Supporting Information

Ultrafast Laser Studies of the Photothermal Properties of Gold Nanocages

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The temperature created by laser excitation in the transient absorption experiments is determined by examining how the period of the symmetric breathing mode of spherical gold particles depends on laser intensity. This analysis assumes that the particles obey Beer's Law and that they have the same elastic constants as bulk gold, but does not require that we calculate the number of adsorbed photons/pulse – which is difficult to do in ultrafast transient absorption experiments.

The first step is to measure transient absorption traces for the particles at different pump intensities. This is shown in Figure S-1. The data show pronounced modulations due to the coherently excited breathing mode. The data are fitted to a damped cosine function (see Eqn. (1) of the paper) to determine the period of the breathing mode.

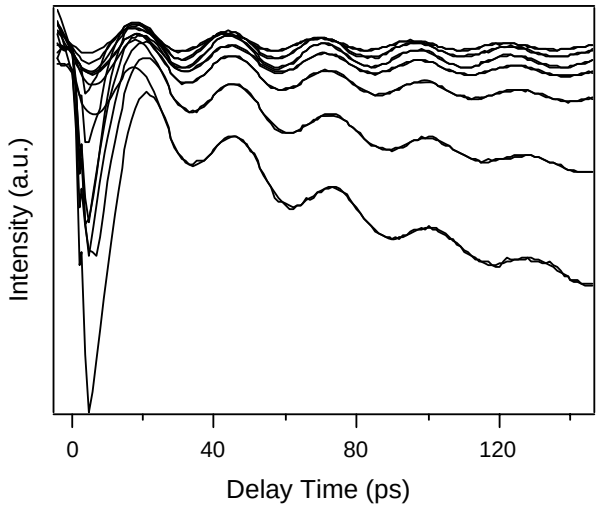

Figure S-1: Transient absorption data for 40 nm radius gold spheres at different pump intensities. The dashed lines show fits to the data using a damped cosine function (see the main text).

The period of the breathing mode is given by:[1]

$$T_{sp}^{br} = \frac{2\pi R}{\chi c_l} \qquad \text{(S-1)}$$

where R is the radius, χ is an eigenvalue determined by $\chi \cot \chi = 1 - (\chi c_l / 2c_t)^2$, and c_l and c_t are, respectively, the longitudinal and transverse speeds of sound of gold. c_l and c_t

(and therefore χ) depend on temperature, and this causes the period to change with pump intensity.[2] The period extracted from the data in Figure S-1 is plotted versus pump intensity in Figure S-2. In our procedure to determine lattice temperature the period versus intensity data is extrapolated to zero intensity. The intercept gives the period at room temperature (25.663 ±0.045 ps), which is used to calculated the radius of the particles via Eqn. (S-1). We have excluded the last point in this analysis, because the calculated temperature for this point is above the melting point (see below). The radius determined from the intercept in Fig. S-2 (using values of c_l and c_t for gold at 300 K) is 39.75 ± 0.07 nm.

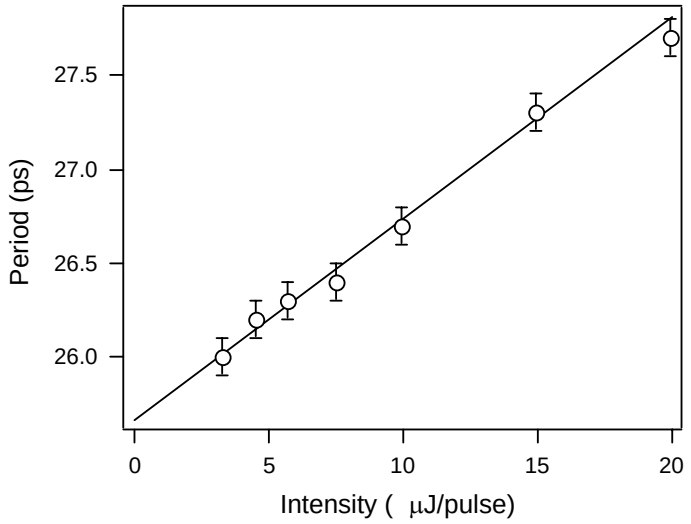

Figure S-2: Period versus pump intensity from the data in Figure S-1. A straight line fit to the data gives $T(\text{ps}) = 25.663 + 0.1074 \times I_0(\mu\text{J})$.

Once we have determined the radius of the particles, the period at any temperature can be calculated using the known temperature dependent elastic constants of gold, which are taken from Ref. [3]. This is shown in Figure S-3. Fitting the calculated points to a straight line gives a relationship between the period and the lattice temperature. For the ~ 40 nm radius particles in our experiments this is $T(\text{ps}) = 25.16 + 0.00170 \times \text{Temp(K)}$. From this relationship we can use the experimentally measured periods to calculate the temperature for each point in Figure S-2. This is shown in Figure S-4.

