Supporting Information

Galvanic Replacement Synthesis of Multi-branched Gold Nanocrystals for Photothermal Cancer Therapy

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Photothermal Transduction Efficiency Calculation

As given by Roper,[1] an energy balance for the system is

$$\sum_i m_i C_{p,i} \frac{dT}{dt} = Q_{NC} + Q_{Dis} - Q_{Surr} \quad (1)$$

where m and C_p are the mass and heat capacity of the solvent (water) and T is the average solution temperature. Q_{NC} is the photothermal energy input from the nanocrystals, expressed as

$$Q_{NC} = I(1 - 10^{-A_{980}})\eta \quad (2)$$

where I is the incident laser power, A_{980} is the optical density of the nanoparticle solution at the laser wavelength of 980 nm (**Fig. 5b**), and η is the photothermal transduction efficiency. Q_{Dis} is the baseline energy input due to absorbance by the solvent and the sample cell without nanoparticles, which was measured independently to be 135.1 mW. Q_{Surr} is the heat loss to the surroundings, expressed as

$$Q_{Surr} = hS(T - T_{Surr}) \quad (3)$$

where h is a heat transfer coefficient, S is the surface area of the sample, and T_{Surr} is the ambient temperature of the surroundings. After an initial transient period, the spatially averaged temperature reaches a steady state maximum value, T_{Max}. At T_{Max}, the energy input is equal to the energy output and equation (1) and (3) can be written as,

$$Q_{NC} + Q_{Dis} = Q_{Surr-max} = hS(T_{Max} - T_{Surr}) \quad (4)$$

Substituting equation (2) into (4), the photothermal transduction efficiency, η, is given by this model as

$$\eta = \frac{hS(T_{Max} - T_{Surr}) - Q_{Dis}}{I(1 - 10^{-A_{980}})} \quad (5)$$

In order to obtain *hS*, a dimensionless driving force temperature θ and a characteristic thermal time constant τ_s are introduced as

$$\theta = \frac{T - T_{Surr}}{T_{Max} - T_{Surr}} \tag{6}$$

$$\tau_s = \frac{\sum_i m_i C_{p,i}}{hS} \tag{7}$$

Substituting equations (6) and (7) into (1), we obtain,

$$\frac{d\theta}{dt} = \frac{1}{\tau_s}\left[\frac{Q_{NC} + Q_{Dis}}{hS(T_{max} - T_{surr})} - \theta\right] \tag{8}$$

For the cooling stage, the laser was shut off, meaning that the input energy is zero. Then equation (8) is simplified as

$$dt = -\tau_s \frac{d\theta}{\theta} \tag{9}$$

After integrating, it gives the expression

$$t = -\tau_s ln\theta \tag{10}$$

The time constant of the system, τ_s, is determined by linear fitting of *t* as a function of –ln(θ) (**Fig. S1**).

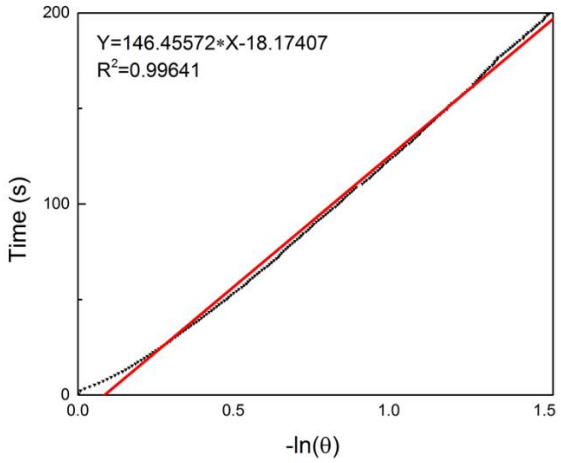

Figure S1. Plot of time versus negative natural logarithm of the temperature increment for the cooling cycle (after 10 min heating) for multi-branched Au NCs with concentration of 200 μg/mL. The linear fit of the data points results in a half-life time τ_s (slope) as shown in the inset.

