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### **Electronic Supplementary Information**

# "Stationary Bubble Formation and Marangoni Convection Induced by CW Laser Heating of a Single Gold Nanoparticle"

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# S1. SEM micrographs of Au NPs



Figure S1. SEM images and corresponding size distribution of Au NPs (BBI, EMGC 150).

# S2. Experimental setup for optical dark-field and bright-field imaging.



Figure S2. Experimental setup.

# **S3.** Dark field images of stationary bubbles



**Figure S3**. (a-d) Optical scattering images of the bubble formation at the laser peak power densities of 0, 10, 34, and 58 mW  $\mu$ m<sup>-2</sup> (scale bar: 10  $\mu$ m). (e) The bubble diameter as a function of laser peak power density.

#### S4. Scattering and absorption spectra of a 150-nm-diameter Au NP

For the calculation of temperature increases of an Au NP ( $T_{NP}$ ), absorption cross section ( $C_{abs}$ ) and scattering cross section ( $C_{sca}$ ) are needed. Note that  $C_{abs}$  and  $C_{sca}$  vary depending on the temperature and a refractive index of surroundings. First, a scattering spectrum ( $C_{sca}$ ) of a 150-nm-diameter Au NP supported on a glass substrate and immersed in water was calculated from Mie theory as shown in Fig. S4a<sup>1</sup>. In principle, Mie theory describes optical absorption and scattering of a dielectric nanosphere immersed in a homogeneous medium having a constant refractive index n<sub>med</sub>. In our case, however, Au NPs are place on the glass cover slip (nglass: 1.52), immersed in water (nwater: 1.33), and exposed to the bubble (n<sub>bubble</sub>: 1.0). To take these disparities in refractive indices of surrounding matrices into account to Mie calculation, an effective refractive index n<sub>eff</sub> averaging/weighting the refractive indices of the medium and the substrate has been devised.<sup>2</sup> It has been reported that Calculated scattering spectra of Au NPs from Mie theory with n<sub>eff</sub> well reproduce actual scattering spectra of Au NPs placed on the glass cover slip and immersed in the medium.<sup>1</sup> For Au NPs placed on a glass ( $n_{glass} = 1.52$ ) and immersed in water ( $n_{water} = 1.33$ ), an effective refractive index of 1.42 (n<sub>eff</sub>) was used for Mie calculation. For the surrounding environment consists of the bubble/glass, n<sub>eff</sub> of 1.12 was used. In experiments, scattering spectra of individual Au NPs were measured and compared with the Mie calculation to choose proper NPs whose diameter are 150 nm (Fig. S4b). It is known that the increases in  $T_{NP}$  result in the damping and broadening of LSPR band owing to the changes in the dielectric function of gold and the refractive index of medium<sup>3</sup>. For the calculation of  $T_{NP}$  below the bubble formation threshold, the decrease in the refractive index of water induces the blue-shift and damping of LSPR band (Fig. S4a). In the same manner, C<sub>sca</sub> of a 150-nm-diameter Au NP in the bubble/glass was calculated as shown in Fig. S4c. Pronounced damping and the red-shift in LSPR band can be ascribed to the temperature-induced changes in dielectric function of gold. At the same time, Cabs of a 150-nm-diameter Au NP in water/glass and bubble/glass were obtained as shown in Fig. S4d.  $C_{abs}$  at 532 nm are summarized in Table S4.

medium/substrate ( $T_{NP}$ )	$C_{abs} / m^2 (532 \text{ nm})$			
water/glass (283 K)	$3.19 \times 10^{-14}$			
water/glass (583 K)	$3.06 \times 10^{-14}$			
bubble/glass (1337 K)	$2.96 \times 10^{-14}$			

Table S4. Cabs of a 150-nm-diameter Au NP



**Figure S4**. (a) Calculated and (b) experimentally measured scattering spectra of a 150-nm-diameter Au NP on glass surface surrounded by water. (c) Calculated scattering spectra of a 150-nm-diameter Au NP in the bubble on glass surface. (d) Calculated absorption spectra of a 150-nm-diameter Au NP on glass surface in water and in the bubble.

