Visible Light Plasmonic Heating of Au/ZnO for the Catalytic Reduction of CO_2

Electronic Supplementary Information

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1. Transmission electron microscopy (TEM) and high resolution TEM images of Au/ZnO catalysts.

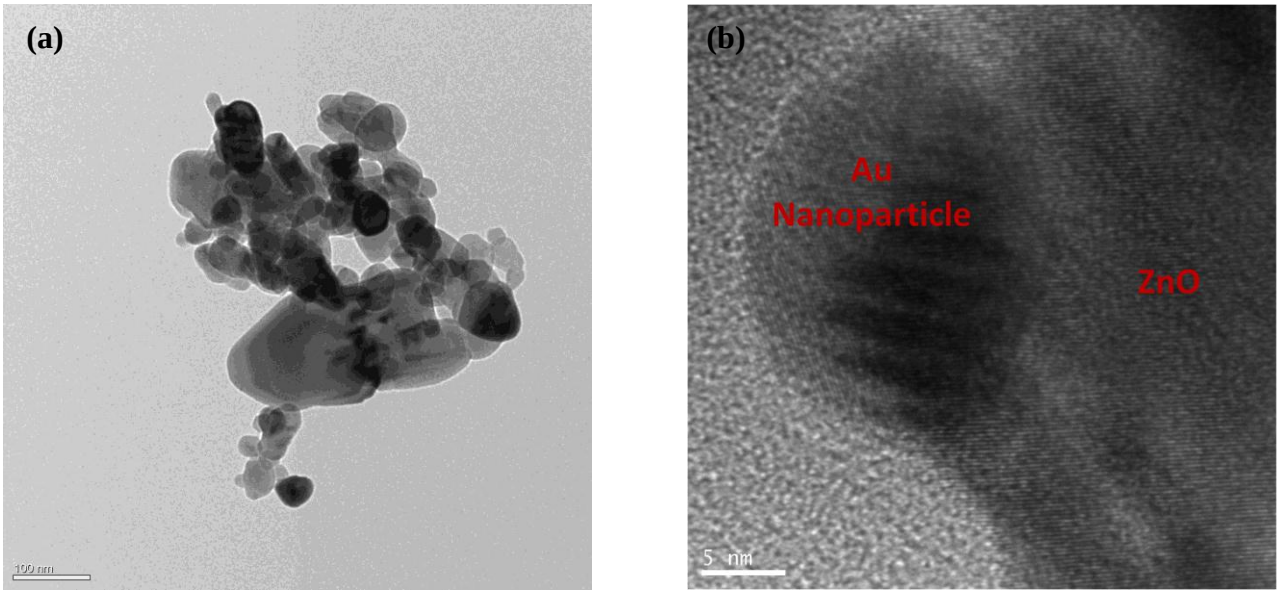

Figure S1. (a) TEM image of the Au/ZnO photocatalysts. Scale bar, 100 nm. (b) High resolution TEM image of the Au/ZnO catalyst. Scale bar, 5 nm.

2. Raman spectroscopic studies of ZnO and Au/ZnO catalysts.

To measure the Au/ZnO catalyst temperature under laser excitation, temperature- and laser intensity-dependent Raman spectroscopic studies of ZnO and Au/ZnO samples were performed.

A Renishaw InVia Raman Microscope with 1.0 cm^{-1} resolution was used to collect the Raman spectra of ZnO and Au/ZnO catalysts. The samples were excited with a 532 nm green laser (CL-532-100). A 5× magnification microscope objective was used in the experiments. Numerical aperture size was 0.12. The experimental laser spot size was measured using a calibration slide and was determined to be ~ 13 µm. A Linkam high temperature stage (THMS 600) and temperature controller (TMS 94) were used to obtain temperature dependent Raman spectra of the samples in the temperature range of 25 °C to 450 °C with 25 °C steps. A series of Raman spectra were also collected for ZnO and Au/ZnO at different laser excitation intensities to measure the temperature change under laser illumination. The temperature dependent Raman spectral broadening is used to determine the Au/ZnO catalyst temperatures under laser excitation.

(a) Temperature dependent Raman Spectra for ZnO.

