Untangling Thermal and Nonthermal Effects in Plasmonic Photocatalysis

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Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry in the Graduate School of Duke University

2019
ABSTRACT

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Abstract

Plasmonic photocatalysis exploits the strong light-matter interactions of small metal nanoparticles and offers a sustainable route for the synthesis of fuels such as hydrocarbons and ammonia (NH₃) using light. Illumination of tailored plasmonic photocatalysts or traditional thermal catalysts with intrinsic plasmonic properties leads to several photo-physical effects including: (1) generation of hot carriers, (2) photothermal heating, and (3) local enhancement of the electric field. Demonstrations of the excitation of localized surface plasmon resonances in plasmonic photocatalysis have shown enhanced reaction rates and improved product selectivity at reduced temperatures, which alleviates several problems found in thermally-driven processes. While the injection of hot carriers from the metal nanoparticles is usually proposed as the dominant mechanism, the contribution of plasmon-induced heating must not be neglected. To understand the underlying mechanism in these plasmon-driven processes, the intertwined thermal and nonthermal effects from light must be untangled. This dissertation summarizes our efforts in establishing theoretical and experimental techniques to accurately distinguish between thermal and nonthermal contributions. The intrinsic plasmonic and catalytic properties of supported rhodium (Rh) and ruthenium (Ru) catalysts are investigated in two model reactions of plasmonic photocatalysis: carbon dioxide (CO₂) hydrogenation and NH₃ synthesis.

We begin with an overview of plasmonic photocatalysis (Chapter 1). Fundamental background along with key challenges and opportunities of this emerging field are discussed. In alignment with recent demonstrations, our initial observation of
reaction rate enhancement and photo-induced product selectivity in CO$_2$ hydrogenation
on Rh-c/Al$_2$O$_3$ is attributed to the unique hot carrier mediated process. The fervent debate
on whether these observed hot carrier effects can be simply explained by plasmonic
photothermal heating motivated our quest to determine the true role of light.

For an improved understanding of the nonthermal contribution in plasmonic
photocatalysis, we must first address the effects of photothermal heating. Chapter 2
describes a multi-thermocouple strategy to monitor the complex thermal profiles of the
catalyst under reaction conditions. Using this method, we derive an effective thermal
contribution for illuminated conditions to understand how photogenerated carriers
enhance the nonthermal reaction rate for CO$_2$ methanation on Rh/TiO$_2$ photocatalysts.
We investigate the effect of support and reaction order for CO$_2$ and H$_2$ to gain insight on
the mechanism of nonthermal reactions.

This approach is then applied to investigate the plasmonic properties of a
traditional thermal Ru-based catalyst for NH$_3$ synthesis in Chapter 3. It is shown that
weak and broadly absorbing plasmonic properties of Ru enables the opportunity to
investigate photothermal heating effects. Light can be used to produce controlled thermal
gradients within the catalyst to achieve a balance between thermodynamics and kinetics.
Due to the contrast in thermal profiles produced under dark thermal and illuminated
conditions, residual effects related to the photothermal heating may be misrepresented as
nonthermal effects. We experimentally capture both photothermal and thermal
contributions via indirect illumination of the catalyst and confirm that this system is
dominated by photothermal effects.
We then employ this indirect illumination technique in plasmon-enhanced CO₂ methanation on a Rh/TiO₂ photocatalyst to verify the proposed hot-carrier mediated process from Chapter 2. The extracted nonthermal methane (CH₄) production rate has a linear dependence on the top surface temperature, distinctly different from an exponential dependence for thermal catalysis. Interestingly, the apparent quantum efficiency from the nonthermal contribution has no dependence on light intensity but maintains a linear dependence on top surface temperatures between 200 and 300 °C. However, past a threshold temperature of ~350 °C, heat begins to affect the light-driven reaction negatively as the reverse reaction of CH₄ reforming is also enhanced by illumination.

Throughout the debate over the dominant mechanism in plasmonic photocatalysis, the observation of product selectivity cannot be explained due to thermal effects. Chapter 5 revisits our initial investigation of plasmon-enhanced CO₂ hydrogenation with our newly established experimental techniques to attest that plasmon-induced product selectivity in the nonthermal reaction occurs through a hot carrier mechanism. Under illumination, the rate of CH₄ is significantly enhanced and this photo-selectivity can be attributed to selective activation of specific reaction intermediates by photo-generated hot electrons.

The strategies by which we discriminate thermal and nonthermal contributions and extract the reaction rate and efficiency of hot carrier driven reactions may be applied universally to any explorations of plasmonic photocatalysis. Our analysis affirms that plasmonic behavior provides new control over the catalytic behaviors of metal nanostructures when the mechanism is thermal, nonthermal, or both.
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List of Abbreviations

AQE – apparent quantum efficiency
DFT – density functional theory
DOS – density of states
IR – infrared
LSP – localized surface plasmon
NC – nanocube
NIR – near infrared
NP – nanoparticle
SEM – scanning electron microscope
sccm – standard cubic centimeters per minute
TEM – transmission electron microscope
UHP – ultra high purity
UV – ultraviolet
XPS – X-ray photoelectron spectroscopy
XRD – X-ray diffraction
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Chapter 1: Introduction to Plasmonic Photocatalysis

1.1 Overview

The insatiable demand for energy has led to increased atmospheric concentrations of carbon dioxide (CO$_2$), while the growing world population necessitates the production of synthetic fertilizers via nitrogen (N$_2$) fixation. Despite the perpetual feedstock of water (H$_2$O), CO$_2$, and N$_2$, the grand challenge in CO$_2$ reduction and N$_2$ fixation comes from their high stability under standard conditions and their low propensity for conversion. Both processes have been achieved on an industrial scale but require high temperature, high pressures, and several recycling steps that consume up to 2% of the world’s energy supply annually.$^1$ Ironically, the Haber-Bosch process for synthetic fertilizer is responsible for about 3% of all CO$_2$ emissions.$^2$ In midst of the global energy crisis, the emerging field of plasmonic photocatalysis brings promise of a sustainable future and a balance between human needs and natural resources. Due to strong light-matter interactions, plasmonic metal nanoparticles (NP) have been heralded as a new class of photocatalysts capable of drastically improving the conversion of solar energy into valuable fuels.$^{1,3}$

Upon illumination, two types of electronic excitations can take place in plasmonic metal NPs.$^4$ Intraband excitations refer to electronic excitations from filled $s$ states below the Fermi level to empty $s$ states above the fermi level (Fig. 1.1i). Localized surface plasmon (LSP) resonance effects such as a collective oscillation of the conduction electrons and large absorption cross-sections occur when the light frequency is resonant with the metal’s plasma oscillation frequency.$^{5-8}$ In addition, excitations from filled $d$
states below the Fermi level to empty $s$ states above the Fermi level are known as interband excitations (Fig. 1.1ii).

