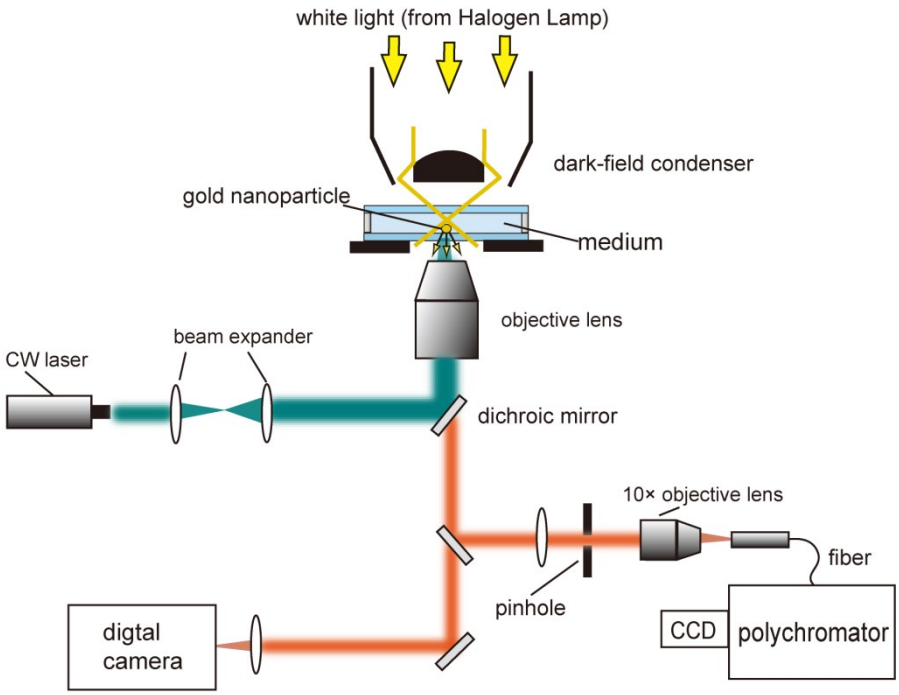

Figure S2-1. Experimental Setup

(a) (b)

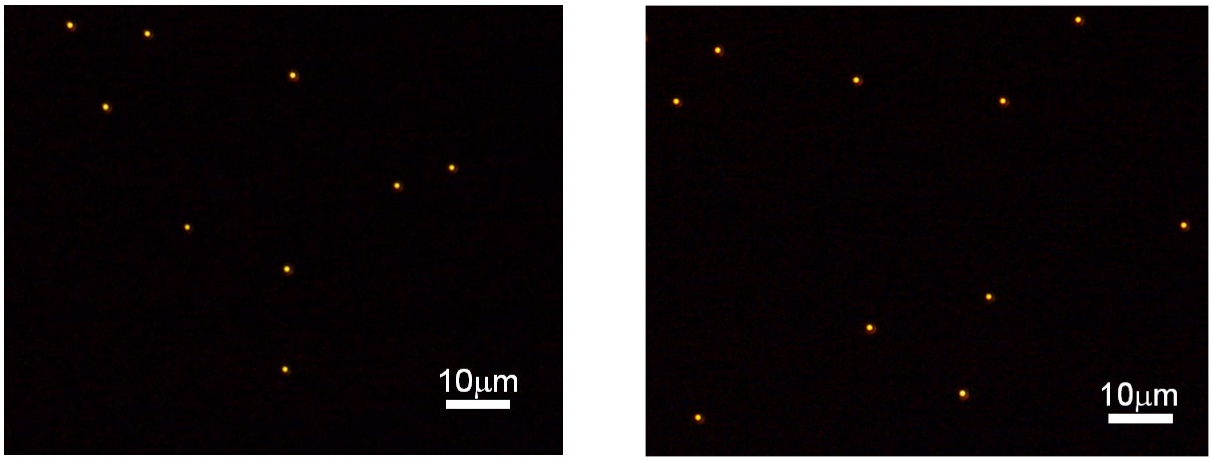

Fig. S2-2. Two typical darkfield images of 100-nm diameter Au NPs supported on a glass substrate and immersed in water (60×, NA=0.70 objective lens): (a) and (b).

