

Supplementary Information

Evolution of light-induced vapor generation at a liquid-immersed metallic nanoparticle

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Figure S1. The Surface plasmon resonance spectrum of a 100 nm nanoparticle in liquid water at 20 and 100 degrees Celsius

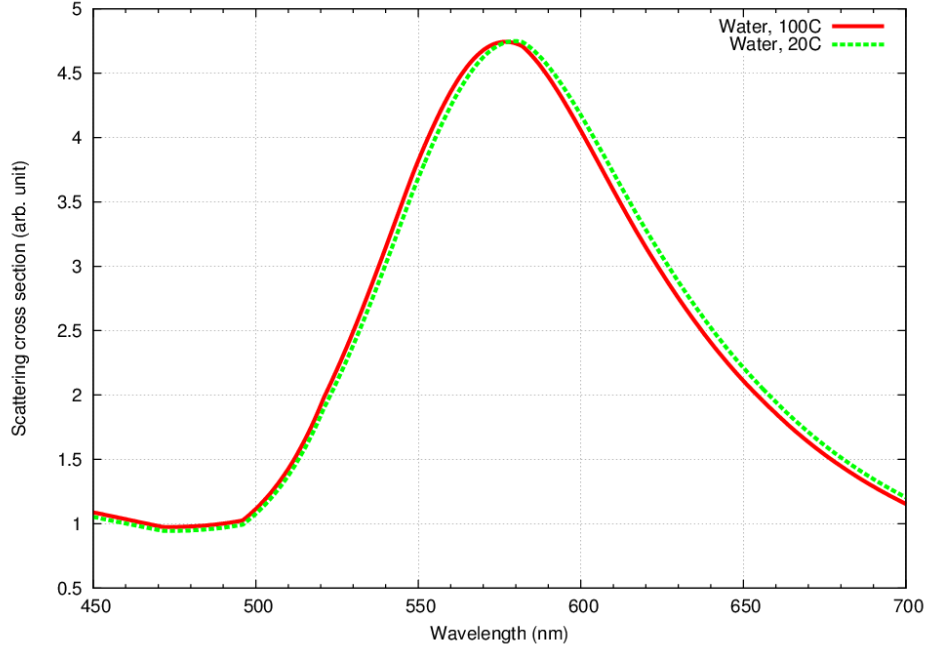


FIGURE S1. Simulated Mie scattering cross-section for an Au NP (100 nm diameter) immersed in 20 and 100 °C water. The resonance peak of the NP in 100 °C water has a ~3 nm blue-shift compared with the one in 20 °C water.

The permittivity of water at 20 °C and 100 °C is 1.7778 and 1.7387^{S1}, respectively, thus

$$\frac{\Delta\lambda^{(373K)}}{\Delta\lambda^{(293K)}} = \frac{\epsilon_{water}^{(373K)} - 1}{\epsilon_{water}^{(293K)} - 1} \text{ can be calculated as 0.95, which means there is only a 5\% difference (2.5 nm)}$$

between the scattering redshift with respect to air ambient (peak at 530 nm) and peak wavelengths in water for 20 and 100 °C.

Figure S2. Calculated Mie absorption efficiency for different size Au nanoparticles.