![Band diagram](image)

**Figure 1.1. Band diagram (energy ($E$) versus momentum ($k$)) depiction of photon absorption in metals.**

(i) $s$-to-$s$ intraband excitations or (ii) $d$-to-$s$ interband excitations. Intraband excitations require a change in momentum whereas interband excitations are direct electronic excitations, which do not require a change in momentum. This figure is adapted with permission from Ref 4.

Both types of transitions contribute to absorption of light, which manifest itself in the optical response of the metals. The decay of plasmons results in photo-induced phenomena including generation of hot carriers, photothermal heating, and local enhancement of the electric field (Fig. 1.2). These nanomaterials have been exploited for a variety of applications such as surface-enhanced Raman (SERS) and fluorescence spectroscopy, optoelectronics, and recently photocatalysis.
1.2 Fundamentals of plasmonics

The remarkable optical properties of plasmonic materials are determined by their dielectric constant, which is a measure of how an electric field affects, and is affected by, a dielectric medium. The dielectric function of metals is strongly frequency dependent and has both real and imaginary components. Generally, the real part (Fig. 1.3a) determines the position of the LSP resonance while the imaginary part (Fig. 1.3b) determines the dephasing.\(^8,18\) This resonance condition depends on the wavelength dependent dielectric function of the nanoparticle (\(\varepsilon_1\)) as well as the dielectric function of the surrounding medium (\(\varepsilon_m\)). When the condition where \(\varepsilon_1 = -2\varepsilon_m\) is satisfied, the
particle is driven into resonance resulting in a strong increase in the absorption and/or scattering at that wavelength.

![Figure 1.3. Dielectric properties of metals.](image)

(a) The real part of the dielectric function, the black line represents the case where \( \varepsilon_1 = -2\varepsilon_{\text{m, air}} \). (b) The imaginary part of the dielectric function. This figure is adapted with permission from Ref 4.

Upon photoexcitation at its LSP resonance, a plasmonic NP can absorb light from an area larger than its physical cross section (Fig. 1.4a).\(^{12}\) Photoexcitation of electrons from filled states to unfilled states generates a nonthermal electron distribution (Fig. 1.4b). Electron oscillations then relax radiatively or non-radiatively on ultrafast timescales of femtoseconds to picoseconds. Radiative relaxation enables re-emission of photons (scattering) while non-radiative relaxation via Landau damping generates hot electrons and holes (absorption). Landau damping is the physical mechanism that contributes to the imaginary, or absorptive, part of the dielectric function of a metal. Within 100 fs, the energy of these charge carriers is redistributed within the nanostructure.
via electron-electron interactions and subsequently electron-phonon collisions into a Fermi-Dirac thermal distribution (Fig. 1.4c).\textsuperscript{19}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic representation of plasmon excitation and relaxation in metal NPs.}
(a) The nanoparticle collects light from an area larger than its physical cross section when illuminated at the LSPR energy. (b) Surface plasmons relax radiatively by scattering and non-radiatively via Landau damping to form hot electron/hole carriers. c) The hot carriers relax into a Fermi-Dirac distribution with a high effective temperature through electron-electron interactions. d) The energy of hot carriers dissipates to the crystal lattice of metal NPs and its environment. This figure is adapted with permission from Ref 12.

Within 10 ps, these hot carriers interact with their surroundings, including transferring to adsorbed molecules, nearby solvent molecules, and scattering off phonons in the metal lattice. This thermalization process leads to direct heating of the plasmonic nanostructure, which eventually reaches equilibrium within the local environment in hundreds of picoseconds (Fig. 1.4d).\textsuperscript{12} Plasmonic properties strongly depend on composition, shape, size and local environment, all of which can be precisely tuned so
that these functional nanostructures can adjustably absorb light at desired wavelengths (Fig. 1.5).\textsuperscript{7,15,20-26}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{\textbf{Tunable plasmonic resonance peaks.} Extinction properties can be tuned by changing size of (a) Au and (b) Ag nanoparticles. (c) Increasing the size of Ag nanoparticles red-shifts the plasmonic peak. This figure is adapted with permission from Ref 15 and 27.}
\end{figure}

Compared to the electric fields of the incident light, local fields can be enhanced from $\sim 10^3$ times at the surface of a single particle (Fig. 1.6a) to $10^6$ times in between two particles separated by $\sim 1$ nm, otherwise known as hot spots (Fig. 1.6b).\textsuperscript{12,15} This feature has been valuable for applications in SERS.
1.3 Advantages of plasmonic photocatalysis

Of the three major light-induced effects, photo-generated hot carriers and photothermal heating have been recognized as key enhancement factors in catalytic reactions. Local light to heat conversion and collective heating effects in metal nanoparticle solutions have been utilized for nanoparticle synthesis where the plasmon-mediated heating can be orders of magnitude more energy efficient than conventional chemical vapor deposition (CVD) or electron beam lithography. Collective heating effects can also benefit exothermic reactions in which higher temperatures lead to increased reaction rates.

Despite the numerous investigations of photothermal heating, hot carrier-mediated processes have become more appealing as it pertains to selective photocatalysis to access reaction pathways that are not possible in purely thermal reactions. These hot carrier mediated processes typically exhibit reaction rates with a more efficient super-
linear dependence on light intensity, \((R_{\text{photo}} \propto \nu, n > I)\)^{6,41-43} and have several advantages over traditional thermal catalysis (Fig. 1.7).

**Figure 1.7. Thermal and plasmonic (electron-driven) molecular dissociation on heterogeneous catalyst surfaces.**
Dissociation of a diatomic molecule via (a) thermal activation, (b) electron-driven process by formation of a transient negatively charged species which decays to a higher vibrational energy state. (c) Electron-driven dissociation with a contribution from secondary electron injections at high incident photon flux (d) Selective targeting of reaction pathways in plasmonic reactions (top) that are unselective in purely thermal reactions (bottom). This figure is adapted with permission from Ref 6.

