Optical Scattering Spectral Thermometry and Refractometry of a Single Gold Nanoparticle under CW Laser Excitation

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ABSTRACT: White light scattering spectra based on dark-field microscopy is a powerful tool for studying localized surface plasmon resonances of single noble metal nanoparticles and for developing their applications in sensing and biomedical therapies. Here we demonstrate the steady-state scattering spectral changes of a single gold nanoparticle under continuous laser heating. The experimental peak shifts allowed the estimation of the particle temperature in the range of 300–700 K with an accuracy of ±20 K on the basis of a spectral calculation exploiting Mie theory. For single gold nanoparticles supported on a glass substrate, progressive red shifts were observed in air, whereas blue shifts were observed in water and glycerol with increasing temperature. The medium has strong influence on peak shifts because of distance-dependent nanoscale medium heating: the shifts strongly depend on the magnitude of the temperature coefficients of a medium refractive index. The laser power-dependent behavior of peak shifts revealed the onset of surface melting occurring at 550–600 K regardless of the medium. Furthermore, experimental shifts also suggested that surface liquid layer grows in thickness with increasing temperature until the whole particle melts: this model has been proposed theoretically as a liquid nucleation and growth hypothesis. Therefore, we showed that the scattering spectral shifts represent an effective measure for the laser-induced morphological alterations of a gold nanoparticle and the nanoscale heating of a medium surrounding the NP.

INTRODUCTION

Plasmonic nanoparticles (NPs) and nanostructures have attracted much attention because of enhanced electromagnetic field in the near-field regime generated by excitation of their surface plasmon resonance (SPR) band.1−4 This enhanced local electromagnetic field can contribute to promote low-yield two-photon-induced photochemical reactions,5,6 nanogap-assisted photolithography,7,8 and plasmon-assisted catalytic activities9,10 as well as SERS (surface-enhanced Raman scattering).11−13 At the same time, heat generation due to strong absorption of plasmonic NPs under visible-light illumination and highly efficient light-to-heat conversion has attracted growing interest in nanoh heater applications.14,15 For instance, the biocompatible nature of Au NPs allows for plasmonic photothermal therapy,16,17 photoacoustic tomography,18,19 and photothermal imaging20−22 by introducing the NPs into living malignant cells. Illumination with the heating laser results in a highly localized temperature increase in NP itself and around the NP, and due to the small scale, it is difficult to measure. The difficulty arises in the measurement of such local temperature when a spatial resolution of several nanometers is required to observe selectively the local heating confined to ∼100 nm area of the NP. A few techniques have been reported to date to demonstrate nanoscale thermometry based on the temperature sensor approach.23−25 For instance, the Kawata group used 40 nm diameter Au NPs coated with thermosensitive polymer, poly(β−isopropylacrylamide) (PNIPAM) to monitor the localized heating effect through the SPR scattering spectral shift.25 The shift occurs as a result of the temperature-induced refractive index change in surrounding polymer medium caused by a phase transition from a swollen hydrated state to a shrunken dehydrated state. Single-particle scattering spectra at different laser powers revealed that the peak wavelength undergoes progressive red shifts as the laser power increases until saturation is reached at ca. 50 °C. However, particle-to-particle variations were observed for peak shift versus laser power curves because of variances in particle size, coating thickness, and particle−substrate distance, showing particle-dependent heating. Moreover, precise calibration of scattering peak shift to temperature increase at the single particle level was difficult because of thermal drift of sample holder on the microscope.

Carlson and coworkers took another approach using a photoluminescent thin film of Al0.94Ga0.06N incorporated with Er3+ to image the temperature profile around optically excited gold NP or lithographically prepared nanodot during laser excitation.26 The calibration of the sensor was necessary to give local temperature of a hot NPs by comparing the measured temperature change of a spherical 40 nm Au NP with the theoretical temperature change calculated from the absorption
cross section, effective medium refractive index, and effective medium thermal conductivity. This is because the true image size of the temperature profile for the NP is much smaller than the collection volume (∼500 nm diameter), and the temperature extracted from the luminescence measurement represents a weighted average temperature from the sample volume. Therefore, the method is not free from the limitation of diffraction limit optics and the particle scale resolution was not attained. Another disadvantage is that the temperature calculation requires precise estimation of the beam diameters of excitation lasers and ill-defined parameters such as the effective thermal conductivity for the system consisting of glass and water.

