Plasmon Resonant Enhancement of Carbon Monoxide Catalysis

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ABSTRACT Irradiating gold nanoparticles at their plasmon resonance frequency creates immense plasmonic charge and high temperatures, which can be used to drive catalytic reactions. By integrating strongly plasmonic nanoparticles with strongly catalytic metal oxides, significant enhancements in the catalytic activity can be achieved. Here, we study the plasmonically driven catalytic conversion of CO to CO2 by irradiating Au nanoparticle/Fe2O3 composites. The reaction rate of this composite greatly exceeds that of the Au nanoparticles or Fe2O3 alone, indicating that this reaction is not driven solely by the thermal (plasmonic) heating of the gold nanoparticles but relies intimately on the interaction of these two materials. A comparison of the plasmonically driven catalytic reaction rate with that obtained under uniform heating shows an enhancement of at least 2 orders of magnitude.

KEYWORDS Plasmon, plasmonic, catalysis, nanoparticle, oxidation

Metal oxides (e.g., TiO2, Fe2O3, PbO) are very promising photocatalysts for a number of applications, including solar fuel production, oxidation of pollutants, and antifogging/self-cleaning coatings for windows and lenses. When gold is dispersed as fine particles (2–5 nm) over select metal oxides, it has been found to exhibit exceptionally high catalytic activity,1,2,16 far exceeding that of the metal oxide and gold catalysts separately.17,18 The catalytic oxidation of carbon monoxide has become an important field of study in and of itself.19–27 For gold nanoparticles on transition metal oxides, the oxidation of CO is an exothermic reaction with extremely low catalytic activation barriers.19 In this work, we explore a fundamentally different mechanism of catalytic enhancement, achieved with plasmonic excitation. By monitoring the temperature of the reaction (using infrared and Raman spectroscopies), we separate the effects of plasmonic heating from exothermic chemical heating. To determine the catalytic enhancement factor, we compare the CO reaction rate achieved under laser irradiation with that observed under uniform heating. We also compare the reaction rate of the Au nanoparticle/Fe2O3 composite with that of its constituent materials, in order to further establish the uniqueness of this catalytic enhancement process.

Experiments are carried out in a microreactor system consisting of a gas delivery system, an optical microscope, and an excitation laser source, as illustrated schematically in Figure 1a. A 532 nm 5 W Spectra Physics solid-state laser is collimated and focused through a Leica DMLM microscope. A 50× long-working distance microscope objective lens with NA = 0.5 and spot size = 1.25 μm is used to irradiate the sample while carbon monoxide (CO) is flowed through the microreactor system. The byproducts of these plasmon-induced reactions are monitored using a Pfeffer Omnistar quadrupole mass spectrometer (QMS). Since the
sensitivity of the mass spectrometer is limited by the background vapors, namely, the unreacted reactants, micrometer-sized channels (similar to microfluidic channels) etched in silicon\textsuperscript{28} are used to reduce the volume of gas flowing through the system to a $20 \times 20 \ \mu m^2$ cross-sectional area. A photograph of these microchannels is shown in Figure 1b. This is a critical step in realizing the full sensitivity of the mass spectrometer for measuring small reactions on the order of the focused laser spot size ($\sim 1 \ \mu m^2$). Gold nanoparticles are deposited in the bottom of the microchannels by electron-beam evaporation of 5 nm thick films of Au. This is known to produce island-like growth of strongly plasmonic nanoparticles separated by only a few nanometers.\textsuperscript{8} Raman and near-infrared spectra are collected with the same objective lens used to irradiate the sample in a Renishaw inVia micro-Raman spectrometer. The catalyst temperatures are determined from the downshifts observed in the Fe$_2$O$_3$ Raman modes. The calibrations of these temperature-induced downshifts were performed in a Linkam THMS temperature-controlled stage. The catalyst temperatures are also determined from the blackbody radiation intensity observed at a wavelength of 980 nm, which increases with the temperature to the fourth power ($I = \sigma T^4$).\textsuperscript{29}