Prior to thermalization, some hot carriers generated in the plasmonic nanostructure may transfer over to an attached material (Fig. 1.8a). Most notably, transfer into unoccupied anti-bonding orbitals, otherwise known as the lowest unoccupied
molecular orbital (LUMO), of adsorbates can weaken chemical bonds and accelerate bond breaking (Fig. 1.7b,c & 1.8a).\textsuperscript{6,43} Specifically, hot carriers can help in two ways: (1) by reducing activation barriers of key steps in chemical reaction and (2) by weakening metal-intermediate interactions to facilitate desorption of products and regeneration of free sites.\textsuperscript{44} Alternatively, plasmon decay can result in direct excitation of charge carriers to states of the adsorbate-metal complex at the interface (Fig. 1.8b).\textsuperscript{19}

![Figure 1.8. Indirect and direct charge-transfer mechanisms.](image)

(a) In the indirect charge-transfer mechanism, plasmon relaxation results in an electron distribution that is characterized by a high concentration of low-energy charge carriers. Those with adequate energy can transfer to lowest unoccupied adsorbate orbitals (LUMO). (b) In the direct mechanism, decay of a resonant plasmon causes direct excitation of an electron to an unoccupied adsorbate state, without the formation of an excited electron distribution in the metal. This figure is adapted with permission from Ref 4.

This direct charge transfer mechanism enables selectivity that is unachievable in thermal catalytic reactions (Fig. 1.7d & 1.8b). Accordingly, the unique control of plasmonic photocatalysis hinges on the design of materials that selectively deposit the energy of photons into targeted adsorbate orbitals associated with the activation of desired bonds.\textsuperscript{7,40,45-50} In an investigation of plasmonic metals, non-plasmonic metals, and their alloys, it was observed that a photon energy threshold exists in each photocatalytic reaction; only photons with energy higher than the energy level of the LUMO can initiate
reactions. By tuning photon and LSP resonance energies so that hot carriers are injected into specific anti-bonding orbitals of specific reaction intermediates, product selectivity may be manipulated. Finally, plasmonic photocatalysis offers a compelling remedy to the exorbitant energy requirements of traditional thermal catalysis while simultaneously extending the stability and lifetime of catalysts.

1.4 Rational design of plasmonic photocatalysts

An ideal plasmonic photocatalyst should have both catalytic and plasmonic components. However, many commonly studied metals such as Gold (Au), Silver (Ag), and Copper (Cu), have resonant frequencies limited to the visible and near-infrared regions and poor catalytic properties. To satisfy both conditions, another level of tunability has been introduced through the synthesis of multi-metallic heterostructures. Bimetallic heterostructures in the form of binary NPs, alloys, and core-shell have been shown to lower costs, offer higher light harvesting efficiency, and promote photocatalytic activity through synergistic effects. More complex core-shell structures with a plasmonic core and a shell of metal-organic-framework (MOF), reduced graphene oxide (r-GO), or semiconductors (Al₂O₃, SiO₂) have also been synthesized. Tailoring the composition and shell thickness of these hybrid core-shell heterostructures maximizes the plasmonic-catalytic efficiency by increasing hot carrier generation/transfer and suppressing photothermal heating or vice versa.

1.5 Recent investigations of thermal vs. nonthermal effects

Currently, there is heated debate on the relative importance of the nonthermal contribution from hot carriers versus the thermal contribution from photothermal heating.
in plasmonic photocatalysis, as the overall enhancement may be due to a combination of these intertwined effects.\textsuperscript{76-78} In parallel to the rational design of plasmonic photocatalysts prone to a specific mechanism, these two mechanisms has been investigated through the temperature-sensitive synthesis of Au@Ag core@shell nanoparticles (Fig. 1.9a).\textsuperscript{30}

**Figure 1.9. Quantifying photothermal and hot carrier effects in plasmon-driven synthesis of Au@Ag core@shell nanoparticles.**

(a) Schematic representation of the temperature-activated synthesis of Au@Ag core@shell nanoparticles in the dark. (b) Apparent rate of the Ag shell growth reaction in the dark as a function of temperature. The inset shows the same data as an Arrhenius plot. (c) Natural logarithm of the apparent rate of silver shell growth as a function of laser irradiation power. This figure is adapted with permission from Ref 31.

Kamarudheen et al., compared the rate of Ag shell growth in the dark at different temperatures monitored by an IR camera with that of plasmon-excited growth at varied laser intensities (Fig. 1.9b,c). For a laser power of 400 mW, the rate measured is comparable to the one observed when the nanoparticle solution is heated to a temperature
of ~50 °C in the dark. However, based on numerical modeling of light propagation and heat diffusion, laser irradiation at 400 mW corresponds to an average solution temperature of 37 °C. Here, collective heating effects can only account for ~30% of the total reaction rate whereas the remaining ~70% are due to hot-electron driven reduction of Ag\(^+\) ions on the Au nanoparticle surface or two photon-mediated reduction of Ag\(^+\) to Ag\(^0\) assisted by the near-field enhancements on the Au nanoparticle surface.

Figure 1.10. Quantifying hot carrier and thermal contributions NH\(_3\) decomposition using a plasmonic Cu-Ru antenna-reactor photocatalyst.  
(a) A 3D representation of \(E_a(\lambda, I)\) for different wavelengths and intensities. (b) Reaction order with respect to \(P_{NH_3}\) in photocatalysis (6.4 W cm\(^{-2}\) white light) and thermal catalysis (427 °C). (c) Schematic energies of elementary reaction steps for NH\(_3\) decomposition. This figure is adapted with permission from Ref 79.
Considering the relationship between reaction rate and temperature, reduced apparent activation energies, $E_a$, have been observed in the presence of illuminated plasmonic photocatalysts$^{67,79,80}$ Using a plasmonic Cu-Ru alloy photocatalyst for NH$_3$ decomposition, activation energies were characterized (Fig. 1.10a) for various illuminated conditions to examine the role of hot carriers in activation barrier reduction.$^{79}$ In thermal reactions, the rate determining step is the associative desorption of N$_2$. The increase in reaction order with respect to NH$_3$ pressure (Fig. 1.10b) and reduction in $E_a$ upon illumination suggests that hot carriers induced by resonant illumination modify the reaction kinetics by reducing the activation barrier for associative desorption of N$_2$ while simultaneously decreasing the surface coverage of adsorbed intermediates (Fig. 1.10c).

