

Supporting Information

Quantifying the photothermal efficiency of gold nanoparticles using tryptophan as an *in situ* fluorescent thermometer

*Ming-Jui Chiu and Li-Kang Chu**

Department of Chemistry, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Rd., Hsinchu 30013,
Taiwan

AUTHOR INFORMATION * To whom correspondence should be addressed. Phone: 886-3-5715131
ext. 33396. Fax: 886-3-5711082. E-mail: lkchu@mx.nthu.edu.tw.

1. The relationship of the fluorescence intensity changes and the temperature

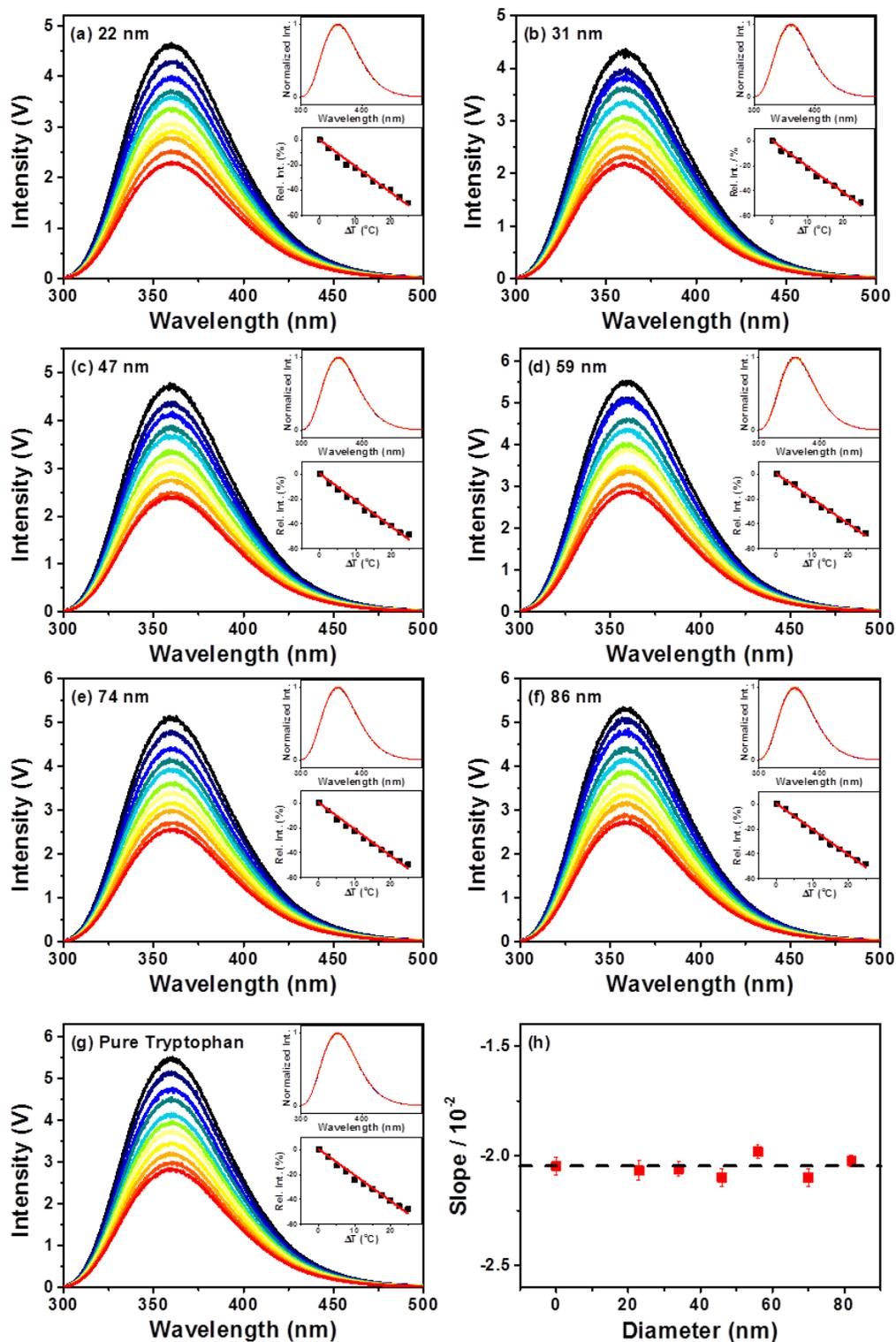


Figure S1. (a)–(g) The temperature-programmed steady-state fluorescence spectra of tryptophan with gold nanoparticles of different sizes at 20–45 °C. The concentration of tryptophan was 0.5 mM. The concentrations of nanoparticles were controlled such that the optical density was 0.2 for an optical

