

Supplementary Information

Quantifying Photothermal Heating at Plasmonic Nanoparticles by Scanning Electrochemical Microscopy

Yun Yu, Jeffrey D. Williams, and Katherine A. Willets*

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, United States

*Corresponding author

kwillets@temple.edu

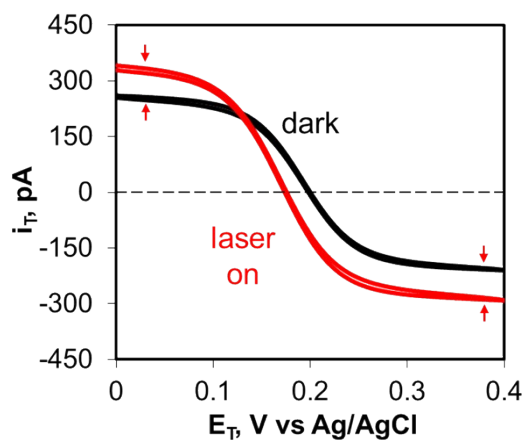


Fig. S1. Steady-state voltammograms obtained with a 460-nm-radius Pt UME before (black) and after (red) a 400 W/cm^2 illumination at the substrate. Scan rate is 50 mV/s . The substrate is glass supported Au nanoparticles. Solution contains 2mM Fe(CN)_6^{3-} , 2mM Fe(CN)_6^{4-} and 0.5M KCl . The tip electrode is placed $10 \mu\text{m}$ from the substrate. Upon illumination, $i_{c,\infty}$ and $i_{a,\infty}$ are enhanced by the same order of magnitude, suggesting that the heating effect only results in an increase of the mass transfer rate, but does not induce the oxidation reaction at the substrate.

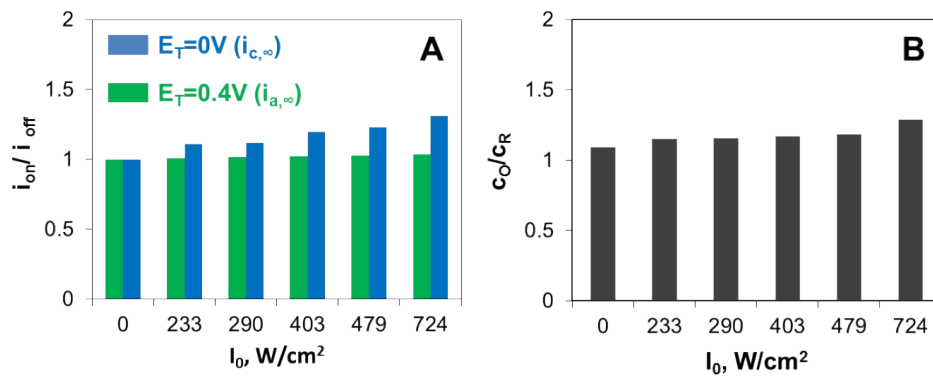


Fig. S2. (A) The plot of i_{on}/i_{off} for $i_{c,\infty}$ ($E_T=0V$, blue) and $i_{a,\infty}$ ($E_T=0.4V$, green) obtained with a 1- μ m-radius Pt UME. (B) c_O/c_R calculated from the data in panel A. Substrate is an unbiased ITO coverslip. Solution contains 2mM $Fe(CN)_6^{3-}$, 2mM $Fe(CN)_6^{4-}$ and 0.5M KCl. The tip electrode is placed 10 μ m from the substrate.

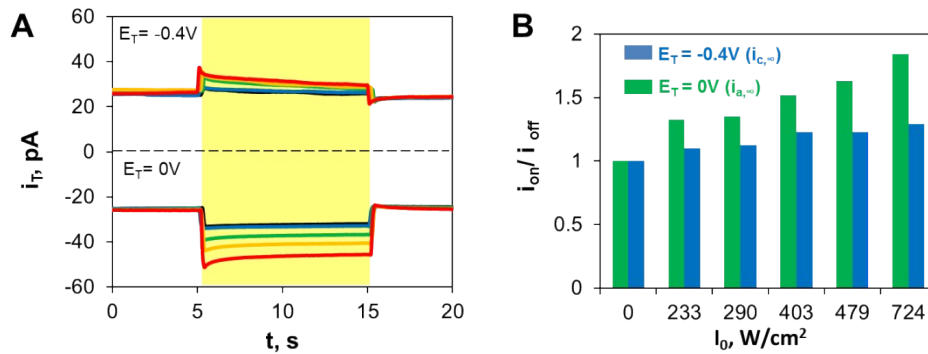


Fig. S3. (A) Current response obtained with a 90-nm-radius Pt tip with $E_T = -0.4V$, $E_S = -0.2V$ (upper section), and $E_T = 0V$, $E_S = -0.2V$ (lower section). The laser was switched on at $t = 5$ s and off at $t = 15$ s. The laser intensities were 724 W/cm² (red), 479 W/cm² (orange), 403 W/cm² (green), 290 W/cm² (blue) and 233 W/cm² (black). (B) The plot of i_{on}/i_{off} for $i_{c,\infty}$ (blue) and $i_{a,\infty}$ (green). Solution contains 2mM $Ru(NH_3)_6^{3+}$ and 0.5M KCl. The tip electrode is placed 10 μ m from the substrate.