Both studies conclude that a hot carrier mediated process is the dominant mechanism. However, theoretical studies have challenged these claims and attribute the enhancement of catalytic reaction rates and reduction in apparent activation energies to plasmonic photothermal heating effects.$^{77}$

### 1.6 CO$_2$ hydrogenation on Rh-based plasmonic photocatalysts

In our own demonstration of plasmonic photocatalysis, aside from the usual observations of reaction rate enhancement and apparent activation energy reduction, photo-induced product selectivity was also observed for CO$_2$ hydrogenation on Rh-c/Al$_2$O$_3$. This Rh-based catalyst consisted of 37 nm nanocubes that strongly absorbed light in the UV region.$^{81,82}$ Unlike typical plasmonic candidates with poor catalytic properties, supported Rh nanoparticles and molecular Rh complexes are widely used as thermal catalysts in hydrogenation, hydroformylation, oxidative coupling, and nitrogen
oxides reduction (in three-way catalytic converters).\textsuperscript{83-88} As a noble metal, Rh is extremely stable against severely oxidative and aqueous environments. This lack of oxide layer formation on Rh allows for direct contact between the Rh nanostructures and adsorbates, a property that is essential for charge transfer in plasmonic photocatalysis. Additionally, the imaginary part of electric permittivity of Rh is larger than Au and Ag.\textsuperscript{89} While this aspect weakens the light concentration capability of Rh nanostructures, it favors the non-radiative decay of plasmons to generate hot carriers for chemical reactions. The superior catalytic activities, plasmonic properties and chemical stability of Rh nanostructures promise a compelling system in which to study plasmonic photocatalysis.

CO\textsubscript{2} hydrogenation on transition metals at atmospheric pressure proceeds through two competing pathways: CO\textsubscript{2} methanation (CO\textsubscript{2} + 4H\textsubscript{2} → CH\textsubscript{4} + 2H\textsubscript{2}O), and reverse water gas shift (RWGS, CO\textsubscript{2} + H\textsubscript{2} → CO + H\textsubscript{2}O).\textsuperscript{90} CO\textsubscript{2} hydrogenation under UV and blue light exhibited selectivity towards CH\textsubscript{4} of >98% and >86%, respectively, much higher than the selectivity of ~60% under thermal conditions (Fig. 1.11a). These results indicated that photons almost exclusively promoted the production of CH\textsubscript{4} with little perturbation in the production of CO. To the best of our knowledge, this is the first report of selective activation among competing pathways in plasmonic photocatalysis. To study the influence of excitation wavelength, varied light sources were also used (Fig. 1.11b). At 350 °C and under the same intensity, photo-enhanced CH\textsubscript{4} production is observed for all light sources used. The rate enhancement was even more significant at lower reaction
temperatures. However, under the same photon flux, the production rate is enhanced to a lesser extent as the excitation wavelength increases.

**Figure 1.11. CH₄ selectivity and production rate under illuminated and dark conditions.**
(a) CH₄ selectivity is plotted as a function of measured chamber temperature, \( T_c \), under dark, UV (365 nm), and blue (455 nm) illumination. (b) Overall CH₄ production rates under dark, UV, blue and NIR (805 nm) at the same intensity and same photon flux. This figure is adapted with permission from Ref 80.

As the mismatch in LSP resonance and excitation widens, lower energy photons are unable to generate hot carriers with the appropriate energy to drive reactions and the photothermal effect becomes more dominant. The activation energy was also reduced from 79 kJ mol⁻¹ in thermal reactions to 50 kJ mol⁻¹ in photo-reactions. Control experiments using pure Al₂O₃ and isotopic labeling experiments with deuterium confirmed that CH₄ and CO were produced from the photocatalytic reactions on the Rh cubes rather than from contaminants or Al₂O₃. No other carbon-containing product was detected in our experiments, and the reaction rates responded to light instantly and reversibly.

In our experiments, the selective photocatalytic CH₄ production emerges from the selective activation of the key intermediate CHO in the CO₂ methanation pathways by
hot electrons. Density functional theory (DFT) calculations were performed for adsorbed CHO and CO, key intermediates established in previous reports for CH₄ and CO production respectively, on the dominant Rh (100) facet in Rh cubes. The computed local density-of-states (LDOS) of the metal-adsorbate systems are presented in Figure 1.12.

![Figure 1.12. DFT calculations of CHO and CO intermediates on the Rh(100) surface.](image)

(a) LDOS for adsorbed CHO on C(p₂), O(p₂), and Rh(d) orbitals. (b) LDOS for adsorbed CO on C(pₓ), O(pₓ), and Rh(d) orbitals. All energies are referenced to the Fermi level. The insets are magnified plots of the anti-bonding regions. This figure is adapted with permission from Ref 80.

The bonding interactions in both the CHO and CO systems lie ~6 eV below the Fermi level, suggesting a minimal role for hot holes in this process. For CHO, the C-O π* anti-bonding bands, which can accept hot electrons to weaken the C-O bond and facilitate CH₄ production, can be easily identified on the C(p₂) and O(p₂) orbitals at ~2.0 eV above the Fermi level (Fig. 1.12a). On the other hand, the very weak and broad anti-bonding Rh-C interactions observed on the C(pₓ) orbital at ~1.0 eV for CO (Fig. 1.12b) suggests a much smaller possibility of accepting UV photo-excited hot electrons by the CO intermediate compared to the CHO intermediate. Thus, the photo-generated hot electrons
preferentially activated the CHO intermediate and enhanced CH₄ production, while only a small enhancement was observed for CO production. Moreover, these results are also consistent with the lower selectivity towards CH₄ observed under non-resonant, lower energy blue light (~85%): the lower energy hot electrons had a lower probability of populating the higher energy (~2.0 eV) anti-bonding orbital of the CHO intermediate and a higher probability of populating the lower energy (~1.0 eV) orbital of the CO intermediate.

While our initial experimental results along with DFT calculations support a hot carrier mediated mechanism, the overall nonthermal effect may be overestimated due to imprecise temperature measurements. Efforts to improve quantification of thermal effects involve nanoscale thermometry techniques such as IR pyrometry, molecular thermometers, scanning probe thermometry, and most notably SERS via analysis of Stokes and Anti-Stokes intensities. However, implementing these techniques while simultaneously monitoring reaction dynamics remains a challenge.