S3. Temperature-dependent absorption cross section spectra of 100-nm diameter Au NP.

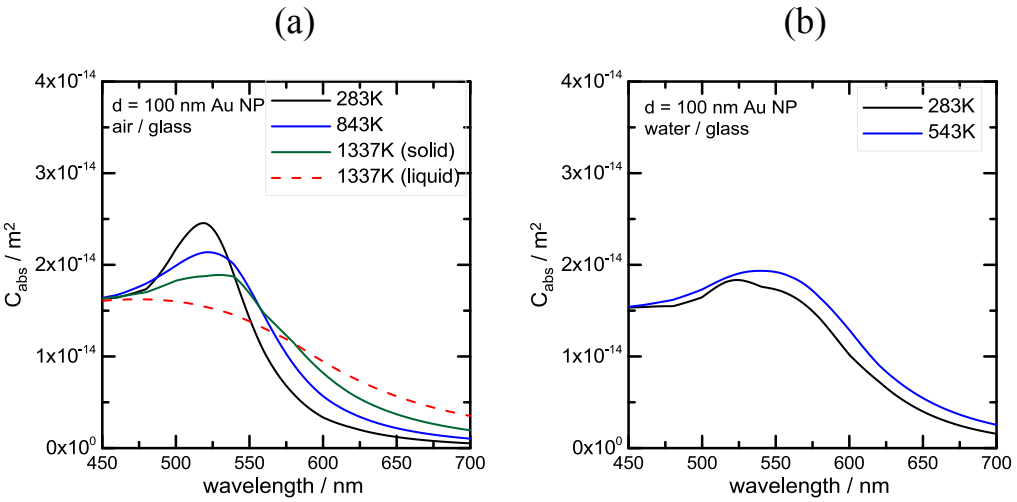

Fig. S3. Temperature-dependent absorption cross section spectra of 100-nm Au NP in air/glass (a) and water/glass (b) calculated by applying Mie theory.[1,2] Experimentally obtained temperature-dependent dielectric functions were used for the calculation.[3] The temperature-inducedt damping of LSPR band has been observed experimentally.[4,5]

1. C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*; Wiley: New York, **1983**.
2. K. Setoura, D. Werner and S. Hashimoto, *J. Phys. Chem. C*, 2012, **116**, 15458–15466.
3. M. Otter, *Z. Phys.* **1961**, 161, 539-549.
4. L. M. Liz-Marzan and P. Mulvaney, *New J. Chem*. 1998, **22**, 1285–1288.
5. S. Link and M. A. El-Sayed, *J. Phys. Chem. B*, 1999, **103**, 4212–4217.

S4. Calculated time evolution of particle temperatures.

The medium temperature T (r, t) surrounding a spherical particle at a distance r from the particle center at time t under the steady-state heating a by CW laser has been derived by Keblinski et al. [1] by solving 1D heat transfer equation in the frequency domain followed by taking the Laplace transformation, as given by eq. S4-1:

$$T(r,t) - T_\infty = \frac{C_{abs} \cdot I}{4\pi r k_{eff}} \left[erfc\left(\frac{r-a}{2\sqrt{Dt}}\right) - exp\left(\frac{r-a}{a} + \frac{Dt}{a^2}\right) erfc\left(\frac{r-a}{2\sqrt{Dt}} + \frac{\sqrt{Dt}}{a}\right)\right] \qquad \text{(S4-1)}$$

in which T_∞ [K] is the bulk temperature, C_{abs} [m^2] is the absorption cross section of the particle , I [W m^{-2}] is the laser peak power density, k_{eff} [W $m^{-1}K^{-1}$] is the effective thermal conductivity of the medium and substrate, a is the radius of the particle, D [m^2 s^{-1}] is the thermal diffusivity of the medium. When the thermal conductance at NP-medium interface is negligible under the steady state excitation condition, the particle temperature, T_p, is approximated by T ($r = a$, t).