Bendix and coworkers performed measurements of the temperature surrounding single Au NPs optically trapped on a lipid bilayer incorporated with fluorescent sensor molecules.25 The heating by a tightly focused laser beam (λ = 1064 nm) was measured by visualizing the melted footprint around the irradiated particle originating from lipophillic fluorescent molecules: the molecules preferentially partition into low-temperature gel phase rather than melted fluid phase due to high temperature. The distance from the particle to the rim of the footprint was observed to be a linear function of laser power. By using the inverse relationship between temperature and distance to a heat source,26 they mapped out the entire temperature profile surrounding the NP, without making assumptions regarding the values of the absorption cross section and the thermal conductivity. Despite their highly advanced and sophisticated measurements, the method suffers seemingly complicated and time-consuming procedures with elaborate techniques for routine access. This underscores the importance of developing alternative simple methods.

Herein we demonstrate a straightforward way to estimate particle temperatures under steady-state laser illumination based on the measurement of purely optical property of a single Au NP, that is, the scattering spectral peak shifts caused by CW laser irradiation. The extinction (absorption and scattering) of a single Au NP is temperature-dependent primarily because of temperature-dependent damping: the spectral broadening occurs as the temperature increases.27,28 Simultaneously, temperature-induced changes in the medium refractive index can bring about the spectral shift. Although the temperature-induced SPR broadening of Au NPs has been previously measured in bulk solutions, the spectral shift has been paid little attention.29,30 This is partially because of limited availability of experimental temperature-dependent refractive index data of n(ω, T) and κ(ω, T) for complex refractive index defined by n = n + iκ.31,32 Therefore, the calculation of temperature-dependent spectra has been explored for only a limited temperature range.33,34 We implemented a method of acquiring temperature-dependent n and κ to calculate temperature-dependent absorption and scattering cross sections by applying Mie theory.34 We then carried out a single-particle scattering spectroscopy that allows us to observe spectral shifts more clearly than the ensemble measurement. We investigated the heating-induced transformations of Au NPs under laser illumination together with the heat-transfer-induced refractive index change in the surrounding medium. Our method is advantageous due to three points: (1) precise determination of laser beam diameter for the estimation of laser power on samples is unnecessary because the temperature information is contained in the experimental scattering spectra, (2) the particle temperature can be obtained without using a calibration coefficient such as a temperature transfer coefficient34 that contains unknown parameters, and (3) the particle temperature determined in that way is not affected by the spatial resolution of the optical setup.

We measured the scattering spectral peak shift of single Au NPs supported on a glass substrate as a function of excitation laser power density in three media: air, water, and glycerol. We observed red shifts in air and blue shifts in water and glycerol. These observations were consistent with the calculated temperature-dependent spectral shifts based on Mie theory. The measurement of temperature-dependent peak shifts has led to intriguing observations of surface melting, particle melting mechanism suggesting liquid nucleation and growth (LNG), and heating-induced refractive index gradient profile of the surrounding medium.

## MATERIALS AND METHODS

Aqueous solutions of Au NPs with nominal diameters of 100 nm (cat. no. EMGC100) and 150 nm (cat. no. EMGC150) were purchased from British Biocell International (BBI). The particles were transformed to spherical shape by irradiating weak-intensity nanosecond laser pulses with a wavelength of 532 nm (∼10 mJ cm−2). The particle images acquired by transmission electron microscope (TEM) and the corresponding size distributions were given in Supporting Information, Figure S1. The Au NPs were spin-coated onto a 24 mm × 32 mm × 0.17 mm coverslip (Schott D263T) that had been cleaned in a plasma reactor (Sakigake, YHS-R (70 W, 20 kHz)) for 120 s. The Au NPs were washed three times with doubly distilled water by placing 0.5 mL of water and spinning on the spin coater. The Au NP-coated glass slide (G/Au/air) was mounted on the scanning stage (Sigma, BIOS-150T) of an optical microscope. Besides this sample preparation, Au NPs on a glass were submerged in water (G/Au/water) or glycerol (G/Au/glycerol) in a 90 °C chamber consisting of two coverslips sandwiched with a 0.3 mm thick silicone rubber spacer.