length of 0.2 cm at 532 nm. The normalized emission contours are shown in the upper insets. The relationships between the relative change of the integrated fluorescence intensity at 300–450 nm ($\Delta I^{FL}/I^{FL}_0$, $\Delta I^{FL}=I^{FL}-I^{FL}_0$) and the temperature changes with respect to room temperature ($\Delta T=T-T_{room}$) for the samples mentioned above are shown in the lower insets. Dots and solid lines represent the observed data and linear fittings, respectively. The excitation wavelength was set at 280 nm for all measurements. (h) The slopes of $\Delta I/I_0$ versus ΔT for pure tryptophan and those containing different sizes of nanoparticles.

2. The fluorescence of gold nanoparticles and mixtures of gold nanoparticles and tryptophan upon 280 nm excitation

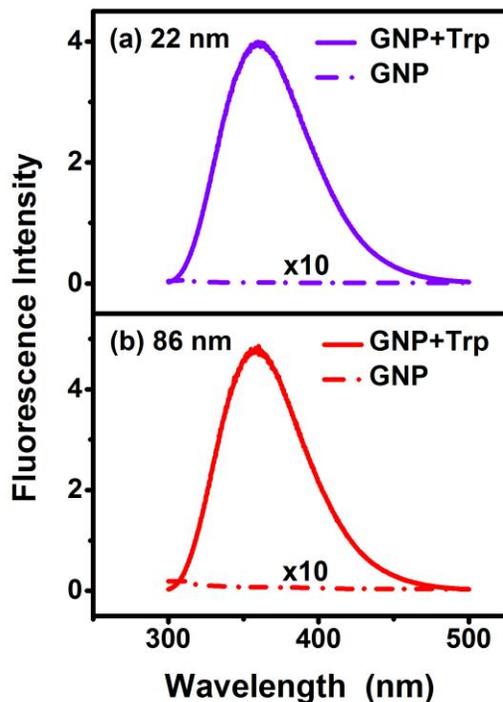


Figure S2. The fluorescence of gold nanoparticles and mixtures of gold nanoparticles and tryptophan upon 280 nm excitation

3. Evolutions of the temperature change of gold nanoparticles of different sizes upon excitation with different laser fluences at 532 nm