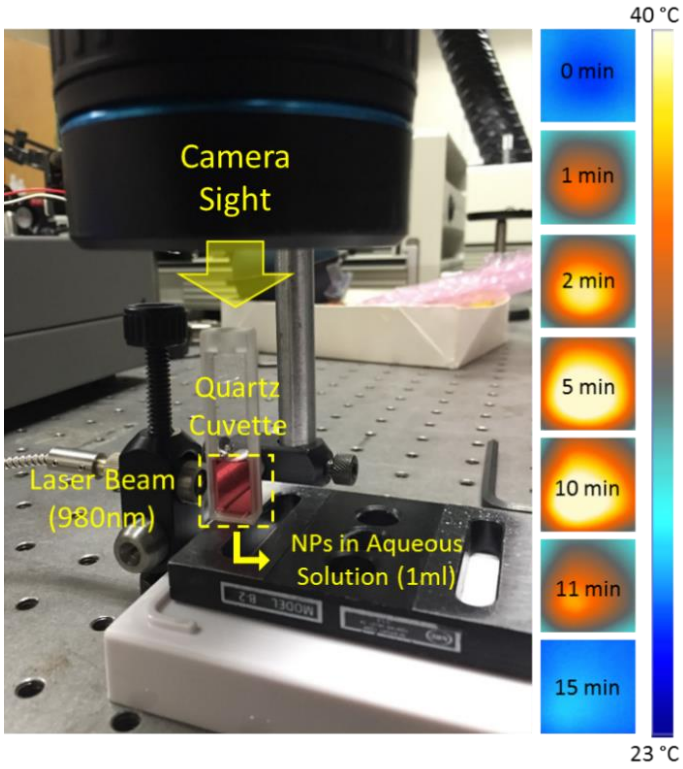

Figure S2. Annotated photograph of the system for photothermal heating experiments.

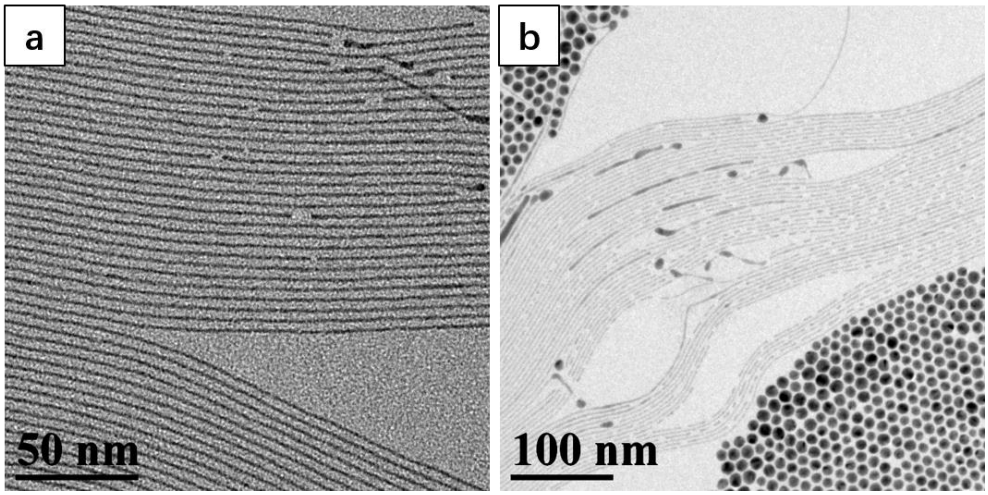

Figure S3. TEM images of (a) Au NWs and (b) Au NWs with Au NPs produced without Cu (I).

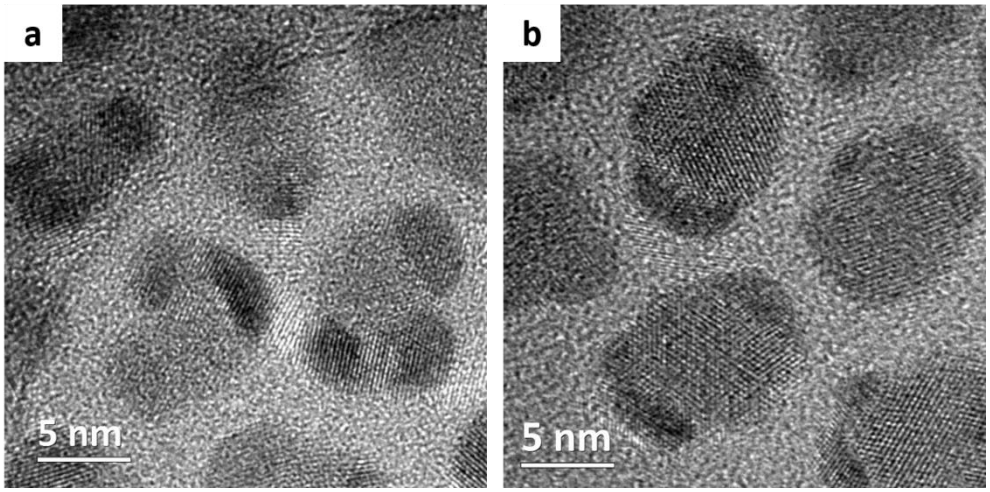

Fig. S4. Additional HRTEM images of NCs obtained at reaction time of 2 min.