The forward light scattering spectra of single Au NPs were measured using a dark-field light microscopy-spectroscopy35–37 setup given in Scheme 1. The spectra were obtained by subtracting the background scattering from the NP and then dividing it by the spectral profile of the white-light excitation source. Laser illumination was carried out through a microscope objective (60x, NA = 0.70) on an inverted dark-field microscope (Olympus IX 71 with a dark-field condenser U-DCD (NA = 0.8 to 0.92)) equipped with two output ports. Output from one port was relayed to a spectrograph consisting of an Acton SP300i polychromator (grating: 150 grooves/mm, blazed at 500 nm) and an Andor CCD camera (type: DU401-BR-DD operated at −60 °C) through a 150 μm diameter pinhole, whereas the output from the other port was used for imaging (Nikon, DS-5M). The excitation of a single Au NP was performed using a focused 488 nm CW laser (NEORK, TC20-4860-4.5) beam. The excitation wavelength was chosen to record a whole range of the SPR scattering spectra. The excitation was also carried out at 532 nm, near the peak position of the SPR band: although only a portion of the spectrum was recorded, the spectral shifts depending on particle temperature were observed as given in Supporting Information. The laser power was measured using a photodiode power meter (OPHIR, Orion). The spatial laser profile was determined by the measurement of scattering signal intensity of 100 nm diameter Au NP while scanning the stage at 100 nm
Scheme 1. Experimental Setup

Temperature-Dependent Dielectric Function of Au.

Temperature-dependent absorption, scattering, and extinction (absorption and scattering) spectra of a Au NP can be calculated as a function of angular frequency \( \omega \) or wavelength \( \lambda = 2\pi/\omega \) by applying Mie theory,34,38 when temperature-dependent dielectric functions \( \varepsilon(\omega, T) \) of the particle, particle radius \( R \), and the permittivity of the surrounding medium \( \varepsilon_m \) are provided. The dielectric function of gold is defined as the sum of the interband term, \( \varepsilon^{IB}(\omega, T) \), which considers the response of 5d electrons to the 6sp conduction band, and the Drude term, \( \varepsilon^{D}(\omega, T) \), which considers free conduction electrons (Drude model), and thus

\[
\varepsilon(\omega, T) = \varepsilon^{IB}(\omega, T) + \varepsilon^{D}(\omega, T)
\]  

Each term in eq 2 is divided into a real part \( \varepsilon_1(\omega, T) \) and an imaginary part \( \varepsilon_2(\omega, T) = 2\nu \kappa \), where \( n \) represents the refractive index and \( \kappa \) represents the absorption coefficient of the metal. Therefore

\[
\varepsilon^{D}(\omega, T) = \varepsilon_1^{D}(\omega, T) + i\varepsilon_2^{D}(\omega, T)
\]

\[
\varepsilon^{IB}(\omega, T) = \varepsilon_1^{IB}(\omega, T) + i\varepsilon_2^{IB}(\omega, T)
\]  

The following eqs 4 and 5 derived previously39,40 were used to obtain \( \varepsilon^{D}(\omega, T) \)

\[
\varepsilon^{D}(\omega, T, R) = 1 - \frac{\omega_p^2}{\omega(\omega - i\Gamma(T, R))}
\]

\[
\Gamma(T, R) = \Gamma_{c-e, ph}(T) + A \nu_e^\frac{\kappa}{R}
\]  

where \( \omega_p \) is the plasma frequency and \( \Gamma \) is the damping frequency, \( \Gamma_{c-e, ph}(T) \) is the damping frequency due to electron–phonon and electron–electron scattering of conduction electrons, \( \nu_e \) is Fermi velocity, and \( A \) is a proportionality constant (\( A = 1 \) for isotropic electron scattering), and \( \varepsilon^{IB}(\omega, T) \)

\[
\varepsilon^{IB}(\omega, T) = K \int_{-\infty}^{\infty} \left[ \frac{\sqrt{y - \omega_p^2}}{y} \left( 1 - f(y, T) \right) \right] \frac{y^2 - \omega^2 + \Gamma_{c-e}^2 - i2\omega\Gamma_{c-e}}{(y^2 - \omega^2 + \Gamma_{c-e}^2)^2 + 4\omega^2\Gamma_{c-e}^2} \, dy
\]

\[
f(y, T) = \frac{1}{1 + \exp \left( \frac{E_g - E_F}{kT} \right)}
\]

\[
o_{ph} = \frac{E_g}{h}
\]

\[
y = \frac{E_g}{kT}
\]  