We calculated the time evolution of particle temperature both in air/glass and in water/glass; the result is given in Fig. S4. The result indicated that the equilibrium T_p is much greater in air/glass than in water/glass. This difference is ascribed to an order of magnitude greater thermal conductivity of water (k_{water}: 0.60 W $m^{-1}K^{-1}$) than that of air (k_{air}: 0.022 W $m^{-1}K^{-1}$). The time evolution of T_p in the steady-state excitation reveals that the temperature rise is much faster than the experimental minimum exposure period, 125 μs and the steady state particle temperature is reached even for the shortest period of laser exposure.

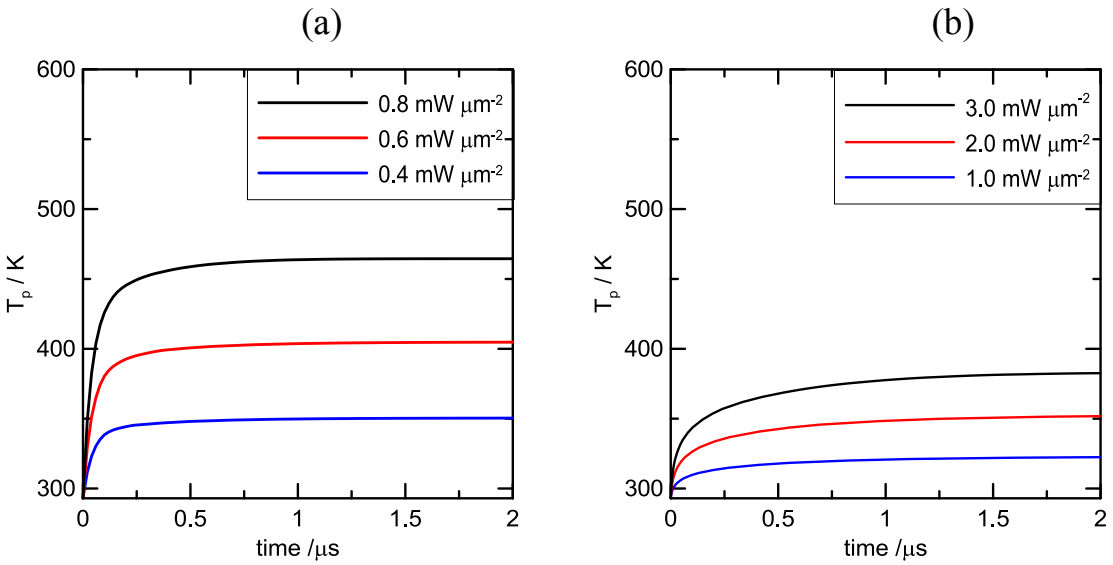

Fig. S4. Calculated time evolution of particle temperatures, T_p for a 100-nm diamter Au NP supported on a glass substrate in air (a) and in water (b). The excitation wavelength is 488 nm and the laser peak power densities are given in the figure.

1. P. Keblinski, D. G. Cahill, A. Bodapati, C. R. Sullivan, T. A. Taton, *J. Appl. Phys.* 2006, **100**, 054305.

S5. 1D heat conduction equation to estimate particle temperature.

According to the analytical solution of a 1D heat conduction equation, the steady-state particle temperature of a sphere of radius a [m], $T(a)$ [K] supported on a substrate and exposed to a medium is given by: [1,2]

$$T(a) = T(\infty) + \frac{C_{abs} \cdot I}{4\pi k_{eff} a} \qquad \text{(S5-1)}$$

where $T(\infty)$ [K] is the ambient temperature, C_{abs} [m^{-2}] the absorption cross section of Au NP at the excitation wavelength, I [W m^{-2}] the peak power density of the excitation laser, and k_{eff} [W m^{-1} K^{-1}] the effective thermal conductivity of the medium and substrate. The C_{abs} value of 100-nm Au sphere at the excitation wavelength of 488 nm is approximately constant regardless of temperature (C_{abs} (air/glass) = 1.94×10^{-14} m^{-2}; C_{abs} (water/glass) = 1.79×10^{-14} m^{-2}). The value of k_{eff} in air/glass is 0.2 ± 0.1 and that in water/glass is 0.8± 0.2. Equation S5-1 suggests the linear relationship between laser intensity, I and particle temperature, $T_p = T(a)$. This relationship was experimentally observed for the CW laser heating of a single Au sphere supported on three different substrates and submerged in various media. [1] Equation S5-1 suggests that the heating rate, the slope of T vs. I is dependent on the medium; the slope in air/glass is greater than that in water/glass. To construct temperature *vs*. laser peak power density given in Fig. 1c and Fig. 3b, we added melting enthalpy (1.22×10^{9} J m^{-3}) at 1337 K and evaporation enthalpy (3.282×10^{10} J m^{-3}) at 3100 K of bulk gold. The length of flat parts necessary for the consumption of melting enthalpy or evaporation enthalpy is medium-dependent; much longer in water/glass than in air/glass.