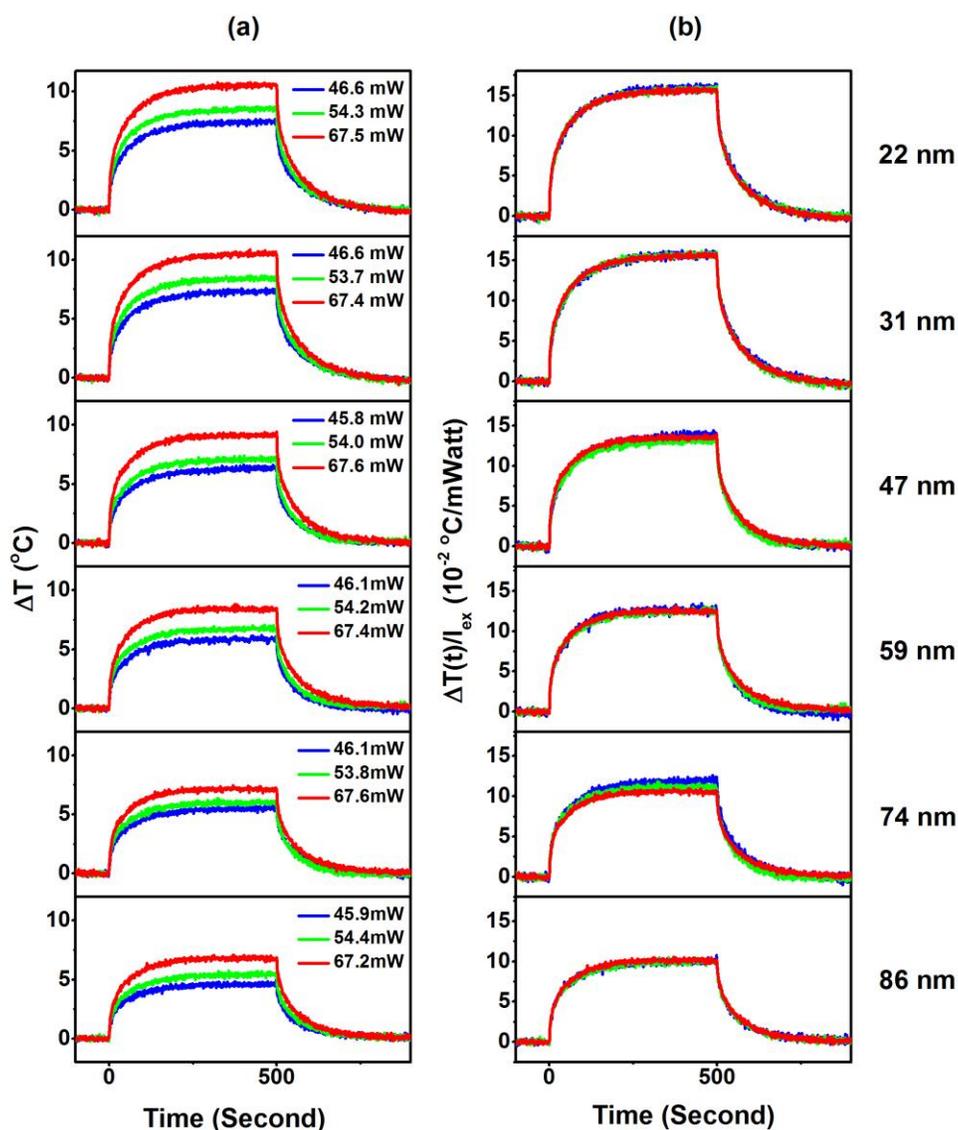


Figure S3. Evolutions of the temperature modulation of gold nanoparticles (0.2 O.D. for 0.2 cm absorption path length) of different sizes upon excitation with different excitation powers from 45.8 to 67.6 mWatt. The diameter of the circular cross section of the 532-nm laser is 0.83 mm. (a) The traces of $\Delta T(t)$ at different excitation powers. (b) The traces of $\frac{\Delta T(t)}{I_{\text{ex}}}$ at different excitation powers. The averaged traces for each nanoparticle are shown in **Figure 6(a)**.

4. Formulization of the heat transport

The alteration in fluorescence results from the temperature change in the heating volume. However, the spatial distribution of the temperature could have been inhomogeneous because no mechanical stirring was employed. The distribution exhibits a temperature gradient from the heating core to the outer layer, which was in contact with the bulk solution. Since the cylindrical volume is defined by the propagation of the 532-nm laser, at least two moieties, the core cylinder (m_2) and the jacketed layer (m_1), should be included to express the heat transport, as shown schematically in **Figure 5**. T_2 and T_1 represent the temperature evolutions of the core cylinder and jacketed layer, and T_0 denotes the ambient temperature of the bulk solution before 532-nm exposure, respectively. As a result, the heat transfer processes for the core cylinder and jacketed layer can be expressed in the following form,

$$m_2 \cdot C \cdot \frac{d(T_2 - T_1)}{dt} = I_{\text{ex}} (1 - 10^{-\text{OD}}) \eta \cdot \frac{m_2}{M} - k_2 (T_2 - T_1) \quad (\text{Eq. S1a})$$