Here \( E_g \) is the interband gap energy of 1.8 eV at the tail, \( E_F \) is the electron energy of state, \( \Gamma_{c-e}(T) \) is the damping frequency due to electron–electron scattering of interband electrons, and \( K \) is a constant. The function \( f(y, T) \) represents the distribution of quasiparticle (plasmon) states. The experimental temperature-dependent dielectric functions of bulk gold have been obtained by Otter at wavelengths form 440 to 640 nm at several temperatures for solid and also for liquid gold.33 By fitting eqs 4 and 5 to the Otter’s data points at four temperatures 283, 583, 843, and 1193 K, we obtained \( \Gamma_{c-e, ph}(T) \) and \( \Gamma_{c-e}(T) \) as a function of \( T \). The best fit to reproduce Otter’s data was obtained by using parameters: \( \Gamma_{c-e, ph}(T) = 6.10 \times 10^{11} + 2.97 \times 10^{11} T \), \( \Gamma_{c-e}(T) = 2.75 \times 10^{14} + 5.35 \times 10^{10} T \), \( K = 2.65 \times 10^{24} \) \( s^{-3/2} \), and \( E_g = 2.55 \) eV. Therefore, we were ready to calculate \( \varepsilon(\omega, T) \) at any temperature. A satisfactory agreement of experimental and computational \( \varepsilon(\omega, T) \) ensures the reliability of calculated optical spectra at given temperatures (Supporting Information, Figure S2).

Multi-Core–Shell Model. In general, the refractive index of the medium surrounding Au NP is temperature-dependent as for the complex refractive index \( \varepsilon(\omega, T) \) of the Au NP. Therefore, the nonlinear optical properties of Au NP are highly sensitive to the refractive index change in the surrounding medium as a result of temperature increase in the close vicinity of a Au NP. Exposure of a Au nanoparticle to a focused laser beam generates a temperature distribution in the surrounding medium due to heat-dissipation-induced medium heating (Scheme 2a).14,15 Note that for CW laser excitation, a steady-state spatial temperature distribution is established within a few hundreds of nanoseconds (Supporting Information, Figure S3). This temperature distribution can be transformed into a refractive index function dependent both on Au NP temperature and on a distance from the NP surface. This temperature-
dependent medium refractive index profile is treated as a NP-core multi-medium-shell system with each shell exhibiting different refractive index of increasing order from inside to outside (Scheme 2b). To calculate the optical properties of the multi core−shell system represented by Scheme 2c, we developed a computational program for multilayered spheres as an extension of the formulations of a coated sphere given by Bohren and Huffman. The idea is to digitize the refractive index distribution around the Au NP surrounded by many layers, each possessing a constant refractive index of a few nanometers. Finally, the extinction (C_{ext}), scattering (C_{sca}), and absorption (C_{abs}) cross sections were obtained as a function of wavelength. Quantitative calculations of the temperature-dependent nonlinear optical properties of Au NPs was performed by combination of the temperature-dependent dielectric functions of a Au sphere with the dielectric constants of surrounding medium consisting of multilayered spherical shells.

## RESULTS AND DISCUSSION

**Au NP Supported on Glass Substrate in Air (G/Au/Air).**

Figure 1a shows the experimental scattering spectral changes of a single 150 nm Au NP supported on a glass substrate and exposed to atmospheric air at various intensities of excitation laser light. The spectra were collected for the particle before, during, and after irradiation of a 488 nm continuous wave (CW) laser. During the irradiation, an appreciable intensity reduction was accompanied by a slight red shift of the spectral envelope (Supporting Information, Figure S4). We employed laser intensities at which the scattering spectra after irradiation coincide with that before irradiation (Supporting Information, Figure S4). This implies that at these laser intensities the laser irradiation causes no shape transformations. Figure 1a demonstrates that systematic spectral red shifts take place with increasing laser intensities (details below). The spectral shifts are caused by the temperature increase in Au NP under laser illumination. The spectral changes are also observed for excitation at 532 nm, as shown in Supporting Information, Figure S5a.