Temperature dependent Raman spectra were taken from 25 °C to 450 °C with 25 °C temperature steps, under 2.6×10^5 W/m^2 *cw* 532 nm laser excitation. The spectral changes of the E_2(high) mode at ~ 438 cm^{-1} were investigated as a function of temperature. The spectra were fitted by Lorentzian line shapes to determine the position and width of the Raman peaks. The broadening of the E_2(high) peak in pure ZnO is used as a calibration curve to determine the temperature of the Au/ZnO catalyst under different laser excitation intensities.[1,2]

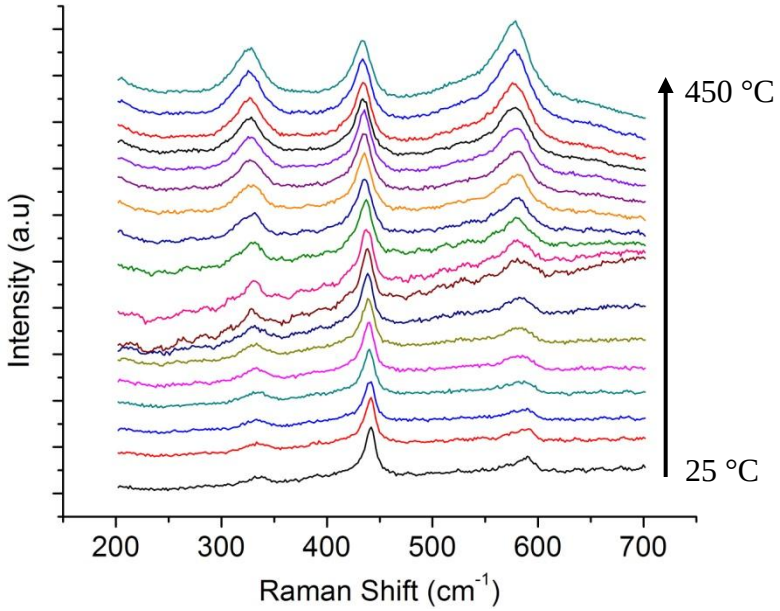

Figure S2. Raman spectra of ZnO at different temperatures under 2.6×10^5 W/m^2 *cw* 532 nm laser excitation.

(b) Theoretical model for the linewidth broadening of the E_2(high) mode.

The temperature dependent Raman linewidth is described by:

$$\Gamma(T) = \Gamma_0 + A\left(1 + \sum_{j=1}^{2} n_j\left(\omega_j, T\right)\right) + B\left(1 + \sum_{j=1}^{3} n_j\left(\omega_j, T\right) + n_j^2\left(\omega_j, T\right)\right)$$

where $\Gamma(T)$ is temperature dependent full width at half maximum (FWHM), Γ_0 is background contribution to linewidths due to impurity and/or defect scattering, $n_j(\omega_j,T)$ is Bose-Einstein distribution function, A is cubic anharmonic coupling constant, and B is the quadratic anharmonic coupling constant.[1-5] The highest experimental temperature accessible in determining our calibration curve for the E_2 mode is ~450 °C. This theoretical expression is fit to experimental data up to ~450 °C to generate a smooth calibration curve. This same theoretical expression can also be used to extrapolate to slightly higher temperatures.