This dissertation details our recent explorations in developing new strategies to characterize the thermal and nonthermal contribution in plasmonic photocatalysis. Here, we define the nonthermal reaction to represent contributions to the overall reaction that cannot be explained or achieved by traditional heating or photothermal heating. Rh and Ru-based photocatalysts with intrinsic plasmonic and catalytic properties are studied in two model reactions: CO₂ hydrogenation and NH₃ synthesis, to gain insight into the underlying mechanisms in plasmonic photocatalysis.
Chapter 2: Monitoring Complex Thermal Profiles of Photocatalysts under Reaction Conditions

The content of this chapter is adapted from our publication (Nano Letters, 2018, 18, 3, 1714-1723).\textsuperscript{105} We acknowledge our coauthors, Dr. Du Zhang, Dr. Neil Qiang Su, and Dr. Weitao Yang at Duke University, for DFT calculations. We acknowledge our coauthors, Ms. Yael Gutierrez and Dr. Fernando Moreno at the University of Cantabria, for the simulations of optical properties of Rh photocatalysts. We also acknowledge our coauthor, Dr. Xiao Zhang, Dr. Matthew E. Reish and Dr. Henry O. Everitt for helpful discussions about experimental design.

2.1 Introduction

Recently, the plasmonic community has generated excitement by demonstrating that the transfer of hot carriers into anti-bonding orbitals of surface adsorbates at the rate-determining step (RDS) may select products and accelerate chemical reactions by weakening certain chemical bonds.\textsuperscript{40,45-49} However, absorbed light also heats these metal nanoparticles, so claims about the beneficial effects of hot carriers must first convincingly distinguish the effects of “nonthermal” hot carriers from those of “thermal” hot surfaces. Unfortunately, it is quite difficult to measure the temperature of individual metal nanoparticles, so this discrimination has primarily depended on calculations that estimate the degree of photothermal heating or on simple measurements of the catalyst’s thermal activity prior to illumination. Often, the bulk and surface temperature of the catalyst bed are different due to compromises in designing the reactor chamber to enable the use of spectroscopic techniques and illuminated conditions.\textsuperscript{106} For traditional thermal
catalytic reactions, comparison of Arrhenius plots enable a temperature correction. However, this simple correction is not possible for plasmon-enhanced catalytic reactions where both thermal and nonthermal effects can contribution to the overall reaction rate.

Here we demonstrate a more comprehensive experimental exploration and discrimination of thermal and nonthermal catalytic activities under illumination. Our exploration uses Rh nanoparticles, already well known as an effective thermal catalyst\textsuperscript{86-88,91,107,108} and recently demonstrated as an effective plasmon-enhanced catalyst through the discovery of its ultraviolet (UV) plasmonic behavior.\textsuperscript{80,81,89,109} Specifically, the CO\textsubscript{2} hydrogenation reaction is investigated, and by using much smaller Rh nanoparticles on a more active titanium dioxide (TiO\textsubscript{2}) support, we dramatically enhance the activity of the catalyst to create conditions under which thermal and nonthermal catalytic behaviors are at work simultaneously and cooperatively. Measurements and a model describing the temperature profile of the catalyst bed are proposed to obtain the effective thermal and nonthermal reaction rates under illumination with and without external heating. Through reaction order studies, our analysis affirms that plasmonic properties provide new control over the catalytic behaviors of metal nanostructures when the mechanism is thermal, nonthermal, or both.

\textbf{2.2 Experimental methods}

\textbf{2.2.1 Synthesis of Rh-based photocatalysts}

Rh nanospheres and nanocubes were synthesized by polyol methods. For Rh nanospheres, 25 mg polyvinylpyrrolidone (PVP, M.W. $\approx$ 55,000, Aldrich) was dissolved in 5.6 ml ethylene glycol (EG, J. T. Baker) in a 20 ml glass vial and stirred in an oil bath
at 160 °C for 30 min. 12 mg rhodium(III) chloride hydrate (RhCl₃·xH₂O, 40% Rh, Pressure Chemical) was separately dissolved in 0.4 ml EG and quickly injected into the hot solution to initiate nanoparticle growth. The reaction mixture was stirred for another 30 min and then cooled to room temperature. The Rh nanocubes were synthesized by a modified slow-injection polyol method. 109 54 mg potassium bromide (KBr, ACS, Acros) was dissolved in 2 ml EG in a 20 ml glass vial and stirred in an oil bath at 160 °C for 1 h. 12 mg RhCl₃·xH₂O and 25 mg PVP were dissolved in 2 ml EG separately and injected into the hot reaction mixture by a two-channel syringe pump at a rate of 1 ml h⁻¹. The injection was paused for 15 min after adding 20 μl of the Rh precursor. After complete injection of the precursor, the reaction mixture was stirred for another 30 min and then cooled to room temperature.

The solution of Rh nanoparticles was washed with deionized water/acetone until no Cl⁻ and Br⁻ were detected in the supernatant. The nanoparticles were dispersed in 20 ml ethanol and impregnated on ~95 mg oxide supports to achieve ~5 wt% Rh loading. The oxide supports were Al₂O₃ (Degussa, Alu Oxide C, specific surface area 85~115 m² g⁻¹) and TiO₂ (Degussa, P25, specific surface area 35~65 m² g⁻¹). The supports were activated in air at 500 °C for 5 h before impregnation. Upon evaporation of the solvent, the obtained solid was ground and calcined in air at 400 °C for 2 h.

2.2.2 Material characterization

Transmission electron microscopy (TEM) images were collected by a FEI Tecnai G² Twin operating at 200 kV. The TEM samples were prepared by dispersing the photocatalysts in ethanol with sonication and depositing on a copper grid coated with a
carbon film (Ted Pella, 01813). Diffuse reflectance ultraviolet-visible extinction spectra were obtained on an Agilent Cary 5000 equipped with an external diffuse reflectance accessory (DRA-2500). The composition of the photocatalysts was measured by a Kratos Analytical Axis Ultra X-Ray Photoelectron Spectrometer (XPS).

### 2.2.3 Gaseous reaction system setup for catalytic reactions

All reactions were carried out in a custom-built gaseous reaction system. The system consists of a gas delivery system, a fixed-bed reactor equipped with a quartz window, LED/laser light sources, an online mass spectrometer, and a multi-thermocouple setup with programmable temperature controller (Fig. 2.1).