Figure 1b shows the temperature-dependent scattering cross section spectra for a 150 nm Au NP calculated as a function of wavelength. For the calculation, the effective refractive index of the medium was set to 1.12 that was determined by the method described in the literature. In G/Au/air, the medium refractive index was assumed to be constant regardless of temperature because the temperature coefficient for the refractive index of a glass substrate assumes a value with an order of $10^{-6}$ K$^{-1}$, two magnitudes smaller than that of liquids. The calculated spectral peak shift is a linear function of the temperature, as given in the Supporting Information, Figure S6. This relationship allows the direct evaluation of particle temperature from the experimental $\Delta \lambda$, as will be given below.

Figure 2 shows the plots of $\Delta \lambda$ as a function of laser peak power density for excitation at 488 nm (for excitation at 532 nm, see Supporting Information, Figure S5b). The black line gives a linear fit to the initial part of the experimental data points. At first, $\Delta \lambda$ increases linearly with the laser intensity. This is because the particle heating is a function of laser power mainly due to light-to-heat conversion with minor contribution of heat dissipation to the surrounding medium. This linear relationship provided the particle temperature that was given as an upper scale in Figure 2. At a particle temperature of $\sim$550 K

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“Steady-state temperature distribution given in panel a was calculated at 5 $\mu$s after the initiation of laser illumination (T_{NP}: constant temperature of NP, T_{m}: medium temperature distribution). The temperature-dependent refractive index functions of water and glycerol are given in Supporting Information, Figure S9. Here the minimum layer thickness is 10 nm and the refractive indices were determined with an interval of 0.001.
(277 °C), however, upward deviation sets in. This behavior can be explained by considering a phase transformation because an entirely solid particle with a constant heat capacity $c_p$ should give $\Delta \lambda$ linearly dependent on the temperature. Here we assume the initiation of surface melting because Mie calculation predicts greater red shifts for solid-core liquid-shell Au spheres when the medium refractive index is independent of temperature. We will discuss the melting mechanism on the basis of literature.

The melting mechanisms that have been proposed so far can be summarized as follows:46

1. Homogeneous melting (HM) hypothesis in which there is no surface melting and melting takes place at bulk melting point
2. Liquid skin melting (LSM) model that considers the formation of liquid layer over a solid core at low temperature but remains unchanged until the whole particle melts at the melting temperature
3. Liquid nucleation and growth (LNG) model in which a liquid layer nucleates and grows with temperature

It has been revealed that NPs exhibit a melting temperature (mp) that depends on particle size because of the effect of the surface-to-volume ratio. A remarkable decrease in the melting temperature was observed for particle diameters less than 5 nm.46−48 For particles lesser than 5 nm, the HM temperature is inversely proportional to the radius of the particle, whereas for larger particles, melting occurs near the mp of bulk gold. Experimentally, the melting temperature of a 38 nm Au NP has been found to be $\sim 1067$ K ($\sim 830$ °C), which is 200 K lesser than that of bulk gold with a mp of 1337 K (1064 °C).39 Distinct from the entire particle melting at above the melting temperature, shape changes were demonstrated to occur at temperatures much lower than the mp of bulk gold. Surface melting or premelting was used to explain the shape transformations of Au NPs49 and Au nanorods50 at temperatures lower than the particle melting temperature. In particular, the temperature stability of Au nanorods against both thermal and ultrafast laser heating was examined by Petrova and coworkers.51 Their thermal heating experiments showed that at temperatures greater than 523 K (250 °C) Au nanorods are transformed into spheres within 1 h. This is significantly below the mp of bulk gold, and they ascribed the structural changes to surface melting. Direct observation of surface melting was performed by femtosecond pump−probe studies. For instance, Ruan and coworkers reported the structural changes associated with melting of 2−20 nm diameter Au NPs using ultrafast electron crystallography.52 By monitoring the peaks in the electron diffraction pattern after optical excitation, they observed reversible surface melting and full melting of the NPs within first 100 ps after excitation. Besides this, Plech and coworkers used ultrafast X-ray

![Figure 1](image1.png)

(a) Experimental light scattering spectra of a 150 nm diameter Au NP on a glass substrate in air under the illumination of various intensities of 488 nm CW laser light. The peak laser power densities were represented by mW μm$^{-2}$. Note the relationship 1 mW μm$^{-2} = 10^9$ W cm$^{-2} = 10^5$ W m$^{-2}$. Three 490 nm cutoff long-pass sharp edge filters were used for the measurement. Particles with peak wavelengths at 572 ± 1 nm were selected for the measurement. Temperature estimation errors: ±20 K (<1.5 mW μm$^{-2}$) and ±60 K (>1.5 mW μm$^{-2}$). (b) Calculated scattering spectral changes at various temperatures for a 150 nm diameter Au in the medium with an effective medium refractive index of 1.12.

