Supporting Information

Ultrafast Relaxation Dynamics in Bimetallic Plasmonic Catalysts

Sangwan Sim[1,2], Alyssa Bierlie[3], Philip Mantos[3], Steven McCrory[3], Rohit P. Prasankumar[1*], Sanchari Chowdhury[3*]

1 Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

2 Division of Electrical Engineering, Hanyang University, Ansan 15588, Korea

3 Chemical Engineering Department, New Mexico Tech, Socorro, NM-87801

*rpprasan@lanl.gov , *sanchari.chowdhury@nmt.edu

Table 1: Different properties of plasmonic and catalytic metals[1]

Metal	Electron-phonon coupling constant at 300K	Electronic heat capacity at 300 K	Density of states at Fermi level	Interband transition threshold
Au	2.6×10^{16} $Wm^{-3}K^{-1}$	67 $Jm^{-3}K^{-2}$	0.3 states/eV/atom	2.4 eV
Ni	1×10^{18} $Wm^{-3}K^{-1}$	464 $Jm^{-3}K^{-2}$	2.2 states/eV/atom	0.25 eV
Pt	1×10^{18} $Wm^{-3}K^{-1}$	1230 $Jm^{-3}K^{-2}$	5 states/eV/atom	Fermi level and *d* band overlaps

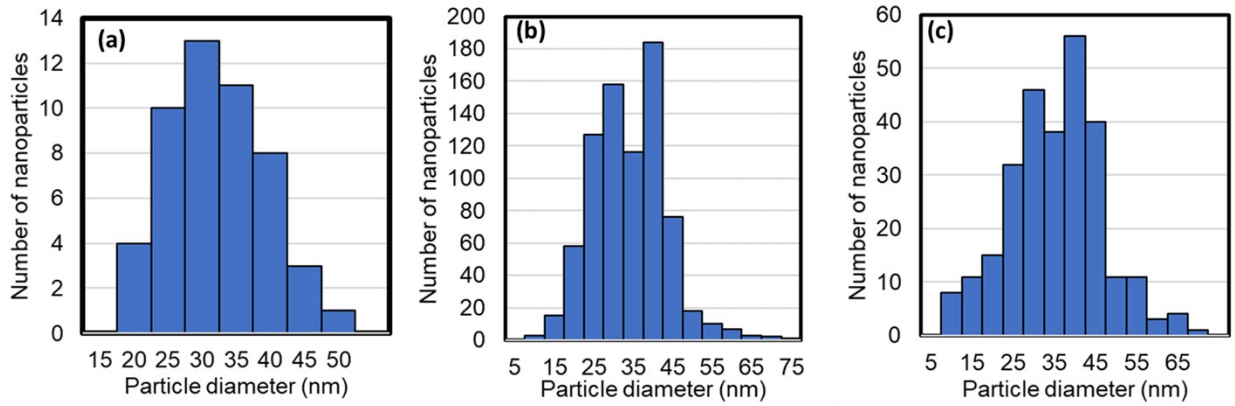

Figure S1: The size distribution histograms calculated from the TEM images for the (a) Au, (b) Au/Ni and (c) Au/Pt bimetallic nanoparticles.

Section 1 : Calculation of maximum temperature rise of the thermalized electrons:

From the two-temperature model, the maximum temperature rise of the thermalized electrons immediately after the pump excitation is given by the following equation,[2]

$$\Delta Temp_e^{max} = \left[Temp_l^2 + 2N_{pp}E_{pp}/\gamma\right]^{1/2} - Temp_l \quad (1)$$

where $Temp_l = 300$ K is the initial lattice temperature, $N_{pp} = 5 \times 10^{17} - 1.2 \times 10^{19}$ cm^{-3} is the absorbed pump photon density, and $E_{pp} = 3.1$ eV is the pump photon energy, and γ is the electronic heat capacity. Assuming that gold absorbs most of the pump photons, we can use gold's electronic heat capacity ($\gamma = 67$ Jm^{-3}K^{-2}) to estimate $\Delta Temp_e^{max}$, which is 10-220 K over the measured pump fluence range. The corresponding maximum lattice temperature rise is $\Delta Temp_l^{max} \sim \gamma Temp_e \Delta Temp_e^{max}/C_l \sim 0.06 - 2.2$ K, where $C_l = 3.5 \times 10^6$ Jm^{-3}K^{-1} is the lattice heat capacity of gold.[3]

Section 2: Calculation of Absorbed Energy Density:

In order to account for the differences in nanoparticle size, optical density, and substrate coverage, the absorbed energy density (U_{abs}) for different nanoparticles is calculated using the following equation[4],

$$U_{abs} = \frac{Energy\ absorbed\ per\ nanoparticle}{Nanoparticle\ volume} = \frac{Abs_{400.} E_{pump.} \pi r_{np}^{2}}{C. \frac{4}{3} \pi r_{np}^{3}} \quad (2)$$

where Abs_{400} is the steady state absorbance of the nanoparticles at 400 nm. E_{pump} is the pump fluence, r_{np} is the radius of the nanoparticle and C is the fraction of the sample area covered by the nanoparticles.

Section 3: Differential Transmission Trace Fitting

The observed differential transmission traces exhibit a biexponential relaxation with two decay time constants, τ_{e-ph} and τ_{ph-ph}, as discussed in the main text. To extract these parameters from the measured $\Delta T/T(t)$ data (where t is the pump-probe time delay), we used the following fit formula, that results from the convolution of the exponential decay function and the Gaussian pump-probe cross correlation[5],

$$\frac{\Delta T(t)}{T} = A_1 \exp\left(\frac{-t}{\tau_{e-ph}} + \frac{(w/2\sqrt{\ln 2})^2}{4\tau_{e-ph}^{\ 2}}\right)\left[1 - \mathrm{erf}\left(\frac{w/2\sqrt{\ln 2}}{2\tau_{e-ph}} - \frac{t}{w/2\sqrt{\ln 2}}\right)\right]$$

$$+ A_2 \exp\left(\frac{-t}{\tau_{ph-ph}} + \frac{(w/2\sqrt{\ln 2})^2}{4\tau_{ph-ph}{}^2}\right)\left[1 - \mathrm{erf}\left(\frac{w/2\sqrt{\ln 2}}{2\tau_{ph-ph}} - \frac{t}{w/2\sqrt{\ln 2}}\right)\right], \qquad (3)$$

where the first and second term on the right-hand side represent the electron-phonon and phonon-phonon scattering dyamics, respectively, and A_1 and A_2 are amplitudes for each term. Table 2 shows the best fitting parameters for Figure 3(a) in the main text. w is the experimentally obtained pump-probe correlation width, which was fixed at ~ 100 fs during the fitting procedure.

Table 2: Best fitting parameters for the normalized $\Delta T/T$ traces in Figure 3(a):

Nanoparticle	A_1	A_2	τ_{e-ph} (ps)	τ_{ph-ph} (ps)
Au	0.526	0.0309	4.25	629
Au/Pt	0.441	0.0925	1.12	782
Au/Ni	0.546	0.0685	0.98	349

References:

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