Plasmon-Mediated Catalytic Oxidation of *sec*-Phenethyl and Benzyl Alcohols: Supporting Information

Geniece L. Hallett-Tapley,¹ M. Jazmín Silvero,¹ María González-Béjar,¹ Michel Grenier,¹ José Carlos Netto-Ferreira^{1,2*} and Juan C. Scaiano^{1*}

¹Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa K1N 6N5, Canada

²Departamento de Química, Universidad Federal Rural do Rio de Janeiro, Seropédica, 23851-970, Rio de Janeiro, Brazil

*Author to whom correspondence should be addressed. Email: <u>tito@photo.chem.uottawa.ca</u> and josecarlos@photo.chem.uottawa.ca

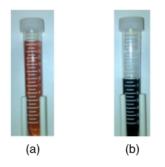


Figure S1. Photo of aqueous (a) 2.5 nM and (b) 13 nM AuNPs.

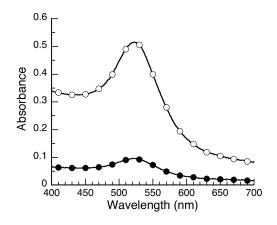


Figure S2. UV-visible spectra of aqueous 2.5 nM (\bullet) and 13 nM (O) AuNP.

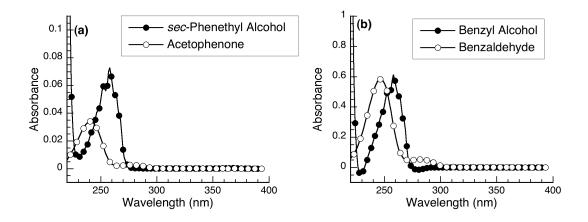


Figure S3. UV-visible spectra of (a) *sec*-phenethyl alcohol/acetophenone and (b) benzyl alcohol/benzaldehyde. Note the spectral overlap at 245 nm (left) and 250 nm (right).

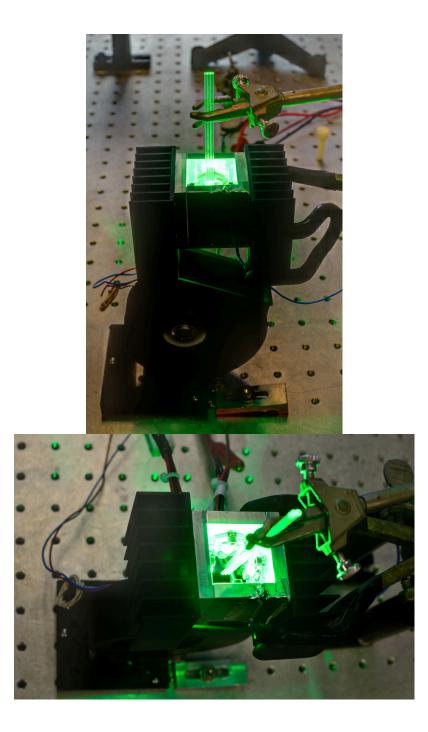


Figure S4. Photos depicting a full view (top) and close up (bottom) of the LED apparatus used for plasmon-mediated catalysis.

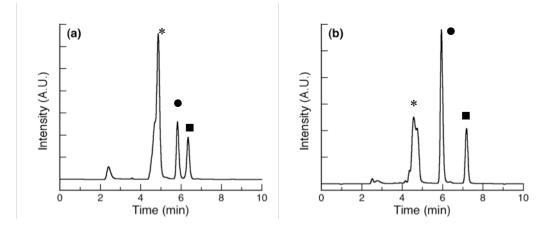


Figure S5. HPLC spectra of (a) *sec*-phenethyl and (b) benzyl alcohol oxidation using 532 nm laser drop excitation following 100 laser shots/drop. Peak identification: H_2O_2 (*), alcohol (•), and carbonyl oxidation product (acetophenone or benzaldehyde) (\blacksquare).