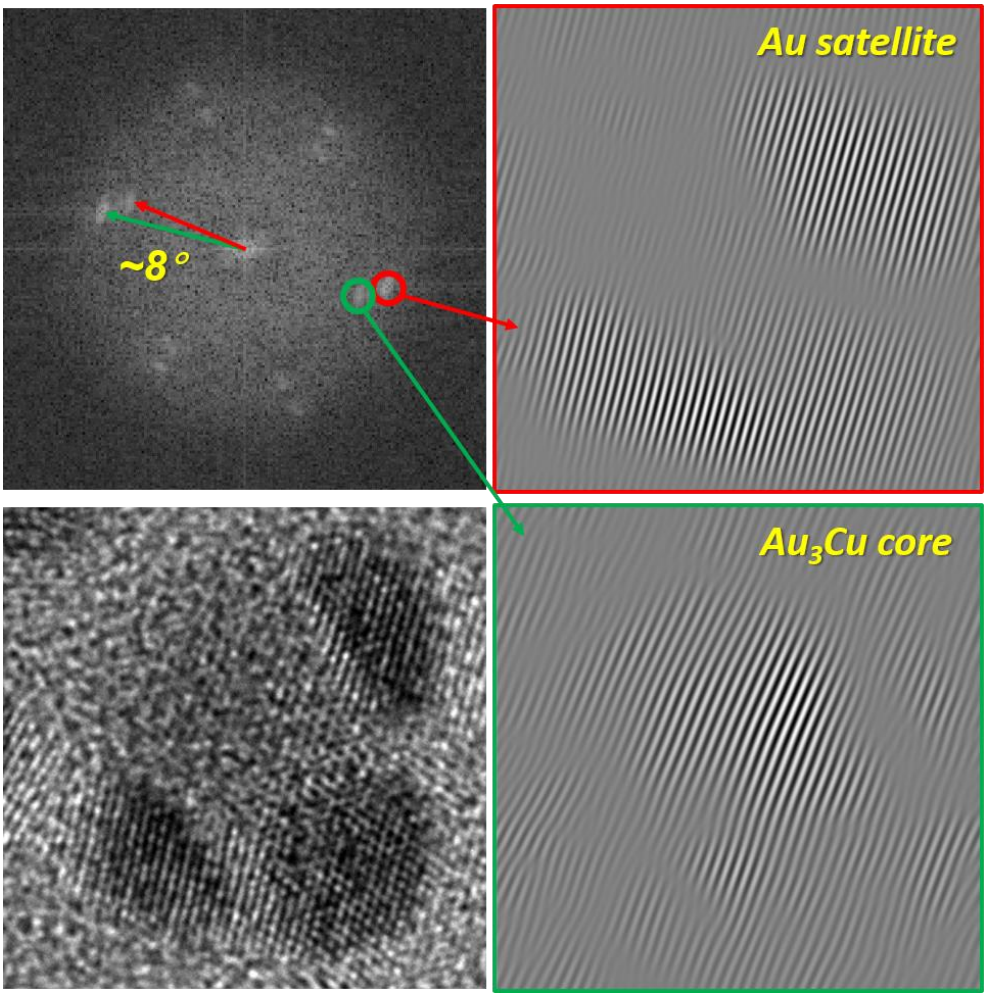

Figure S5. FFT filter analysis of Au_3Cu-Au heterostructure seeds. Based on the HRTEM image analysis in Figure 2a, The Au_3Cu domain has wider lattice spacing (closer green FFT spots). The FFT filter shows that all the domains have minimal lattice orientation mismatch of ~8°, confirming the epitaxial growth proposed in Figure 2. The green and red FFT spots reflect the periodicity in the center and satellite domains, respectively.