1. K. Setoura, Y. Okada, D. Werner, S. Hashimoto, *ACS Nano*, **2013**, *7*, 7874–7885.
2. M. Carlson, A. Khan, H. H. Richardson, *Nano. Lett*. **2011**, 11, 1061-1069.

S6. Modification of the glass substrate below the gold nanoparticles.

CW laser illumination of a single Au NP supported on a glass substrate ((Schott D263T, T_{glass}=860 K, T_{soft}=1006 K)) in air enabled the formation of a crater on the surface below the NP when the particle temperature increases to temperatures near the melting point of gold, as revealed by the atomic force microscopy (AFM) measurement (Fig. S6).

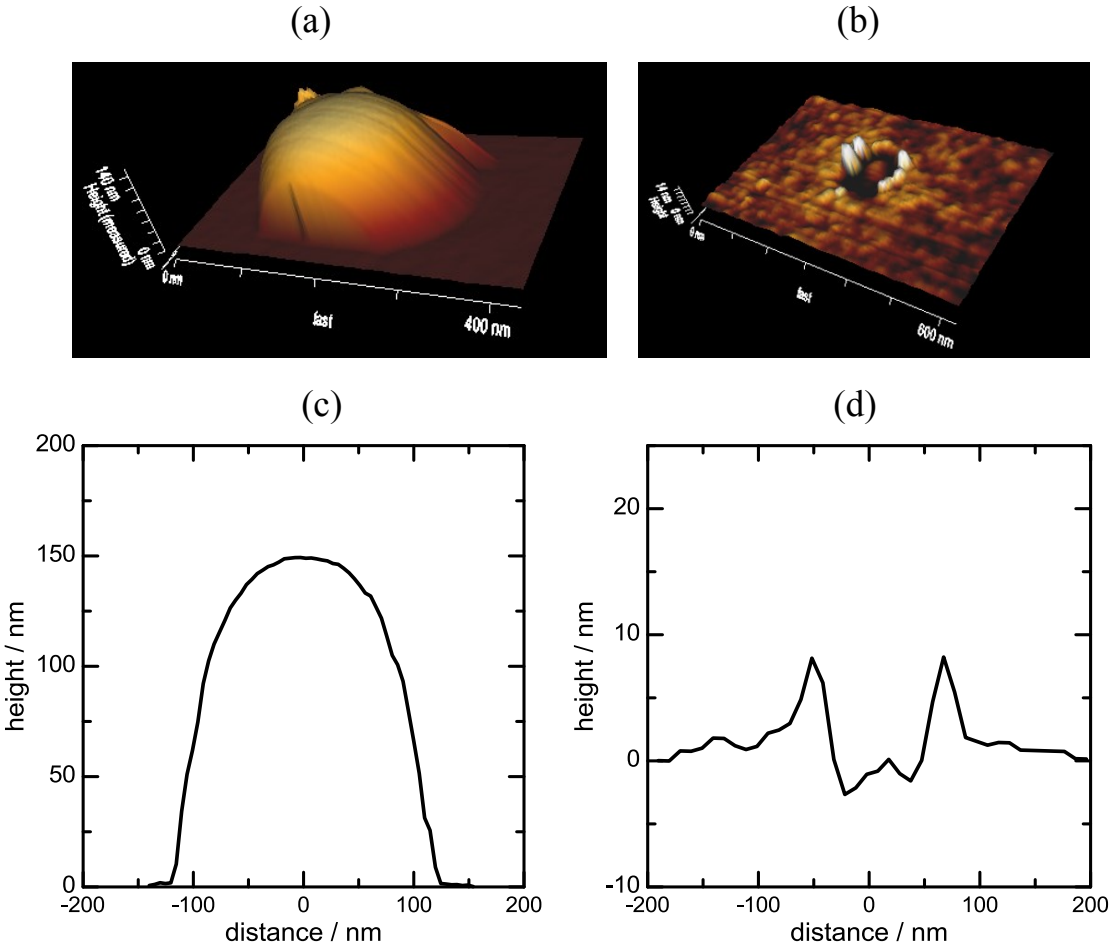

Fig. S6. (a) AFM height image of a 150-nm Au NP exposed to the illumination of 532nm CW laser with a peak power density of 11.6 mW μm^{-2} for 10s. The particle temperature was estimated as 1100 K. (b) AFM height image of a glass surface when the particle was removed by a cantilever. (c) The height profile of a Au NP given in (a). (d) The height profile of a glass surface shown in (b). AFM measurement: Nano wizard II (JPK instruments); cantilever: Olympus OMCL-AC240 (radius of curvature: 7 nm; spring constant: 2 N m^{-1}).

As shown in Fig. S6-b, a crater with a limb was found to form on a glass surface when the Au NP illuminated by a laser was removed. The crater formation was ascribed to a melting of the glass surface heated by the heat transfer from the particle.

S7. Scattering spectral changes of single Au NPs in water on a glass substrate.