![Figure 2](image2.png)

Figure 2. Scattering spectral shift $\Delta \lambda$ as a function of laser peak power density (lower scale) or particle temperature (upper scale). The black line represents a linear fit to the initial part of the data points. The red line represents the relationship corresponding to an LSM (liquid skin melting) model with a core diameter of 144 nm and shell thickness of 3 nm. The blue curve represents a fitting based on a solid-core−liquid-shell model with various shell thickness from 1 to 70 nm. The green horizontal line represents $\Delta \lambda = 25.5$ nm for 150 nm diameter liquid Au.
diffraction to monitor the lattice expansion and cooling of 61.5 (±8%) nm Au NPs. They observed a loss of long-range lattice order at elevated temperatures, which was attributed to premelting of the particles. They concluded that the observation is consistent with the development of a core−shell structure, with the surface melting layer acting as a liquid viscous shell.

A different view that denies the concept of premelting came from a molecular dynamics (MD) simulation by Wang and coworkers. They showed that facets on the surface of icosahedral Au NPs softened but remained ordered and did not premelt below the particle melting temperature. This may represent a view similar to HM. However, another MD simulation by Wang and coworkers revealed that liquid-like regions form on the Au NP surface prior to melting: they attributed this to orientation-dependent surface premelting. With temperature increase, these liquid-like surface regions not only increase in area but also deepen into the inner regions of the NP prior to the formation of contiguous liquid layer on the surface. Shim and coworkers also concluded by MD study that the premelting phenomenon of surface atoms is observable prior to the melting of whole Au particle. Judging from a number of experimental and computational studies, it seems likely that the concept of surface melting that occurs at a temperature much lower than the mp of bulk gold can be accepted in the field.

The onset of surface melting observed in the present study, 550 K, is more-or-less similar to the values of previous measurements. The value may depend on the measurement method, particle shape and size, and heating periods and methods (thermal heating or pulsed laser heating with various pulse durations). Importantly, our optical measurement reflects the direct response of Au NP. To assess the effect of surface melting on Δλ properly, we calculated the temperature-dependent scattering cross section spectra for a 150 nm Au NP with solid-core and liquid-shell by varying the shell thickness. The red line in Figure 2 shows a Δλ versus T curve for a solid Au NP (d = 144 nm) surrounded by a 3 nm thick liquid shell. Even for such a thin layer of a liquid shell, the core−shell structure gives a remarkably greater positive value of Δλ. However, the constant shell thickness cannot explain the experimental laser power-dependent curve that deviates positively from linear increase because a constant slope is always expected for a constant core size. This deduction strongly suggests that the thickness of the liquid shell should increase continuously with increasing particle temperature. The blue curve shows the temperature-dependent Δλ values that were calculated for the core−shell structure of increasing shell...
thickness from 1 to 70 nm with increasing temperature. The blue curve converges with a green horizontal line that represents the $\Delta \lambda$ value for a liquid Au NP at 1337 K. At a shell thickness of 40 nm, the blue curve nearly saturates at a maximum shift of 25.5 nm. Therefore, further liquid-shell growth cannot be distinguished from the liquid Au NP. The blue curve simulates satisfactorily the experimental $T$ versus $\Delta \lambda$ in the nonlinear region. This is significant because the present experimental result can clearly dictate the NP melting mechanism. The occurrence of surface melting has been pointed out experimentally and by MD simulations. However, a clear distinction between LSM and LNG has not been made previously because of experimental limitations. The present result of temperature-dependent $\Delta \lambda$ behavior strongly suggests the occurrence of LNG and can be the first clear evidence in support of the LNG mechanism for Au NP.