When Au nanoparticles are irradiated with light at their plasmon resonance frequency in a dilute Fe(CO)$_5$/CO gas environment, crystalline Fe$_2$O$_3$ (in the hematite phase) is deposited. This process is called plasmon resonant chemical vapor deposition (PRCVD) and is described in a previous publication.\textsuperscript{30} Figure 2a shows the mass spectrometer signals of CO$_2$ and O$_2$ plotted during a 1300 s laser exposure (48 mW at 532 nm). Figure 2b shows the corresponding temperature data (as determined from the calibrated Raman and infrared emission spectra) taken during the same 1300 s laser exposure. During the first 500 s, the temperature remains constant at a value of 330 °C, due to the plasmonic heating of the nanoparticles. During this time, Fe$_2$O$_3$ nanocrystals are deposited.\textsuperscript{30} Throughout the first 500 s of laser exposure, the CO$_2$ and O$_2$ concentrations (Figure 2a) remain unchanged. After 500 s, the CO$_2$ concentration increases and the O$_2$ concentration decreases as they are produced and consumed in the reaction $2CO + O_2 \rightarrow 2CO_2$, respectively. The sudden increase in temperature observed after 500 s is caused by the exothermic CO oxidation, which becomes strongly catalyzed by the newly formed Fe$_2$O$_3$–Au nanoparticle composite. This highly exothermic reaction ($\Delta H = -532$ kJ/mol) causes the temperature to increase rapidly, exceeding 1000 °C after 550 s. The drop in temperature observed after 770 s is caused by blockage of the microchannel, which restricts the flow of reactants and is, therefore, not related to the reaction kinetics. If, at any time, the laser is turned off, the reaction stops and the temperature drops to room temperature. As described in our previous work,\textsuperscript{30} we observe the formation of carbon nanotubes at these elevated temperatures (above 700 °C). The precipitation of carbonaceous material occurs by the reaction $2CO \rightarrow C + CO_2$. While this reaction has a lower negative heat of formation ($\Delta H = -173$ kJ/mol) than the oxygenation reaction described above, it becomes thermodynamically (entropically) favorable at these high temperatures.

The catalytic activity of this Au nanoparticle/Fe$_2$O$_3$ composite is then evaluated in purified CO, in which the Fe(CO)$_5$ has been removed, to prevent further deposition of Fe$_2$O$_3$. Figure 3 shows the mass spectrometer signals of CO$_2$ plotted during a 5 s laser exposure (48 mW at a wavelength of 532 nm). Here, we observe a rapid increase in the CO$_2$ concentration when the laser is incident on the Fe$_2$O$_3$–Au nanoparticle composite. However, when Au nanoparticles are irradiated in a region with no Fe$_2$O$_3$, no change in the CO$_2$ signal is observed, as shown in Figure 3. Similarly, when we irradiate Fe$_2$O$_3$ alone with no Au nanoparticles, we observe

\begin{figure}
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\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) Schematic diagram of the microreactor system. (b) Silicon microchannels with glass cover and metal eyelets.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{(a) Quadrupole mass spectrometer data and (b) infrared temperature data taken during laser irradiation in CO.}
\end{figure}
no production of CO$_2$. We, therefore, conclude that this reaction is not driven solely by the thermal (plasmonic) heating of the gold nanoparticles but relies intimately on the interaction of these two materials. Metal nanoclusters on metal oxide supports are known to produce catalytic efficiencies that exceed those of the two constituent materials by themselves.$^{1,2}$ However, in these prior studies, nanocluster sizes less than 5 nm were required in order for significant catalytic enhancement to be achieved.$^1$ The nanoparticle sizes used in this plasmonic work are 1 order of magnitude larger than this. Furthermore, these previous studies were carried out under uniform heating, rather than laser irradiation. As shown below, these Au nanoparticle/Fe$_2$O$_3$ composites show no detectible catalysis under uniform heating. Therefore, the CO gas reaction kinetics we observe in this work originate from a fundamentally different catalytic mechanism.