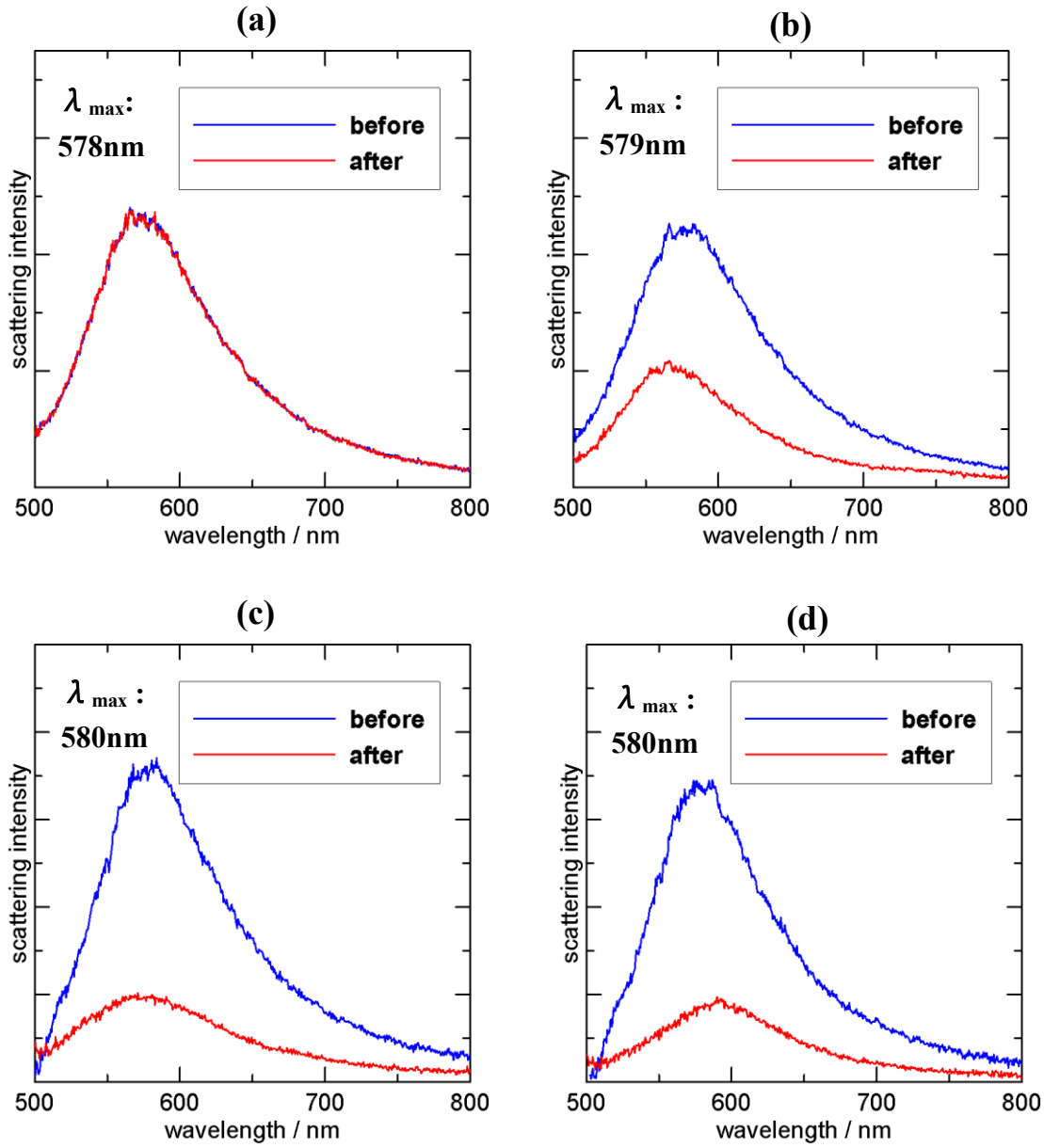

Fig. S7. Scattering spectral changes of single Au NPs on 10-ms illumination of 488-nm CW laser with various laser peak power densities: (a) 10 mW μm^{-2}, (b) 20 mW μm^{-2}, (c) 30 mW μm^{-2}, and (d) 40 mW μm^{-2}, focused with an objective (60×, NA: 0.70) in water on a glass substrate. Note that 1.0 mW μm^{-2} = 10^5 W cm^{-2} = 10^9 W m^{-2}.

S8. 2D temperature distributions.

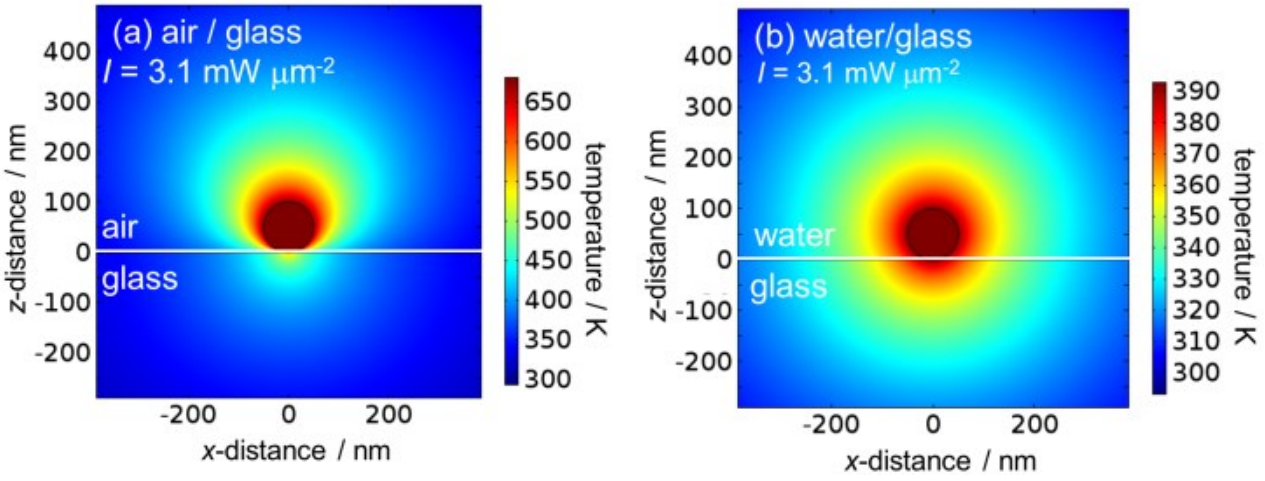

Fig. S8. Calculated 2-D temperature distributions for a 100-nm diameter Au NP supported on a glass substrate and exposed to air (a), and water (b) under the same excitation laser intensity of 3.1 mW μm^{-2} at the excitation wavelength of 488 nm. The dark circle in the center in each figure represents Au NP. The steady-state temperature is appreciably higher in (a) than in (b). The calculation was performed using COMSOL Multiphysics 4.3a.