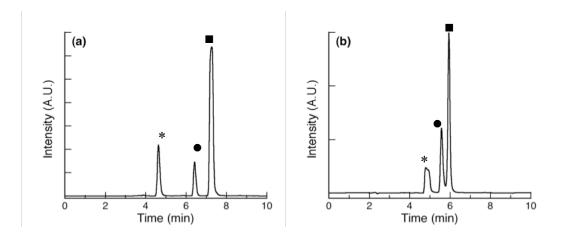


Figure S6. HPLC spectra of (a) *sec*-phenethyl and (b) benzyl alcohol oxidation using 530 nm LED excitation for 25 minutes. Peak identification: H_2O_2 (*), alcohol (\bullet), and carbonyl oxidation product (acetophenone or benzaldehyde) (\blacksquare).



Figure S7. Photo of LED capillary tubes containing *sec*-phenethyl alcohol, H_2O_2 and AuNP following 20 minutes of irradiation. Note deep violet color in the areas exposed to LED light.

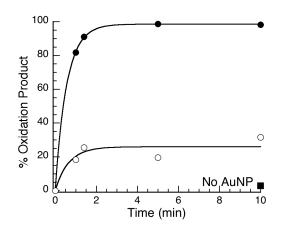


Figure S8. Acetophenone (\bullet) ($\lambda_{\text{monitor}} = 245 \text{ nm}$; 80°C) and benzaldehyde (\bigcirc) ($\lambda_{\text{monitor}} = 250 \text{ nm}$; 40°C) conversion as a function of microwave irradiation. Note the reduced conversion to oxidation products in the absence of AuNP (\blacksquare).

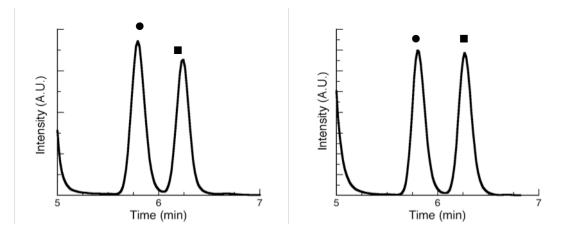


Figure S9. HPLC spectra of 0.28 M *sec*-phenethyl alcohol oxidation (a) in the presence and (b) absence of 0.28 M isopropanol. Spectra are expanded onto the retention times of the alcohol and oxidation product to compare relative peak heights ($\lambda_{monitor} = 245$ nm). Peak identification: alcohol (\bullet), acetophenone (\blacksquare).

Calculation of AuNP concentration

AuNP concentration was calculated using the absorbance at 522 nm for the 2.5 nM and resuspended AuNP colloidal solutions (Figure S2) and the equation below (1):

$$[AuNP] = \frac{Abs @ 522 nm [AuNP]}{Abs @ 522 nm 2.5 nM AuNP} \times 2.5 nM$$
(1)

For the data presented in Figure S2:

$$[AuNP] = \frac{0.514}{0.096} \times 2.5 \text{ nM} = 13.4 \text{ nM}$$

Calculation of % Conversion to Alcohol Oxidation Products:

AuNP plasmon-mediated *sec*-phenethyl and benzyl alcohol oxidations were selective to carbonylic oxidation products – acetophenone and benzaldehyde, respectively. The integration values (area under the curve) for the peaks in the HPLC spectra corresponding to the alcohol and oxidation product were used to approximate the % conversion to oxidation products. For *sec*-phenethyl alcohol, the values were monitored at 245 nm due to the overlap in the absorption spectra at this wavelength, as is illustrated in Figure S3a. Likewise, the values for benzyl alcohol oxidation were extracted at 250 nm, due to overlap in the UV-visible spectra at this particular wavelength (Figure S3b). % conversions were calculated as is shown below (2):

 $\% \text{ conversion ox. product } = \frac{\text{Area under the curve ox. product}}{(\text{Area under the curve alcohol}) + (\text{Area under the curve ox. product})}$