Figure S-4 is the primary result of this analysis. This gives a relationship between the pump laser intensity and the lattice temperature. From fitting the data in Figure S-4 we obtain the relationship $\text{Temp(K)} = 296 + 63.2 \times I_0(\mu\text{J/pulse})$. The last point is excluded from this fit because the calculated temperature is above the melting point of gold. We estimate an error of about ± 5% for the calculated temperature.

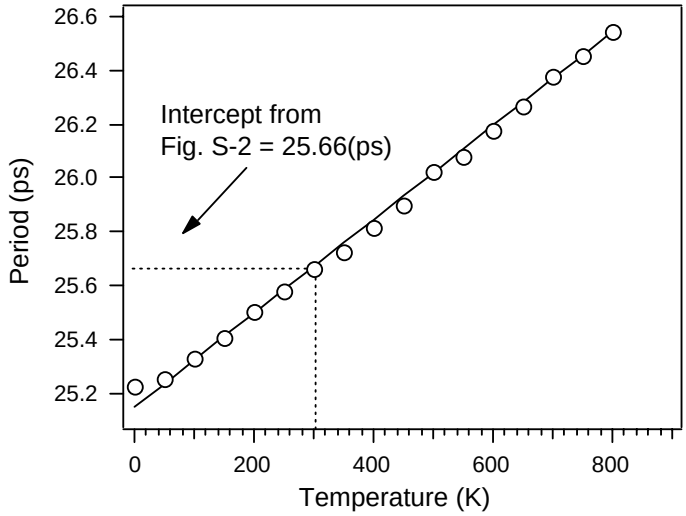

Figure S-3: Period versus temperature calculated using the radius of the particles determined from the intercept in Fig. S-2.

Note that tabulated values of c_l and c_t are only available up to 800 K for gold.[3] Thus, the data points at ~10 μJ/pulse and 15 μJ/pulse represent an extrapolation of the temperature versus period relationship derived from Fig. S-3. We believe this extrapolation is valid because data for other fcc metals (Al, Zn and Cd) shows that the speeds of sound vary linearly with temperature up to the melting point.[2,3] Beyond the melting point Eqn. (S-1) is not valid, so analyzing the measured periods to determine temperature is not appropriate.[2]

The temperature rise in the nanocages will be less than that for the spheres because the nanocages do not absorb light as efficiently at the pump wavelength. Using the dielectric constant data from Ref. [4], the relative absorption of the 68 nm nanocages (2:1 ratio of gold to silver) compared to pure gold is estimated to 0.74 ± 0.02 (in this calculation the

dielectric constants of silver and gold were simply averaged to give the dielectric constant of the nanocages). The same difference in the absorption coefficients of the nanocages compared to spheres is obtained if reflectivity data from the CRC Handbook is used. Taking into account the different absorption coefficients gives the relationship $\text{Temp(K)} = 296 + 46.8 \times I_0(\mu\text{J/pulse})$ for the nanocages. This relationship is used to calculate the temperatures achieved at high power in the text: specifically, 17 μJ/pulse (the maximum power where we still observe modulations, showing that the nanocages are still intact) corresponds to 1100 ± 100 K, and 20 μJ/pulse (the damage threshold of the sample) corresponds to 1200 ± 100 K.

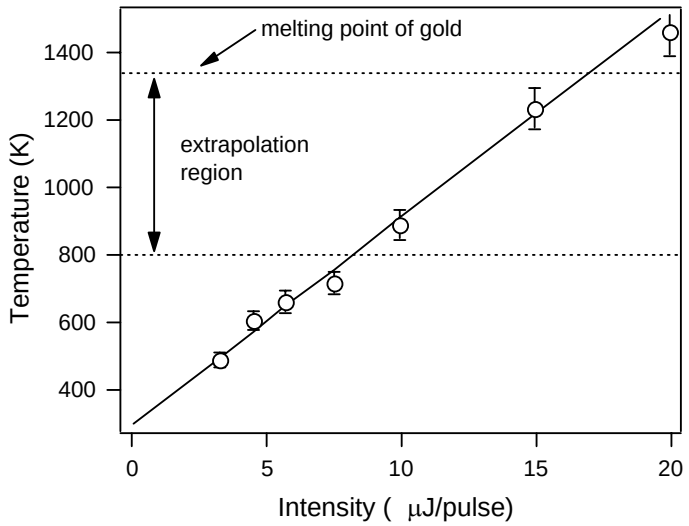

Figure S-4:Temperature versus intensity derived using the relationship between period and temperature obtained from Fig. S-3.

1 Bullen, K. E.; Bolt, B. A. *An Introduction To Seismology,* 4th Edition, Cambridge University Press: Cambridge, 1985.

2 Hartland, G. V.; Hu, M.; Sader, J. E.; *J. Phys. Chem. B* **2003**, *107*, 7472.

3 Simmons, G.; Wang, H. *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook*, The MIT Press: Cambridge, 1971.

4 Quinten, M. *Z. Phys. B-Cond. Matt.* **1996**, *101*, 211.