**Figure 2.1. Gaseous reaction system for investigations of plasmonic photocatalysis.**
(a) Photograph and (b) schematic of the gas delivery system composed of a fixed-bed reactor equipped with a quartz window, LED/laser light sources, an online mass spectrometer, and a multi-thermocouple setup with programmable temperature controller. (c) Close-up view of the reaction chamber and LED liquid light guide.
Reactant gases are obtained from Airgas and the flow rates are individually controlled using mass flow controllers (GFC, 200 sccm, Aalborg). The photocatalytic reactor (Harrick, HVC-MRA-5) has a stainless-steel body, a copper catalyst cup, and a detachable quartz window. The reactor is equipped with two ports underneath to circulate cooling water from a water chiller. The catalyst cup has a diameter of ~6 mm and a height of ~3 mm. The quartz window has a diameter of 8 mm to enable illumination of the catalyst surface. The temperature of the photocatalyst was controlled by a PID temperature controller kit (Harrick, ATK-024-3). The light sources used include light-emitting diodes (LEDs) of varied intensity and wavelength (Prizmatix, UHP-F: 365 nm, 385 nm, 405 nm, 455 nm, 525 nm, broad spectrum white light) or an NIR laser diode (Opto Engine LLC, MDL-H-800-200MW, 805 nm). Emission spectra (Fig. 2.2) of all light sources are measured with a CCD-based spectrometer (Thorlabs, CCS200).

![Emission spectra of light sources](image)

**Figure 2.2. Emission spectra of light sources.**
Light-emitting diodes (LEDs) include 365 nm, 385 nm, 405 nm, 455 nm, 525 nm, broad spectrum white light. NIR laser diode is at 805 nm.
The effluent gas was analyzed by a quadrupole mass spectrometer (Hidden, HPR-20) equipped with a Faraday cup and secondary electron multiplier detector. The responsivity for each reactant and product gas was calibrated with commercial calibration gas or house-made gas mixtures with known composition.

2.2.4 Operation of catalytic reactions

Powdered Rh photocatalysts were loosely packed into the copper catalyst cup and were thick to ensure complete absorption of light for the catalytic measurements. The Rh photocatalysts were first reduced under 60 standard cubic centimeters per minute (sccm) H₂ and 40 sccm Ar at 350 °C for 2 h and then the gas flow was switched to a mixture CO₂, H₂, and Ar with desired ratio and a total flow rate of 250 sccm. For illuminated conditions, the light source was coupled into a liquid light guide with a diameter of 5 mm and delivered to the top of the catalyst through the quartz window. The LEDs were controlled by 0-5 V analog signal while the NIR laser was manually controlled and the resulting output power was measured with a thermopile power meter (Thorlabs, PM310D). For each condition, at least 30 minutes elapsed before ten sequential measurements were made to ascertain the steady-state concentration of each gas and the associated reaction rates and uncertainties. All reactions were operated under atmospheric pressure.

For each analyte of interest, mass spectrometer signals were calibrated using calibration gases (Gasco, Inc.) over a range of concentrations and with Ar gas as an internal standard. For example, the CH₄ reaction rate was calculated according to the following equation:
\[ R_{\text{CH}_4} \left( \text{\textmu mol g}^{-1} \text{s}^{-1} \right) = \frac{\left( \frac{\text{CH}_4}{\text{Ar}} \text{ ratio} \right) \left( f_{\text{Ar}} \text{ sccm} \right) \left( 10^6 \text{ \mu mol mol}^{-1} \right)}{\left( 60 \text{ s min}^{-1} \right) \left( 22400 \text{ ml mol}^{-1} \right) \left( m_{\text{catalyst}} \text{ g} \right)}, \]  

where \( f \) is the flow rate of the feeding Ar.

### 2.2.5 Calculation of the penetration depth

The penetration depth (\( \delta \)) is defined as the depth at which the intensity of the radiation inside the material falls to \( \frac{1}{e} \) of its original value. The penetration depth for an electromagnetic wave at normal incidence is given by

\[ \frac{1}{\delta} = \frac{4\pi}{\lambda} k, \]  

where \( \lambda \) is the wavelength of the illuminating electromagnetic field and \( k \) is the imaginary part of the refractive index of the material, which can be calculated from its effective dielectric function. To obtain \( k \), the catalyst is modeled as an oxide host with inclusions of dipolar metallic NPs (Rh spheres or cubes) using Maxwell-Garnett effective medium theory.\(^\text{110}\) The effective dielectric function (\( \varepsilon_{\text{eff}} \)) is thereby given through

\[ \frac{\varepsilon_{\text{eff}} - \varepsilon_h}{\varepsilon_{\text{eff}} + 2\varepsilon_h} = f \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h}, \]  

where \( \varepsilon_h \) and \( \varepsilon_i \) are the dielectric functions of the host oxide\(^\text{111}\) and Rh inclusions\(^\text{112}\), respectively. \( f \) is the volume density of inclusions embedded in the host, derived for each experimental configuration from the weight percentage of Rh (wt%) considering the
Rh NP volumes and the Rh and oxide densities. From the value $\epsilon_{eff}$, $k$ is calculated through $k = Im(\sqrt{\epsilon_{eff}})$ to estimate the penetration depth.

### 2.2.6 Density Functional Theory (DFT) calculations

All the periodic boundary condition (PBC) calculations in this work were performed with the Vienna Ab initio Simulation Package (VASP).\textsuperscript{113} The Perdew-Burke-Ernzerhof (PBE)\textsuperscript{114} exchange-correlation (xc) functional was used along with its corresponding projected augmented wave (PAW) pseudopotentials. The semi-empirical D2 model\textsuperscript{115} was applied to describe the van der Waals interactions. A plane-wave cutoff of 500 eV was chosen. The Gamma centered $2\times3\times1$ k-point grid was used for the structural relaxations (converged to 0.01 eV Å\textsuperscript{-1}), and $8\times12\times1$ for the projected LDOS calculations and for the plotting of band densities. Periodic boundary conditions were used in all three directions for the fcc Rh model. A vacuum of $>15$ Å was used in the x-direction to separate the Rh(100) surface slabs (parallel to the yz-plane) containing 4 layers of Rh atoms. The two adsorbed CHO groups separated by bare Rh surface, two H groups, and two CO groups were placed on the exposed Rh(100) surface. The optimized structures of the supercell models are generated with GaussView.\textsuperscript{116} The band density plots are produced with VESTA.\textsuperscript{117}
2.3 Results and discussion

2.3.1 Direct measurements of catalyst temperature

2.3.1.1 Modified reaction chamber with inserted thermocouples

The catalyst temperature can be difficult to measure due to evolving reaction conditions and limitations in the reactor design. The addition of a light component further complicates this situation. In the original commercial reactor, the internal chamber thermocouple ($T_c$, 0.8 mm sheath diameter) is located within the heating block and is used to regulate the thermal contribution from the heating element and maintain a set temperature (Fig. 2.3). Although the sample cup is made of copper, a highly conductive material, the remoteness of the $T_c$ to the catalyst bed coupled with dynamic reaction conditions necessitates improved methods to study the catalyst temperature.