The accurate measurement of $\Delta \lambda$ was increasingly difficult at high laser powers, leading to temperatures above $\sim$700 K (427 °C). At these temperatures, the scattering spectra after laser irradiation no longer coincide with those before the laser irradiation. Such an example of a spectral change was given in the Supporting Information Figure S7 together with AFM images before and after irradiation. Additionally, the particle-to-particle difference in $\Delta \lambda$ arises that makes difficult the accurate determination of $\Delta \lambda$ values. Apparently, irreversible particle shape transformation must be taking place at these high laser power regions. The possibility that the particles were buried in glass substrate can be ruled out because the softening temperature of the glass substrate is expected to occur at $\sim$873 K ($\sim$600 °C).

**Au NP on Glass Substrate Submerged in Water (G/Au/Water) and Glycerol (G/Au/Glycerol).** The scattering spectral peak position (also the extinction spectral peak position) has been known to depend on medium refractive index. At ambient temperature for a given diameter of Au spheres, progressive red shifts of the spectral peak were observed with increasing medium refractive index along with appreciable intensity enhancement. In this study, effective medium refractive index was determined to be 1.12 in G/Au/air, 1.41 in G/Au/water, and 1.50 in G/Au/glycerol environments at ambient temperature. Therefore, the experimental scattering spectral peak positions are clearly distinguishable for the three media: the peak positions in G/Au/water are appreciably red-shifted compared with those in G/Au/air, and further red shifts occur in G/Au/glycerol.

In the preceding section, with the increase in temperature, we observed the scattering spectral red shifts that are consistent with our calculation in G/Au/air environment. On the contrary, the calculation predicts temperature-dependent blue shifts both in G/Au/water (Figure 3a) and in G/Au/glycerol (Figure 3b) systems (calculated spectra: Supporting Information, Figure S8a and S8c). This suggests that temperature-dependent refractive index changes in the surrounding medium overwhelm the NP’s own temperature-dependent optical response in the overall spectral peak position. The blue shifts originate from the decreasing refractive index of the solvents with increase in temperature.

Figure 3c shows the experimental spectral shift $\Delta \lambda$ as a function of peak power density of 488 nm laser light for a 100 nm Au NP in water (see Supporting Information, Figure S8b for experimental scattering spectra). The progressive blue shifts were indeed observed depending on the laser power applied. The experimental laser peak power density-dependent $\Delta \lambda$ is not linear but parabolic. It is noteworthy that the multi-core-shell model incorporating experimentally obtained temperature-dependent refractive index of superheated water (Supporting Information, Figure S9a) reproduced the experimental parabolic behavior of $\Delta \lambda$ versus particle temperature, Figure 3c. Because of greater efficiencies of heat transfer to the surrounding medium, greater laser intensities are required to attain Au NP temperatures equivalent to those in air. Inspection of Figure 3c reveals that at laser power densities $>4.3$ mW $\mu$m$^{-2}$ (or $T > 550$ K) a deviation to smaller $\Delta \lambda$ (or upward deviation) took place. This is most likely due to the onset of surface melting, as already observed in air because the formation of liquid shell causes the red shift of the scattering spectrum. (See Figure 2.) The onset value is similar to that observed in G/Au/air. It is reasonable to assume the onset of surface melting to be similar regardless of the surrounding medium. This point will be referred to again later.

In G/Au/glycerol, temperature-dependent blue shifts were observed for a $\Delta \lambda$ versus laser power density curve, Figure 3d (see Supporting Information, Figure S8d for scattering spectra). The calculated $\Delta \lambda$ versus particle temperature was linear (Figure 3b) because of the linear temperature dependence of the refractive index of glycerol (Supporting Information, Figure S9b). The onset of surface melting in glycerol determined by the upward deviation from the linear decrease in $\Delta \lambda$ is 600 K (327 °C). This value is not exactly the same as 550 K in G/Au/air and G/Au/water but similar considering the experimental errors given in Figures 2 and 3. Accordingly, the onset of surface melting is determined to be 550–600 K with an error of ±40 K. The onset value depends solely on the particle temperature, not affected by the presence of solvents.

Further temperature increase again causes greater negative shifts of $\Delta \lambda$ with increasing temperature in both water and glycerol. The observation is primarily explained by high-temperature coefficients of medium refractive index. Because of this, the effect of surface melting on $\Delta \lambda$ can be canceled out. Here higher degree of surface melting, that is, increase in liquid layer thickness resulting in net red shift, is necessary to observe clearly the effect of surface melting in the scattering spectra.