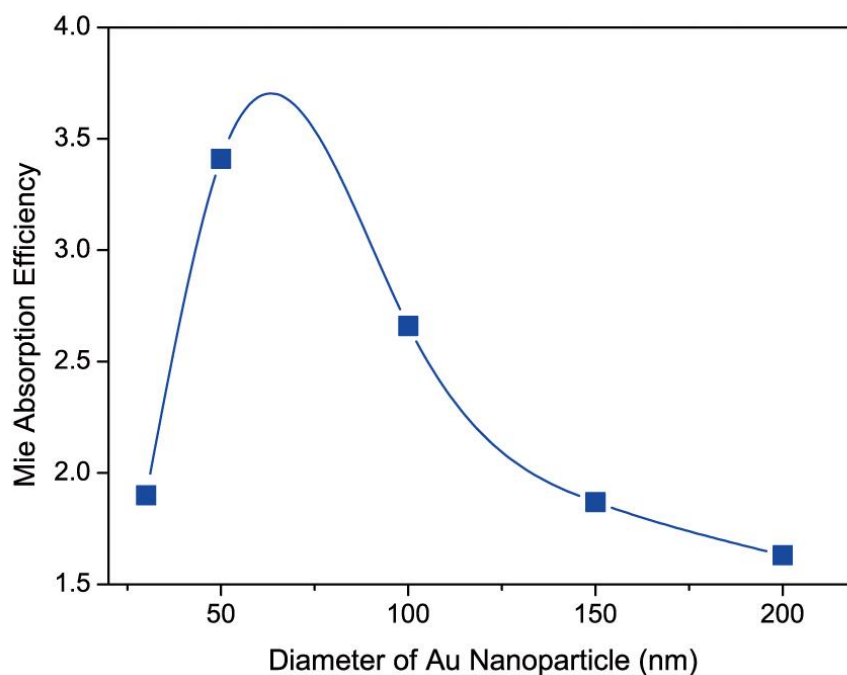


FIGURE S2. Calculated Mie absorption efficiency (absorption cross-section divided by the cross-section area πR_{NP}^2) for Au nanoparticles in water with diameters varying from 30 nm to 200 nm, at the laser excitation wavelength of 532 nm. The squares indicate calculated absorption efficiencies for the nanoparticle diameters at which the measurements were performed (see Fig. 1d). The main reason for decreasing absorption efficiency for Au NP with diameter larger than ~ 70 nm is that the resonance peak of the NP redshifts with increasing radius, such that the excitation wavelength of 532 nm is no longer on resonance. In addition, with larger size, the scattering becomes more pronounced relative to absorption.

Figure S3. Raman spectra for Figure 2a and 2c in the main text.