#### **S5.** Fragmentation in the stationary bubble

Here, we will briefly describe the dynamics on fragmentation of a single Au NP in the stationary bubble, parts of which were reported in our previous work<sup>4</sup>. Individual 100-nm-diameter Au NPs supported on the glass substrate and immersed in water were employed in the experiments. A tightly focused 488-nm CW laser was used as an excitation light source. The irradiation period of the CW laser was set to 125 µs, 10 ms, and 5 s with a programmable shutter. CW-laser-induced morphological changes of single Au NPs in the bubble were monitored by scattering microspectroscopy and SEM after each irradiation. Figure S5 shows the SEM images on the morphological changes of an Au NP at each irradiation period at a fixed laser power density of 40 mW  $\mu$ m<sup>-2</sup>. The intensive irradiation induced an increase in  $T_{NP}$  above the bubble formation threshold. Continuous irradiation of an Au NP in the bubble resulted in the huge  $T_{NP}$  jump because of the poor thermal conductivity of the bubble. Maximum temperature of the NP  $(T_{p max})$  was estimated to be 4200 K from the heat conduction equation at this laser power. At temperatures above the boiling point of gold (3129 K), thermally-induced morphological change of an Au NP could occur<sup>5,6</sup>. At the irradiation period of 125 µs (Fig. S5b), a film-like structure was observed around the original Au NP. This morphological changes are attributed to the melting from NP surface. At the irradiation period of 10 ms, small fragments with diameters ranging from 10 to 20 nm were observed around the original core particle (Fig. S5c). This fragmentation is ascribed to surface evaporation from the core particle. When the irradiation period increased to 5 s, the core particle completely disappeared, *i.e.*, the original Au NP was fragmented into multiple smaller NPs with diameters of 10 to 20 nm with the passage of time under CW laser illumination. Irradiation period of 30 s employed in the present work was much longer than the time scale on the thermally-induced morphological change of an Au NP in the bubble. In the previous report, an average diameter of the fragments  $D_{Au} = 12 \pm 6$  nm, the interparticle distance  $\Delta = 14$  nm, and the number of fragments  $N_{NP} = 20$  were obtained from SEM images.



**Figure S5**. A series of SEM images of the thermally-induced morphological change of an Au NP in the bubble at each irradiation period at a constant laser intensity of 40 mW  $\mu$ m<sup>-2</sup>(scale bar: 100 nm).

### S6. Calculated absorption spectra of fragments of Au NPs



**Figure S6**. (a) Calculated absorption spectra for Au NPs of diameters of 6, 12, 18 nm in a bubble on glass surface at 583 K. The detailed computational method is shown in S.4 in ESI.

#### S7. FEM modeling of heat conduction and fluid convection

Figure S7a shows the 2D geometry for FEM analysis. The geometry consists of a glass substrate, water, a bubble, and a point heat source. The height of water domain ( $H_{water}$ ) was set to 300 µm, which is the same as the thickness of silicone rubber spacer used in the experiment. Other heights and widths were determined considering Rayleigh number. The point heat source was put at the position where the single NP existed. A contact angle of the bubble on the glass substrate was estimated to be 140° on the basis of experimental results. In this FEM analysis, computational variables were only two: input energy for the heat source and the bubble diameter. Physical constants of the domains are summarized in Table S7. For the calculation of temperature field, the boundary condition of a room temperature (293 K) was set at the all outer boundaries. To calculate Marangoni convection, a shear force represented in Eq. S7-1 was applied at the bubble surface. A temperature derivative of the surface tension of water is -1.6 × 10<sup>-4</sup> [ N m<sup>-1</sup> K<sup>-1</sup> ] as shown in Fig. S7b<sup>7</sup>. For other boundaries in water domain, u = v = 0 (No slip) was applied.



Figure S7. (a) FEM geometry and (b) temperature derivative of surface tension of water.

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	Thermal conductivity	Density	Dynamic viscosity	Heat capacity
	[W m <sup>-1</sup> K <sup>-1</sup> ]	[kg m <sup>-3</sup> ]	[ Pa s ]	[ J kg <sup>-1</sup> K <sup>-1</sup> ]
water	0.6	998	$0.84 \times 10^{-4}$	4180
bubble (air)	0.024	1.2	$0.18 \times 10^{-4}$	1020

**Table S7**. Physical constants for FEM analysis (at room temperature)

glass	1.0	2650	N/A	860

S8. Calculated convective velocity of Marangoni convection as a function of  $\Delta T_{BT}$  for a 8.6-µmdiameter bubble.



**Figure S8**.  $\Delta T_{BT}$  *vs* convective velocities at *y*-distances of (a) 100 nm, and (b) 250 nm for three different *x*-distances.

### S9. Convective velocity of Marangoni convection as a function of the bubble diameter



Figure S9. Calculation results on the convective velocity as a function of the bubble diameter at y-distances of (a) 100 nm, and (b) 250 nm for three different x-distances. Experimental data is also plotted together.

#### REFERENCES

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