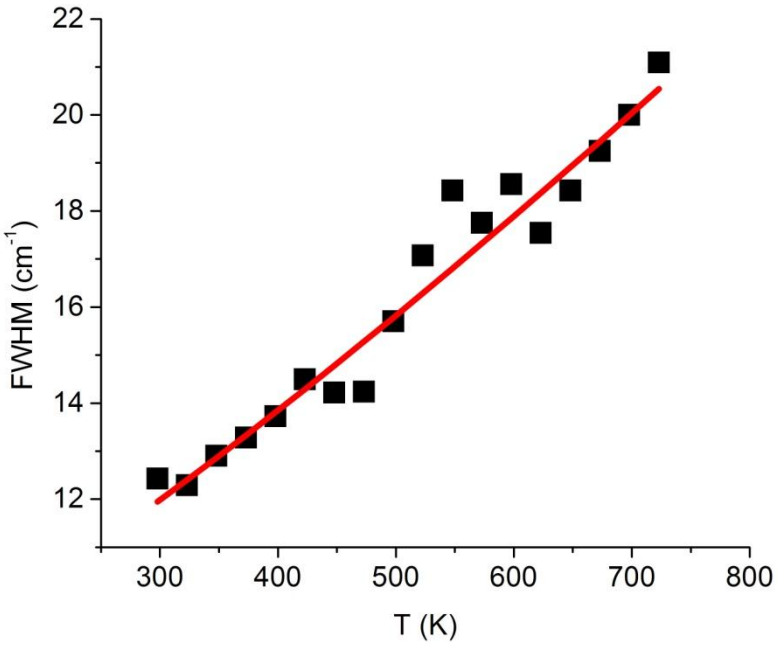

Figure S3. FWHM of E_2(high) mode of ZnO as a function of temperature (black squares) under 2.6×10^5 W/m^2 *cw* 532 nm laser excitation. The red line is the fit based on the theoretical model described in the text.

(c) Raman spectra of ZnO and Au/ZnO at room temperature under different laser excitation intensities.

Raman spectra were collected for both ZnO and Au/ZnO samples at room temperature under different laser intensities. The FWHM of ZnO remains the same under all laser excitation intensities. Au/ZnO, however, shows significant broadening as laser intensity increases, a clear indication of the plasmonic heating due to the Au nanoparticles. The broadening is linearly dependent on the laser intensity. The steady state temperature of the Au/ZnO sample at different laser excitation intensities is determined by measuring its FWHM at a specific laser intensity and comparing this value to the calibration curve and theoretical model of the temperature dependent FWHM measured for pure ZnO. As discussed in the main text, there is evidence that the local heating near the Au particles in the Au/ZnO samples may be higher than the steady state temperature measured with this Raman method.

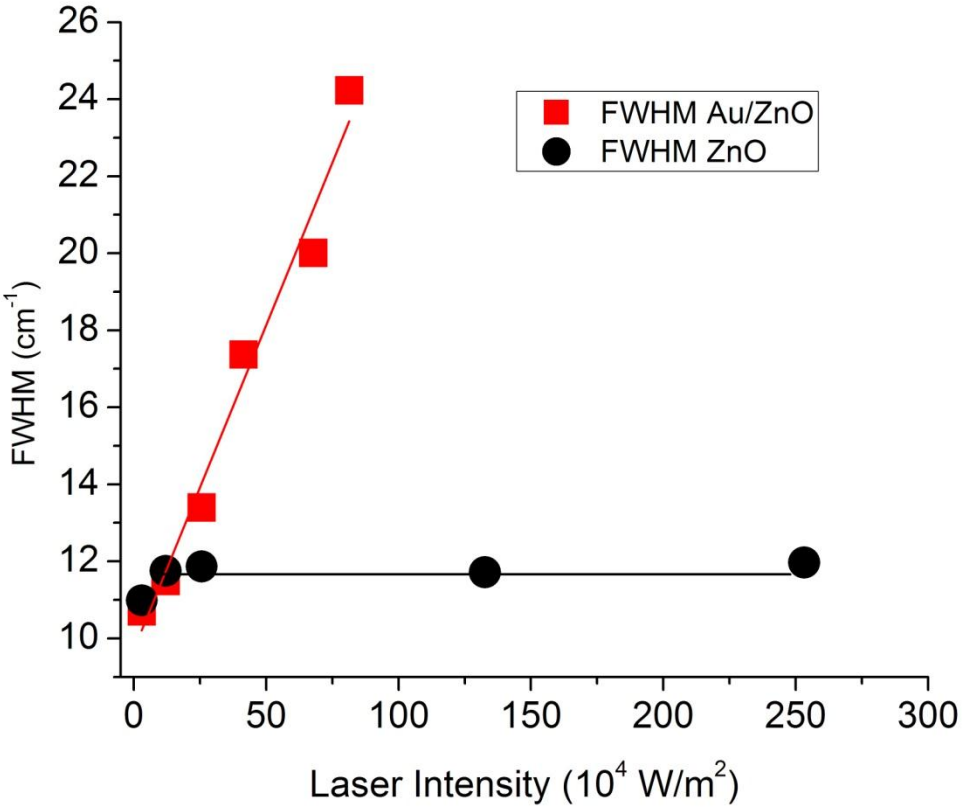

Figure S4. FWHM of E_2(high) mode of ZnO (black circles) and Au/ZnO (red squares) under different 532 nm laser excitation intensities at room temperature. The red line is a linear fit of the FWHM increase of the Au/ZnO sample.