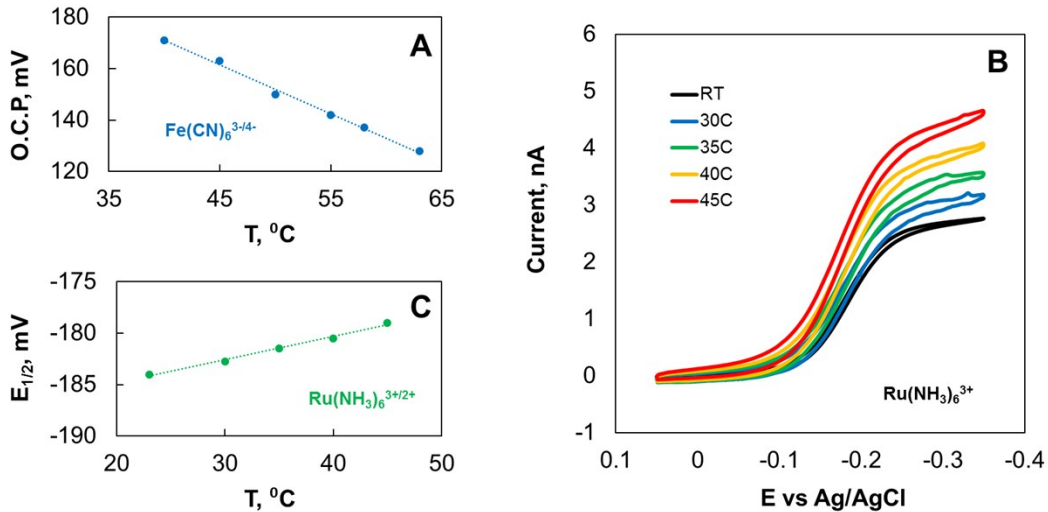


Fig. S4. (A) Open circuit potential (O.C.P.) measured as a function of temperature (T) using a 5- μm -radius Pt UME. Solution contains 2mM $\text{Fe}(\text{CN})_6^{4-}$, 2mM $\text{Fe}(\text{CN})_6^{3-}$ and 0.5M KCl. O.C.P. is equivalent to $E_{eq} = E^0 + (RT/F) \ln(c_O/c_R)$. (B) Steady-state voltammograms obtained with a 5- μm -radius Pt UME at different temperatures. Scan rate is 20 mV/s. Solution contains 2mM $\text{Ru}(\text{NH}_3)_6^{3+}$ and 0.5M KCl. (C) Half-wave potential ($E_{1/2}$) of the voltammograms in panel B as a function of temperature (T). For a Nernstian process, $E_{1/2} = E^0 - (RT/F) \ln(D_O/D_R)$. The electrochemical cell is placed inside a temperature controlled water bath. Temperature coefficients -1.65 mV/K for $\text{Fe}(\text{CN})_6^{3-/4-}$ and +0.46 mV/K for $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ are obtained by subtracting the results in panel A and C by the temperature coefficient for Ag/AgCl,^{S1} and are consistent with the values (-1.53 mV/K for $\text{Fe}(\text{CN})_6^{3-/4-}$, +0.46 mV/K for $\text{Ru}(\text{NH}_3)_6^{2+/3+}$) reported previously.^{S2}

Finite-element Simulation

COMSOL Multiphysics (version 5.2a) was used to simulate the mass transfer and heat transfer processes. The simulation geometry is shown in Fig. S5.