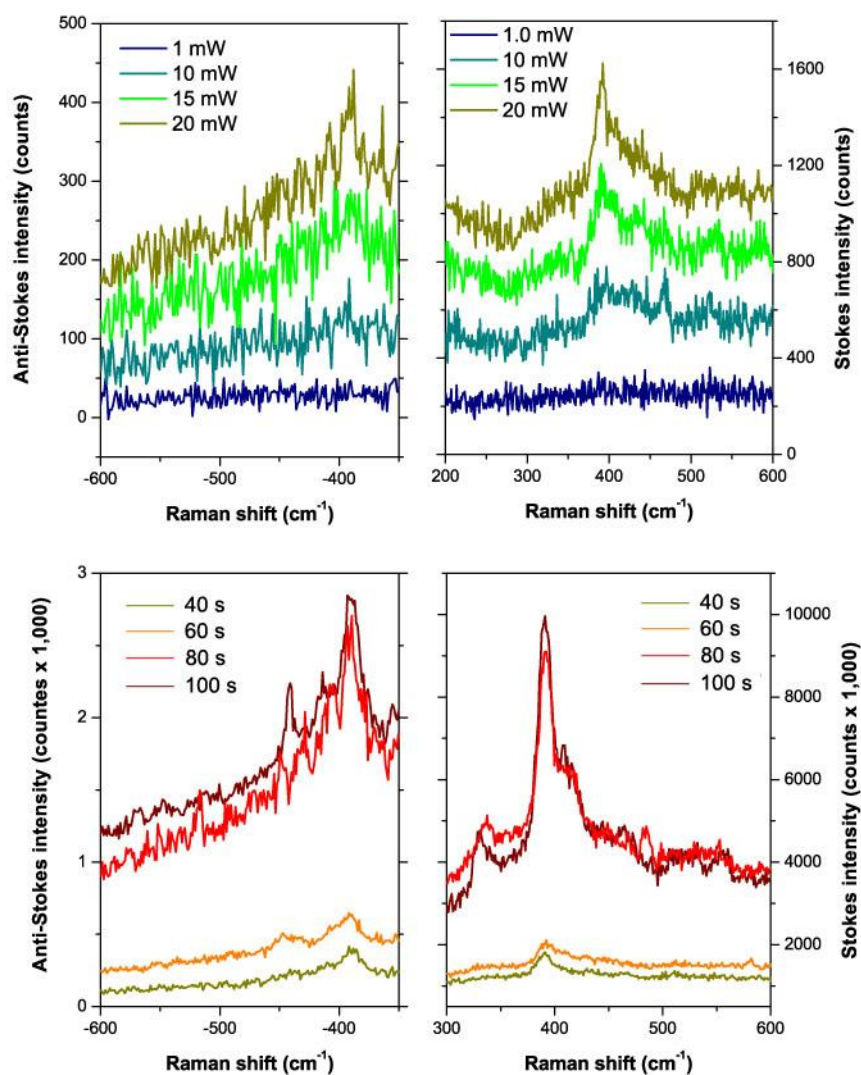


FIGURE S3. Top: Raman response of a pMA-coated single Au NP (in CCD counts) as a function of Raman shift (x -axis) under different incident laser powers. **Bottom:** Raman spectra at 25 mW incident power for different excitation times. Each characteristic Stokes spectrum exhibits strong optical pumping of the Au-S vibrational mode at 390 cm^{-1} .

Figure S4. Determination of nanobubble thickness.

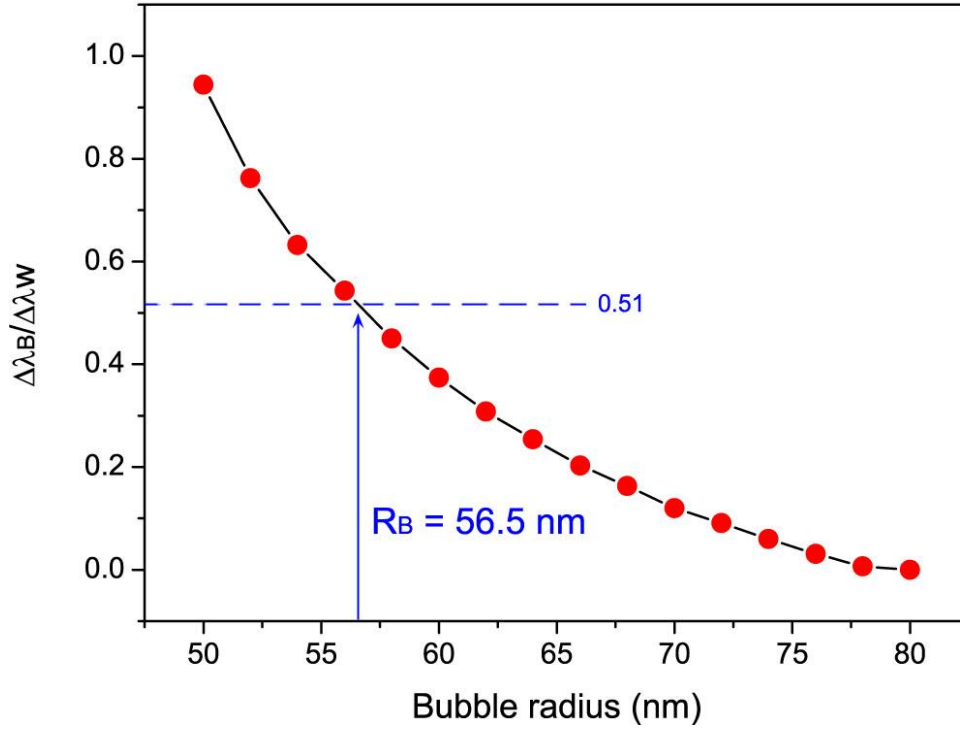


FIGURE S4. Ratio of wavelength redshift for a gold nanosphere with a diameter of 100 nm embedded in a vapour bubble to that in water, $\Delta\lambda_B/\Delta\lambda_w$, calculated using Mie scattering theory. The thickness of the nanobubble layer surrounding the Au nanoparticle responsible for the observed blueshift is deduced to be 6.5 nm ($R_B=56.5$ nm, as indicated by the arrow) by direct comparison of the calculated $\Delta\lambda_B/\Delta\lambda_w$ with the experimental value of 0.51 (indicated by the dashed line). We use $\epsilon_{\text{water}}^{(373K)}=1.74^{S1}$ in the calculation for the Au nanosphere in a vapour bubble to account for the surrounding hot (373K) water when a steam bubble is present; $\epsilon_{\text{water}}^{(293K)}=1.78^{S1}$ was used for the Au nanosphere embedded in cold water; $\epsilon_{\text{air}}=1.00$ was used for the Au nanosphere embedded in air. The empirical (Johnson and Christy) dielectric function^{S2} for Au was used in all Mie calculations.