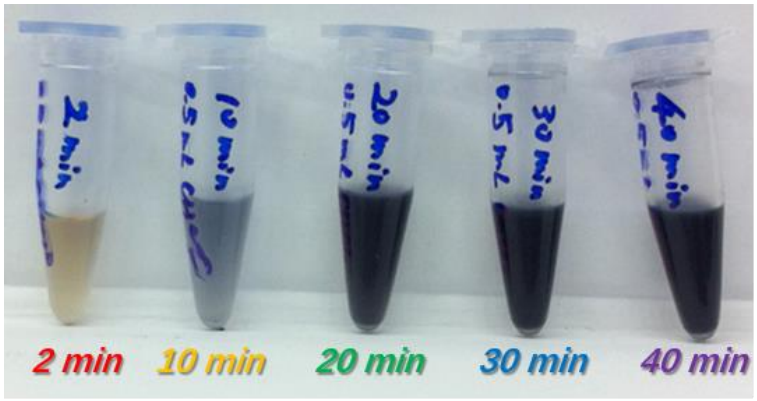

Fig. S6. Photograph of chloroform dispersions of particles obtained at the indicated reaction times.

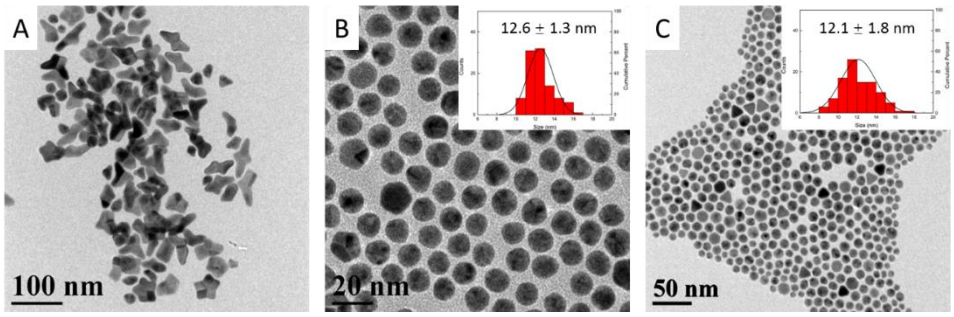

Fig. S7. TEM images of NCs obtained at reaction temperatures of 90 °C (a), 120 °C (b), and 150 °C (c). The insets in panels (B) and (C) show the corresponding NC size distributions.

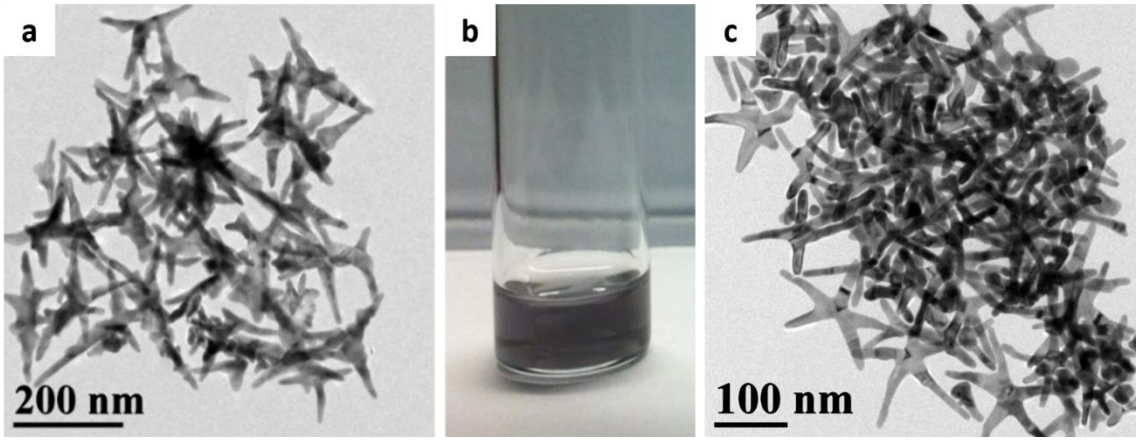

Fig. S8. TEM images of PEGylated multi-branched Au NPs in water (a) before and (c) after laser radiation. Panel (b) shows a typical photograph of the aqueous dispersion.