$$m_1 \cdot C \cdot \frac{d(T_1 - T_0)}{dt} = I_{\text{ex}} (1 - 10^{-\text{OD}}) \eta \cdot \frac{m_1}{M} + k_2 (T_2 - T_1) - k_1 (T_1 - T_0) \quad (\text{Eq. S1b})$$

where M represents the total mass of the heating volume, and $M = m_1 + m_2$; m_i and k_i denote the masses involved in the heat volume and the apparent heat transfer coefficient. By rearranging **Eqs. S1a** and **S1b**,

$$\frac{dT_2}{dt} - \frac{dT_1}{dt} = \alpha - \beta (T_2 - T_1) \quad (\text{Eq. S2a})$$

$$\frac{dT_1}{dt} = \alpha + \gamma (T_2 - T_1) - \kappa (T_1 - T_0) \quad (\text{Eq. S2b})$$

where $\alpha = \frac{I_{\text{ex}} (1 - 10^{-\text{OD}}) \eta}{M \cdot C}$, $\beta = \frac{k_2}{m_2 \cdot C}$, $\gamma = \frac{k_2}{m_1 \cdot C}$, $\kappa = \frac{k_1}{m_1 \cdot C}$, and $\frac{m_2}{M} = \frac{\gamma}{(\beta + \gamma)}$. By accounting for the

temperature change, $\Delta T_2 = (T_2 - T_0)$, $\Delta T_1 = (T_1 - T_0)$, and $\Delta T_2 - \Delta T_1 = (T_2 - T_1)$, and by employing the Laplace transform for solving the differential equations **S2a** and **S2b**, the evolutions of ΔT_1 and ΔT_2 can be determined,

$$\Delta T_2 = \alpha \left(\frac{(\kappa + \gamma - \beta) e^{-\beta t}}{\beta(\beta - \kappa)} + \frac{(\kappa - \beta - \gamma) e^{-\kappa t}}{\kappa(\beta - \kappa)} + \frac{(\beta + \gamma + \kappa)}{\beta \cdot \kappa} \right) \quad (\text{Eq. S3a})$$

$$\Delta T_1 = \alpha \left(\frac{\gamma e^{-\beta t}}{\beta(\beta - \kappa)} + \frac{(\kappa - \beta - \gamma) e^{-\kappa t}}{\kappa(\beta - \kappa)} + \frac{(\beta + \gamma)}{\beta \cdot \kappa} \right) \quad (\text{Eq. S3b})$$

The fluorescence alteration of tryptophan is attributed to the temperature modulation from the core cylinder and jacketed layer. Assuming the fluorescence intensity is proportional to the masses in the core cylinder and jacketed layer, the temperature evolution can be expressed in the following form,

$$\Delta T(t) = \frac{\Delta FL(t)}{FL(t=0)} \cdot \xi = \frac{\Delta FL_1(t)}{FL(t=0)} \cdot \xi + \frac{\Delta FL_2(t)}{FL(t=0)} \cdot \xi = \frac{m_1}{M} \Delta T_1 + \frac{m_2}{M} \Delta T_2 \quad (\text{Eq. S4})$$

Thus, we can derive the following form to illustrate the temperature evolution from the fluorescence alteration,

$$\Delta T(t) = \alpha \left[\frac{(\kappa - \beta - \gamma)}{\kappa(\beta - \kappa)} e^{-\kappa t} + \frac{(M\gamma + m_2(\kappa - \beta))}{\beta(\beta - \kappa)M} e^{-\beta t} + \frac{(M(\beta + \gamma) + m_2\kappa)}{\beta \cdot \kappa \cdot M} \right] \quad (\text{Eq. S5})$$

Substituting m_2/M to use $\frac{m_2}{M} = \frac{\gamma}{(\beta + \gamma)}$, we can obtain the evolution of the temperature in the following form,

$$\Delta T(t) = \frac{\alpha}{\kappa \cdot \beta \cdot (\beta - \kappa)} \left[\beta(\beta + \gamma - \kappa)(1 - e^{-\kappa t}) - \frac{\kappa\gamma(\gamma + \kappa)}{(\beta + \gamma)}(1 - e^{-\beta t}) \right] \quad (\text{Eq. S6})$$

which is as the same as **Eq. 6**.