TEXT S1. Calculation of temperature inside a nanobubble

a) Steam temperature

To determine the temperature inside the nanobubble, we assume that the steam generated inside the bubble is saturated. The pressure of the saturated steam is determined by the vapor pressure of water

as a function of temperature. We assume that, once formed, the nanobubble is in steady-state and the steam pressure is balanced by the Laplace pressure due to surface tension at the water-steam interface. The Clausius-Clapeyron Relation (CCR) is used to represent the relation between the vapor pressure of water and the temperature. We therefore have

$$C \exp\left(-\frac{h}{k_B T_s}\right) = p_0 + 2\gamma(T_s)/R_B, \quad (\text{S8})$$

where the left side is the CCR and the right side is the Laplace pressure, T_s is the absolute temperature (in Kelvin) of saturated steam inside the bubble, p_0 is the atmosphere pressure (set to 1 atm), k_B is Boltzmann constant, h is the enthalpy of water evaporation per water molecule, and γ is the surface tension coefficient, which is a function of temperature ($\gamma(T) = -0.2222T + 142.2$ mN/m^{S3}). The parameters in the CCR for water are $C=95$ GPa and $h=7082 \times 10^{-20}$ J. With $R_B=56.5$ nm, T_s is solved from Eq. (S8) to be 464K with a corresponding steam pressure of 1.49MPa. The refractive index of steam at the state of a temperature of 464K and a pressure of 1.49MPa is calculated to be $n=1.002$ for the wavelength of laser excitation 532 nm, using Eq. A1 in Ref. S1 as well as the reference therein. This result is consistent with our previous assumption that the refractive index of steam is set to 1, which was used in our determination of the vapour shell thickness.

b) NP surface temperature

When the system is in steady state, the law of energy conservation must be observed, which means the absorbed power must be equal to the dissipated power. By applying Fourier's law for the heat transfer at the Au-steam interface, we have

$$P_{abs} = G_{g,s} S_{NP} (T_{NP} - T_s), \quad (\text{S9})$$

where P_{abs} is the optical input power absorbed by the Au NP, $G_{g,s}$ is the effective thermal boundary conductance at the Au-steam interface, $S_{NP} \equiv 4\pi R_{NP}^2$ is the surface area of the nanoparticle, and T_{NP} is the surface temperature of the nanoparticle. Similarly, at the steam-water interface, we have

$$P_{abs} = G_{s,w} S_B (T_s - T_w), \quad (\text{S10})$$

where $G_{s,w}$ is the effective thermal boundary conductance at the steam-water interface, $S_B \equiv 4\pi R_B^2$ is the outer surface area of the nanobubble, and T_w is the temperature of the surrounding hot water, assumed to be 373K.

Noting that $P_{abs} = \sigma P_{inc}/A$, where σ is the effective absorption cross-section of the Au nanoparticle after nanobubble formation, P_{inc} is the incident power of the laser, and $A \equiv \pi D^2/4$ is

the laser spot area with a diameter $D = 1 \mu\text{m}$, we obtain $P_{abs} = 0.62 \text{ mW}$ for a single Au NP with 100 nm diameter, given that $P'_{inc} = 24 \text{ mW}$ (a 25mW input power multiplied by 96% transmission of the glass cover slide), and $\sigma = 0.0202 \mu\text{m}^2$ as calculated using Mie scattering theory.

Measuring the thermal boundary conductance/resistance is a topic of fundamental importance^{S4}. By inserting $P_{abs} = 0.62 \text{ mW}$, $R_B = 56.5 \text{ nm}$, $T_s = 464 \text{ K}$, and $T_w = 373 \text{ K}$ into Eq. (S10), we obtain $G_{s,w}$, the effective thermal boundary conductance, to be $170 \text{ MW}/(\text{m}^2\text{K})$. Interestingly, this conductance is found to be quite comparable to the reported nanoscale thermal conductance of the Au-water interface^{S5} ($G_{g,w} = 105 \text{ MW}/(\text{m}^2\text{K})$) and the platinum-water interface^{S6} ($130 \text{ MW}/(\text{m}^2\text{K})$). Since our effective thermal conductance at the steam-water interface is on the same order as that at the metal-water interface, we speculate that such a high thermal conductance may be induced by the condensation-evaporation balance at the interface between the saturated steam and the surrounding water. While an unsaturated steam layer is a thermal insulator, this saturated steam layer may be perceived as a good thermal conductor. Although acoustic mismatch and phonon scattering are often used to account for interfacial thermal behavior, a microscopic nanoscale heat transfer theory involving interfacial phase-transition dynamics would be required to explain such a high value of $G_{s,w}$, comparable to its metal-water counterpart.