Mie calculation predicts that vapor bubble formation surrounding the Au NP, that is, formation of a shell with a refractive index of 1.0 (over a few nanometers thick), can cause a significant blue shift. At ambient pressure, superheated water molecules directly surrounding the Au NP undergo vaporization as a result of explosive evaporation when heated to near the spinodal temperature of $\sim$573 K ($\sim$300 °C). Bubble nucleation threshold temperature in water for 500 nm diameter gold was determined experimentally to be 600 K (327 ± 112 °C). Lapotko’s group studied the bubble formation by a single-particle light extinction spectroscopy on excitation of Au NP and NP clusters by a nanosecond laser pulse. Plech and coworkers employed a femtosecond laser excitation and X-ray probe method for the observation of bubble generation from Au NPs in solution. For CW laser excitation, Hünn and coworkers captured the images of micrometer-sized bubbles from Au NP clusters embedded in polyelectrolyte film submerged in water. In our CW laser experiment, at laser peak power densities $<7$ mW $\mu$m$^{-2}$ (excitation at 532 nm) in water, we could not observe scattering spectral signals ascribable to bubble formation. This might be due to the fact that our steady-state detection system is not sensitive enough to detect nanometer-sized transient or dynamic bubbles even if they exist. At laser peak power densities $>20$ mW $\mu$m$^{-2}$,
(excitation at 532 nm), however, we could actually captured the image of a micrometer-scale bubble and its scattering spectrum, as given in the Supporting Information, Figure S10. In this case, particle destruction took place presumably due to explosive evaporation of a Au NP heated above the boiling point.64

CONCLUSIONS

We measured the scattering spectral peak wavelength shifts of single Au NPs supported on a glass substrate as a function of excitation laser power ($\lambda = 488$ nm) in three environments: air, water, and glycerol. With increasing laser intensity, we observed systematic red shifts in air and blue shifts in water and glycerol. These observations were consistent with the calculated temperature-dependent spectral shifts based on Mie theory. The red shifts were observed in air as an intrinsic optical property of Au NP because of negligibly small temperature coefficients of the refractive indices of air and glass. Heating-induced development of medium refractive index gradient is the origin of observed blue shifts in water and glycerol because of large temperature coefficients of the refractive indices in both liquids. The experimental peak shifts enabled the estimation of the particle temperature in the range of 300–700 K with an accuracy of ±20 K. In situ measurements of scattering spectral shifts revealed that the onset of surface melting for a 100 nm diameter Au NP on a glass substrate in air on irradiation of 488 nm CW laser, the calculated spectral change of laser-heated 150 nm gold sphere embedded in glass, laser-temperature, calculated transient temperature curves for a CW laser-heated 150 nm gold sphere, irrespective of the surrounding medium. Furthermore, increasingly greater deviation of the spectral peak shifts from a linear function of a laser power provided the definitive evidence of the melting mechanism of Au NP: a LNG process. Accordingly, we showed that the scattering spectral shifts are useful as a quantitative measure for temperature-induced alterations of a Au NP under CW laser excitation and the nanoscale temperature profile of a medium surrounding the NP.

ASSOCIATED CONTENT

 Supporting Information

 TEM micrographs of Au NPs, calculated and experimental $n$ and $\kappa$ of bulk gold as a function of wavelength at various temperatures, calculated transient temperature curves for a CW laser-heated 150 nm gold sphere embedded in glass, laser-induced scattering spectral changes of a single 150 nm Au NP on irradiation of 488 nm CW laser, scattering spectral change of a 150 nm diameter Au NP on a glass substrate in air on illumination of 532 nm CW laser light, the calculated spectral peak shift as a function of the temperature of a 150 nm diameter Au NP supported on a glass substrate in air, AFM cross sectional profiles of a 100 nm diameter Au NP before and after laser irradiation and corresponding scattering spectral change, experimental and calculated scattering spectra of 100 nm Au NP in water and glycerol measured at 589 nm, and darkfield image and light scattering spectra demonstrating the formation of photothermal bubble. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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The effective medium refractive index at ambient temperature was estimated by the measurement of the scattering spectra of randomly selected 100 particles for (99 ± 4.5) nm diameter Au NPs (the size distribution was determined by TEM images): 1.12 for air/glass, 1.41 for water/glass, and 1.50 for glycerol/glass samples.