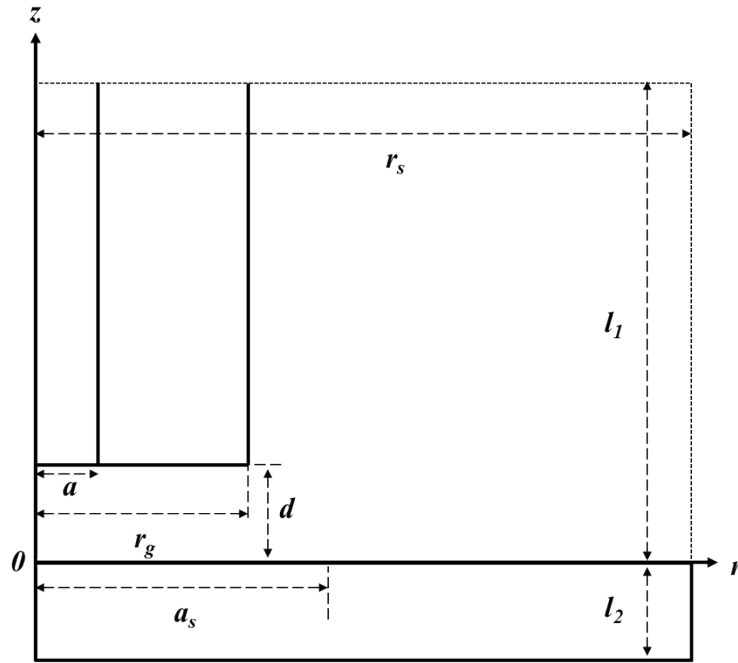


Fig. S5. Geometry of the simulation space.

To simplify the calculation, no convective flow is incorporated in the mass-transfer model. The steady-state diffusion of the redox species is simulated by solving the differential equation below:

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} = 0; 0 \leq r \leq r_s, 0 \leq z \leq l_1; \quad (\text{S-1})$$

where r and z are the coordinates in directions parallel and normal to the tip electrode plane, respectively. r_s and l_1 are the radius and the height of the electrochemical cell, respectively. c is the concentration of redox species. The boundary conditions are shown below:

$$c = 0; 0 \leq r \leq a, z = d; \quad (\text{S-2})$$

$$c = c^*; r_g < r \leq r_s, z = l_1; 0 \leq r \leq r_s, z = 0; r = r_s, 0 \leq z \leq l_1; \quad (\text{S-3})$$

$$\frac{\partial c}{\partial n} = 0; a < r \leq r_g, z = d; r = r_g, d \leq z < l_1; \quad (\text{S-4})$$

where a is radius of the tip electrode, d is the tip-substrate distance, r_g is the radius of the glass sheath of the tip electrode, c^* is the bulk concentration, and $\partial c / \partial n$ is the normal derivative of concentration. The tip current was evaluated by integrating the normal flux to the tip electrode:

$$i_T = 2\pi F D(T) \int_0^a \left[\frac{\partial c}{\partial n} \right]_{z=d} r dr; \quad (\text{S-5})$$

where $D(T)$ is the temperature (T) dependent diffusion coefficient of the redox species, determined by the following relationship according to Stokes–Einstein equation:

$$\frac{D(T)}{D_0} = \frac{T * \mu(295K)}{(295K) * \mu(T)} \quad (\text{S-6})$$

where D_0 is the diffusion coefficient at room temperature, and $\mu(T)$ represents the temperature dependent viscosity of the solution^{S3}:

$$\frac{\mu(T)}{\mu_0} = 10^{\left(\frac{247.8}{T - 140} - \frac{247.8}{295 - 140} \right)} \quad (\text{S-7})$$

where μ_0 is the viscosity at room temperature.

Steady-state heat transfer is simulated by solving the following differential equation:

$$\rho C_p u \nabla T = \nabla(k \nabla T) + Q \quad (\text{S-8})$$

where the velocity $u=0$ (no convective flow), and the heat source $Q=0$ (no heat adsorption by solution or glass) is assumed to simplify the calculation. Eq. S-8 in the reduced form becomes

$$\nabla(k_g \nabla T) = 0; 0 \leq r \leq r_g, d \leq z \leq l_1; 0 \leq r \leq r_s, -l_2 \leq z \leq 0; \quad (\text{S-9})$$

$$\nabla(k_w \nabla T) = 0; 0 \leq r \leq r_s, 0 \leq z \leq l_1; \quad (\text{S-10})$$

where k_g is thermal conductivity of glass, k_w is the thermal conductivity of water, and l_2 is the thickness of the substrate. The boundary conditions are shown below:

$$T = 295K + \Delta T; 0 \leq r \leq a_s, z = 0; \quad (\text{S-11})$$

$$T = 295K; r_g \leq r \leq r_s, z = l_1; r = r_s, 0 \leq z \leq l_1; \quad (\text{S-12})$$

$$\nabla T = 0; 0 \leq r \leq r_g, z = l_1; r = r_s, -l_2 \leq z \leq 0; 0 \leq r \leq r_s, z = -l_2; \quad (\text{S-13})$$

where a_s is the radius of the laser spot, and ΔT is a constant temperature increase at the laser spot.

References

- S1 L. Yang, *Techniques for Corrosion Monitoring*, 2008, Woodhead Publishing, U.K., pp.55.
- S2 U. Kumar Sur, F. Marken, N. Rees, B. A. Coles, R. G. Compton and R. Seager, *J. Electroanal. Chem.*, 2004, 573, 175-182.
- S3 A. Tarik, *Engineering Fluid Mechanics*, 2012, Ventus Publishing, Holland, pp. 17–18.