The effective interfacial thermal conductance at the Au-steam interface can be estimated by the following two methods. First, since solids usually have well-defined densities of states of phonons relative to liquids, we can suspect that phonon coupling at the Au-steam interface is better than at the steam-water interface; therefore a moderate enhancement $G_{g,s} = 2G_{s,w} = 340 \text{ MW}/(\text{m}^2\text{K})$ can be expected. On the other hand, based on the hypothesis that the interfacial heat transfer in this system is a series of processes analogous to serial resistances in an electrical circuit, we can write $1/G_{x,y} = 1/G_x + 1/G_y$, where G_x and G_y can be any combination of G_s , G_w , G_g , accounting for the bulk (nanoscale) contributions to the interfacial conductance from steam, water, and Au. If we consider that saturated steam possesses ideal thermal conducting and interfacial coupling properties, G_s can be assumed to be much larger than the other two conductances. Therefore $G_w = G_{s,w} = 170 \text{ MW}/(\text{m}^2\text{K})$ results, leading to $G_g = G_{g,s} = 275 \text{ MW}/(\text{m}^2\text{K})$. Both conductances estimated by the above two methods are similar, however, we choose the lesser value $G_{g,s} = 275 \text{ MW}/(\text{m}^2\text{K})$. As a result, for $R_{NP} = 50 \text{ nm}$, $P_{abs} = 0.62 \text{ mW}$, and $T_s = 464 \text{ K}$, and we obtain $T_{NP} = 536 \text{ K}$ from Eq. (S9).

Nevertheless, because the temperature obtained in the SERS experiment is for an introduced pMA layer coated on the NP surface, even with T_s and T_{NP} determined, it is still challenging to

estimate the temperature theoretically, due to a lack of detailed knowledge of the thermal coupling properties of the Au/water-molecule and water-molecule/steam interfaces. We assume that the perturbation of the molecular layer to the entire temperature field is negligible, hence an average temperature for the molecular layer is calculated to be $(T_{NP} + T_s)/2 = 500$ K, not far from the experimental temperature (465 K) determined from our SERS measurements.

Table S1. Experimental data for Figure 4c in the main text.

NP distance (μm) Power (mW)	0.05	0.1	0.2	0.4	0.8	1.6
1000	(96,0)	(80,0)	(55,0)	(35,0.1)	(8,32)	(0, ∞)
900	(92,0)	(74,0)	(52,0)	(33,0.1)	(5,45)	(0, ∞)
800	(87,0)	(69,0)	(48,0)	(31,0.5)	(3,60)	(0, ∞)
700	(82,0)	(62,0)	(45,0.1)	(28.5,1.2)	(1, ∞)	(0, ∞)
600	(75,0)	(57,0)	(42,0.5)	(26,2.5)	(1, ∞)	(0, ∞)
500	(70,0.1)	(55,0.3)	(38,1)	(22.5,4.1)	(0, ∞)	(0, ∞)
400	(64,0.5)	(50,0.5)	(34,2)	(21,6.5)	(0, ∞)	(0, ∞)
300	(53,1)	(42,1)	(28,3.5)	(18.5,8.2)	(0, ∞)	(0, ∞)
200	(42,1.3)	(35,2.5)	(25,6.8)	(14.7,11.9)	(0, ∞)	(0, ∞)
100	(30,3.2)	(23,6.4)	(16,9)	(10.2,15.3)	(0, ∞)	(0, ∞)

Table 1. Experimental data of final bubble size and bubble start-up time depending on laser power and average NP surface-to-surface separation. The data format is (x, y) , such that the generated bubble is of diameter x μm , with start-up time y sec.

By interpolating the experimental data in Table 1, we present in Fig. 4c a color map of the final bubble diameter, as well as contour lines of the start-up time. Three regions can be clearly identified within the color map, as delimited by the assisting contour lines.

MOVIE S1. Microbubble coalescence

This movie shows the coalescence of microbubbles resulting in a larger microbubble. The laser has an incident power of 150 mW.

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