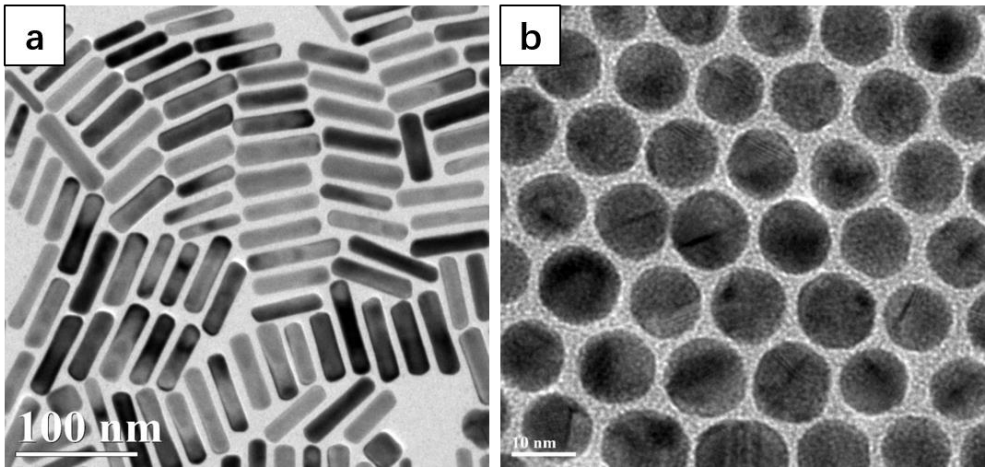

Fig. S9. TEM images of (a) 75×20 nm Au nanorods and (b) ~10 nm Au nanoparticles.

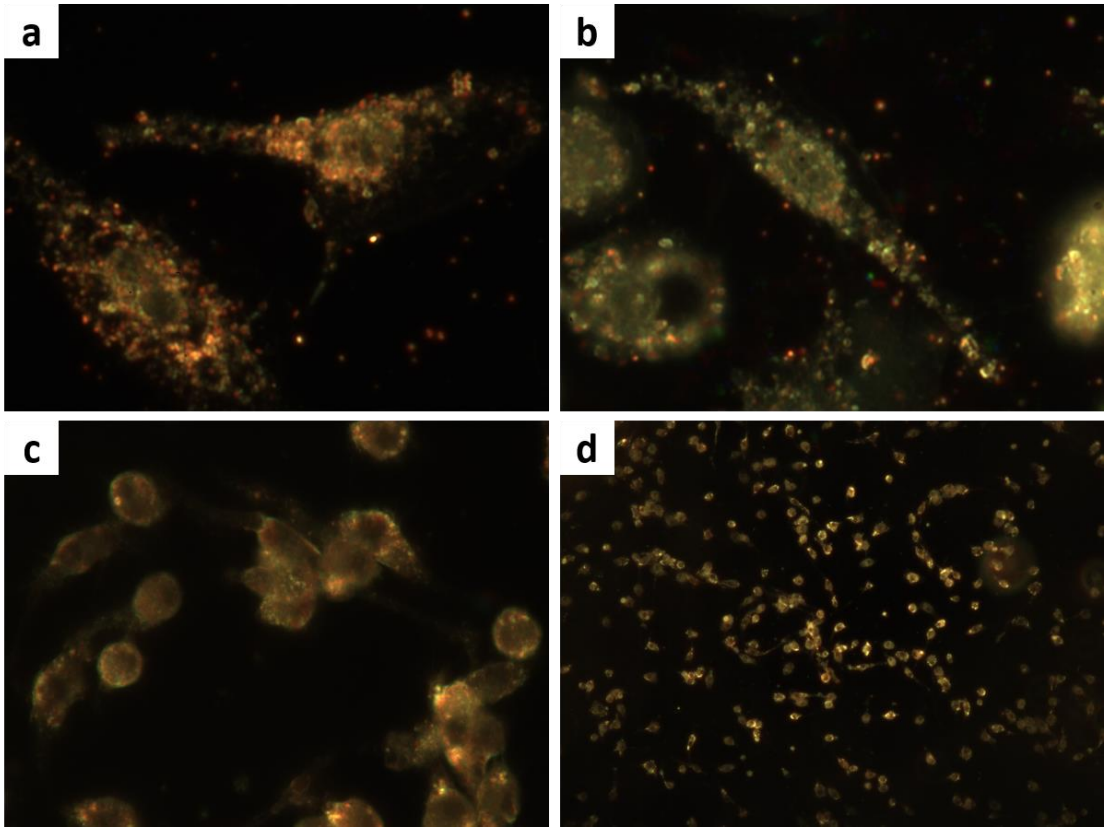

Fig. S10. Dark field image of multi-branched Au NPs in (a-b) HeLa and (c-d) macrophage cells.

References

1. D. K. Roper, W. Ahn and M. Hoepfner. Microscale Heat Transfer Transduced by Surface Plasmon Resonant Gold Nanoparticles. J. Phys. Chem. C 2007, 111, 3636-3641.