3. Schematic and photograph of experimental setup.

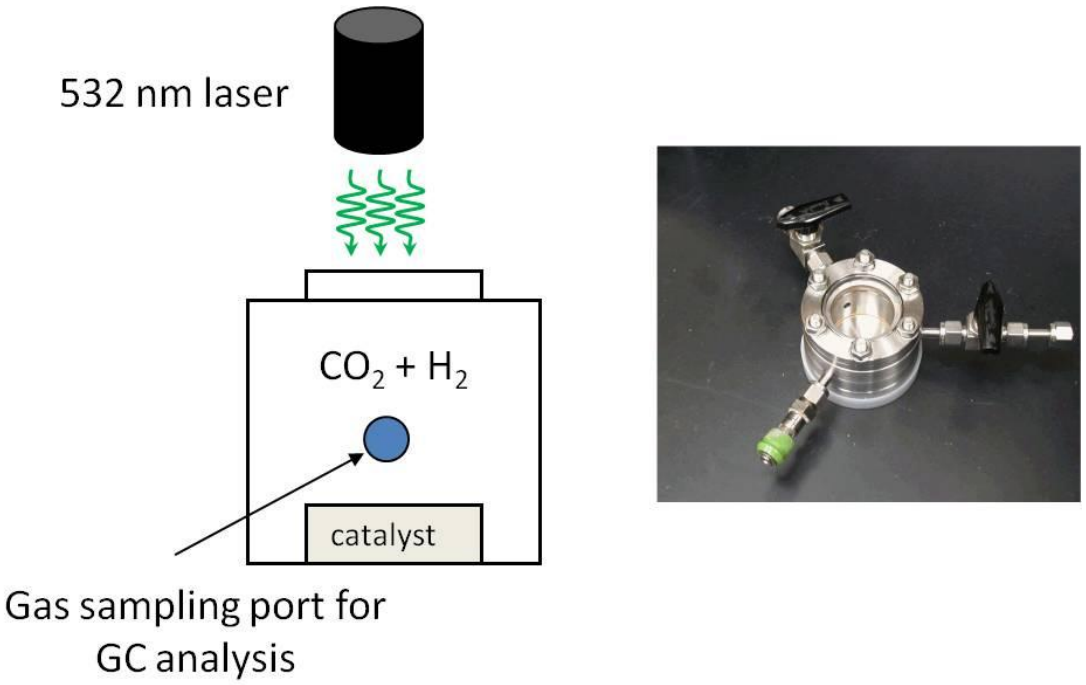

Figure S5. The schematic of the experimental setup for CO_2 reduction reactions and a photograph of the photocatalysis cell.

4. Thermodynamic calculations for the CO_2 conversion reaction mechanism.

Calculations of the CO_2 conversion were performed for the following four different reaction schemes:

Reaction scheme 1: $CO_2 + H_2 \leftrightarrows CO + H_2O$ (Reverse water-gas shift (RWGS))

Reaction scheme 2: $CO_2 + H_2 \leftrightarrows CO + H_2O$ (RWGS); $CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$ (Methanol synthesis)

Reaction scheme 3: $CO_2 + H_2 \leftrightarrows CO + H_2O$ (RWGS); $CO + 3H_2 \leftrightarrows CH_4 + H_2O$ (CO-methanation)

Reaction scheme 4: $CO_2 + H_2 \leftrightarrows CO + H_2O$ (RWGS); $CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$ (Methanol synthesis); $CO + 3H_2 \leftrightarrows CH_4 + H_2O$ (CO-methanation)

Among the 4 schemes considered, only reaction scheme 3 is consistent with the observed products in the photocatalytic reduction of CO_2 using Au/ZnO photocatalysts.

References:

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