![Diagram](image)

Figure 2.3. Schematic of modified reaction chamber for multi-thermocouple setup.
(a) Side view, thermocouples are inserted from the gas outlet port and through a flat mesh catalyst holder. $T_1$ and $T_2$ are positioned at the center of the top and bottom surface of the catalyst, respectively. $T_c$ is the original built-in thermocouple that measures the temperature of the heating block. (b) Top view shows the relative positions of the three thermocouples.
To monitor the thermal profile of the catalyst, K-type thermocouple probes with a sheath diameter of 0.5 mm (Omega) are inserted into the reaction chamber through the gas outlet port and bent upwards to the desired top and bottom surface positions (Fig. 2.4a). In a proof of concept experiment, fine fused quartz wool was used as a catalyst holder to allow facile insertion of the thermocouples. However, due to the fibrous nature of the quartz wool, it was difficult to maintain a flat bottom surface and replicate setups between batches of experiments. Instead, a piece of micronic stainless steel filter cloth (635 Mesh T316, 20 micron opening, TWP Inc.) was cut into a 6 mm diameter circle and punctured with a 25 gauge needle through the middle. This created a ~0.5 mm hole for the inserted top surface thermocouple (Fig. 2.4b). Subsequently, the catalyst is loaded over the mesh holder and just barely covers the tip of the $T_1$ thermocouple (Fig. 2.4c). The tip is covered to prevent direct illumination from light sources and changes in the location of the thermocouple due to flowing gases. When the tip is exposed, the flowing gases can easily change the top surface terrain and form a cavity around the thermocouple, thus resulting erroneous temperature measurements. However, having a minimal amount of catalyst covering the tip ensures more accurate and reliable measurements of the top surface temperature of the catalyst under reaction conditions. For all future experiments, $T_1$ and $T_2$ represent the temperature measured at the center of the top and bottom surface of the catalyst, respectively.
**Figure 2.4. Photographs of multi-thermocouple setup.**
(a) 0.5 mm sheath diameter thermocouples are inserted through the gas outlet port and bent to central positions to measure the top and bottom surface temperature. (b) Stainless steel mesh holder with hole for inserted $T_1$ thermocouple. (c) Catalyst is loaded over mesh holder and barely covering the tip of $T_1$ thermocouple.

Initially, the thermocouples were inserted through a punctured hole rubber sleeve stopper into the gas outlet port (Fig. 2.5a). However, over time, the two holes caused leakage of flowing gases. Instead, a compression thermocouple assembly was integrated using a piece of rubber and a ¼” Swagelok nut (Fig. 2.5b and c). This compression design secured the thin thermocouples in place and provided a leak tight seal for flowing gas applications.

**Figure 2.5. Inserted thermocouple assembly.**
(a) Red rubber sleeve stopper is used as a make-shift port for thermocouples (b) Compression assembly for inserted thermocouples to prevent gas leaks, (c) Close-up view.
2.3.1.2 Reactant gas versus inert gas mixture

While light can cause the top surface temperature to rise due to photothermal heating effects, the release of heat from exothermic reactions can also influence the catalyst temperature. To quantify and deduce the origin of the increase in temperature, the thermal profile of a Rh-s/TiO$_2$ catalyst is compared for light and dark conditions for CO$_2$ hydrogenation with a mixture of reactant gases (CO$_2$, H$_2$, and Ar) versus a mixture of inert gases (H$_2$, and Ar) (Fig. 2.6).

![Graph](Image)

**Figure 2.6.** Measured $T_1$ as a function of set $T_2$ for flowing mixtures of reactant gases and inert gases. $T_1$ is measured for dark thermal conditions and under 3.2 W cm$^{-2}$ blue illumination. The total flow rate is maintained at 250 sccm. The reactant gas mixture is composed of a 1:3:1 ratio of CO$_2$:H$_2$:Ar while the inert gas mixture is composed of 3:2 ratio of H$_2$:Ar.

To maintain a total flow rate of 250 sccm, CO$_2$ is replaced with additional Ar for the inert gas mixture. At room temperature, the thermal conductivities of CO$_2$ and Ar are 16.8 and 17.7 mW m$^{-1}$ K$^{-1}$, respectively with slight differences at higher temperatures.$^{118}$ However, since the reactant gas mixture contains flowing CO$_2$, H$_2$, and Ar with a 1:3:1
ratio, the influence of CO$_2$ on the overall thermal conductivity of the gas is minimal. Under dark thermal conditions, a set $T_2$ temperature produces nearly identical $T_1$ temperatures for both gas mixtures. Slight deviations occur at higher temperatures due to the exothermic heating from the reaction.

For the inert gas mixture, the change in $T_1$ temperature upon the addition of light represents the contribution from photothermal heating. For the reactant gas mixture, the change in $T_1$ temperature for illuminated conditions includes both photothermal heating and exothermic heating. Comparing illuminated conditions under reactant gases versus inert gases isolates the amount of temperature increase due to exothermic heating. Since the amount of exothermic heating is directly correlated to the amount of catalyst used and specific reaction conditions, simply focusing on the temperatures only reveals half the story. Simultaneous measurements of reaction rates and temperature profile of the catalyst is required to understand the role of light in plasmonic photocatalysis.

2.3.2 Simultaneous measurements of reaction rates and thermal profiles

In conjunction with the online continuous gas sampling from the mass spectrometer, a handheld temperature data logger (Omega, RDXL6SD-USB) records the temperatures measured by our multi-thermocouple setup in real time. Figure 2.7 shows a schematic of the main components of our modified reaction chamber under reaction conditions.
Figure 2.7. Schematic representation of reaction chamber for in situ measurements of top- ($T_1$) and bottom- ($T_2$) surface temperatures of the catalyst bed. Blue shading indicates the route taken by the flowing gases.