In order to distinguish this plasmonically driven catalysis from standard thermally driven catalysis, we uniformly heated the same gold nanoparticles in the same gas environment to 350 °C without laser irradiation. This is slightly higher than the temperature achieved by plasmonic heating (see Figure 2). The CO$_2$ mass spectrometer signal of this reaction is plotted in Figure 4. Once the CO gas flow is turned on, there is an increase in the CO$_2$ signal, since the Au nanoparticles themselves are slightly catalytic. The CO$_2$ production rate begins to decrease after 3 min, as the catalytic surface becomes coked with amorphous carbon and Fe$_2$O$_3$. This is a well-known problem in catalysis, limiting catalytic performance and lifetime. The same uniform heating reaction was repeated at temperatures of 550 and 900 °C, resulting in more severe coking of the sample surface that could be clearly seen by scanning electron microscopy. These results are very different from those observed under laser irradiation, where the CO$_2$ signal, and hence reaction rate, increased monotonically for 15 min. Here, we observe a reaction rate that is comparable to that achieved under laser irradiation (picoamperes); however, the reaction area is 2–3 orders of magnitude larger than that of the plasmonically driven reactions in Figures 2 and 3, indicating that superior catalytic performance is obtained with plasmonic excitation.

In order to quantify the plasmonic enhancement in the catalytic activity, we compared the CO$_2$ production rate of these Au nanoparticle/Fe$_2$O$_3$ composites under laser irradiation with that under uniform heating.

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In order to quantify the plasmonic enhancement in the catalytic activity, we compared the CO$_2$ production rate of these Au nanoparticle/Fe$_2$O$_3$ composites under laser irradiation with that under uniform heating. Figure 5a shows the mass spectrometer signal for CO$_2$ plotted versus time at a base substrate temperature of 300 °C. The laser is pulsed on and off 10 times with 50 s pulse durations. With the laser on, the CO$_2$ signal rises significantly above the baseline. This
was repeated at several different base substrate tempera-
tures. Figure 5b shows the average CO$_2$ quadrupole mass
spectrometer (QMS) signal under laser irradiation compared
with that under uniform heating over a wide range of base
substrate temperatures. The data show that the laser-
induced catalysis is at least 2–3 orders of magnitude higher
than that of uniform heating. We see no detectible change
in the baseline CO$_2$ signal, even after 25 depositions of Fe$_2$O$_3$
onto the substrate. This 2–3 order-of-magnitude en-
hancement is a lower limit for the plasmonic enhancement,
since the uniform heating data are limited by the noise in
our system.

As a final control experiment, we performed the same
experiment with 785 nm light, which is below the plasmon
resonance energy of the Au nanoparticles. Here, we ob-
served no decomposition of Fe(CO)$_2$ or CO and no deposi-
tion of material on the substrate, even at laser powers 10
times higher than those used with 532 nm. Therefore, in
order for sufficient electric fields to be achieved and signifi-
cant heating to occur, the laser energy must match the
plasmon resonance frequency of the nanoparticles. Also,
regions on the substrate without nanoparticles were irrad-
iated, and no decomposition of CO or deposition of Fe$_2$O$_3$
was observed.

While the amount of CO is known and the amount of CO$_2$
produced can be quantified from the mass spectrometry
data, there are several difficulties associated with determi-
ning the rate constant of these plasmonically driven reactions.
As mentioned above, the Au nanoparticle/Fe$_2$O$_3$ composites
are formed during an early stage of the process and continue
to grow and change their configuration during the reaction
process. These changes can also vary the activation energy
of the reaction with the time, which in turn affects the rate
constant of the reaction. Another difficulty is the undiff-
ferentiated CO$_2$ byproduct from the two oxidation reactions:
2CO + O$_2$ → 2CO$_2$ and 2CO → C + CO$_2$ at high tempera-
tures. The main difficulty, however, in quantifying the rate
constant of this reaction is that the temperature changes
dramatically over the course of the reaction and is non-
uniform over the catalytic surface area.

In conclusion, we demonstrate plasmonically driven
catalysis of CO on Au nanoparticle/Fe$_2$O$_3$ composites. The
catalytic performance of these composites greatly exceeds
that of the Au nanoparticles and Fe$_2$O$_3$ alone, when irrad-
iated with visible light. Control experiments indicate that the
plasmonically driven catalytic reaction rate is several orders
of magnitude higher than that obtained under uniform
heating, without irradiation. We conclude that this enhanced
catalytic reaction is not driven solely by the thermal (plas-
monic) heating of the gold nanoparticles but relies on the
interaction between the plasmonic nanoparticles and the
metal oxide catalyst. The improved catalytic processes
described in this work will likely be extended to other
applications such as solar energy conversion and storage.

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