Using this new setup, we replicate experiments in which the internal chamber thermocouple ($T_c$) was used to set the temperature and assumed to represent the actual temperature of the catalyst. Figure 2.8a illustrates the dependence of $T_1$ and $T_2$ on illumination intensity by a modest intensity UV LED (UV Intensity, $I_{uv} < 3$ W cm$^{-2}$, 365 nm) with a ~3 mm thick Rh-s/TiO$_2$ catalyst thermostatically held at $T_c = 300^\circ$C and 350 $^\circ$C using 50 sccm CO$_2$, 150 sccm H$_2$, and 50 sccm Ar. The flowing gas produces $T_2 < T_c$ for all light intensities while $T_1$ increases rapidly from below to well above $T_c$ with increasing light intensity. Temperature gradients $> 100^\circ$C across a 3 mm thick catalyst are observed at the highest light intensity, so the set point temperature $T_c$ neither represents the average temperature nor the thermal profile of the catalyst.
Figure 2.8. Measured $T_1$ and $T_2$ temperatures as a function of $I_{uv}$ for $T_c = 300$, 350 °C.
Under dark thermal conditions, $T_1 < T_2$ whereas illumination increases the surface temperature and results in $T_2 > T_1$. The reactions are carried out with a ∼3 mm thick Rh-s/TiO$_2$ catalyst and 50 sccm CO$_2$, 150 sccm H$_2$, and 50 sccm Ar. This figure is adapted with permission from Ref 105.

On the Rh-s/TiO$_2$ catalyst, CO$_2$ methanation (CO$_2$+4H$_2$→CH$_4$+2H$_2$O) is the dominant reaction pathway. For a given $T_c$, the CH$_4$ reaction rates exhibit monotonic increases with increasing $I_{uv}$ (Fig. 2.9) until plateauing (e.g. $I_{uv} \approx 0.6$ W cm$^{-2}$ for $T_c = 350$ °C) because the reaction becomes diffusion limited (i.e. CO$_2$ conversion >10%). Prior experimental and theoretical investigations of the reaction mechanism on supported Rh and ruthenium catalysts suggest that CO$_2$ first dissociatively adsorbs as CO and O, then CO is hydrogenated to CHO. The dissociation of CH-O into CH and O is identified to be the RDS of CO$_2$ methanation, followed by fast hydrogenation of CH to produce CH$_4$. 

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Figure 2.9. Measured total reaction rates and CO$_2$ conversion for $T_c = 250$, 300, 350 °C as a function of light intensity.
The reactions are carried out with a ~3 mm thick Rh-s/TiO$_2$ catalyst and 50 sccm CO$_2$, 150 sccm H$_2$, and 50 sccm Ar. This figure is adapted with permission from Ref 105.

The observed photo-enhanced reaction rate (Fig. 2.9) includes both “thermal” and “nonthermal” contributions, but how may these be parsed? An important clue comes from the methane/photon ratio which is commonly referred to as the quantum efficiency or quantum yield. This ratio is defined as the difference in the illuminated and dark reaction rates at a common chamber temperature divided by the photon flux.$^{47,120}$

$$\frac{\text{methane}}{\text{photon}} \text{ratio} = \frac{R_{\text{illuminated}} - R_{\text{dark}}}{\text{photon flux}}$$  \hspace{1cm} (2.4)

However, inadequate accounts of the thermal effect may misrepresent the relationship between nonthermal reaction and photon flux. Using this definition, we
measure a methane/photon ratio as large as ~800% under low intensity UV illumination ($I_{uv} \approx 0.4$ W cm$^{-2}$) with $T_c = 350$ °C (Fig. 2.10).

![Graph showing methane/photon ratios for different temperatures.]

**Figure 2.10.** Methane/photon ratios at the $T_c = 250, 300, 350$ °C as a function of $I_{uv}$. The methane/photon ratio is calculated as difference between methane production rate under light and in the dark at the same $T_c$, divided by photon flux. The reactions are carried out with a ~3 mm thick Rh-s/TiO$_2$ catalyst and 50 sccm CO$_2$, 150 sccm H$_2$, and 50 sccm Ar. This figure is adapted with permission from Ref 105.

This clearly seems unphysical, as if each photon creates a hot carrier that breaks bonds of as many as eight different intermediate adsorbates at the RDS.$^{121-123}$ Furthermore, this ratio decreases with increasing light intensity, as if adding more photons makes the reaction less efficient. The only explanation is that somehow the subtraction of thermal effects was incomplete. Indeed, the critical assumption that illumination only generates nonthermal contributions is incorrect because it omits the effects of photothermal heating and the associated thermal gradient, effects clearly seen
in Figure 2.8. Thus, to ascertain the extent of any nonthermal contributions, the reaction rate caused by photothermal heating must also be characterized and subtracted, just as the reaction rate for unilluminated thermal heating was.

### 2.3.3 Plasmonic properties of Rh-s/TiO$_2$

Our proposed method for separating the photothermal and nonthermal contributions of the reaction rate first considers the wavelength-dependent light penetration depth of the catalyst constituents. TEM image of small Rh spheres supported on TiO$_2$ indicate an average size of ~6 nm (Fig. 2.11a). The LSP resonance peak of Rh spheres in an ethanol suspension resides in the deep UV region (Fig. 2.11b). However, the tail of its plasmon resonance extends into the blue/violet spectral region and absorbs light from both LEDs.$^{81,89,109}$

---

**Figure 2.11. Characterization of Rh-s/TiO$_2$.**
(a) TEM image of Rh-s/TiO$_2$ indicating Rh nanospheres with diameter of 6.3 ± 0.8 nm. (b) Measured absorbance (solid lines) of Rh-s/TiO$_2$ (black), Rh-s in an ethanol solution (red), and pure TiO$_2$ support (blue), overlaid with the estimated penetration depth of Rh-s/TiO$_2$ (black dotted line). Vertical lines show the central wavelengths of the UV and blue LEDs. This figure is adapted with permission from Ref 105.
As for the TiO$_2$ support, its $\sim$3 eV (413 nm) bandgap strongly absorbs light from the UV LED (365 nm) but is transparent to the blue LED (455 nm) used. The non-resonant excitation of Rh nanoparticles by the UV and blue LEDs produces hot electrons with near free-electron behavior, which is plasmonic in nature.$^{80,124}$ The penetration depth into the Rh-s/TiO$_2$ catalyst, modeled as a uniform distribution of Rh nanoparticles on a continuous TiO$_2$ host with the correct 5:95 mass ratio of constituents, is only $\sim$0.1 μm for both LEDs, indicating that the absorption is dominated by the Rh nanoparticles. Even if the porous structure of the TiO$_2$ support and the light scattering at the gas-solid interface were considered, the 3 mm thick Rh-s/TiO$_2$ catalyst still absorbs all illumination in much less than 1 μm depth. Obviously, nonthermal reactions requiring direct light-matter interactions, which involve hot-electron-driven reactions,$^{47,48}$ photo-modification of catalyst composition,$^{125}$ and enhanced near field,$^{81}$ can only occur in this thin layer, and the temperature of that thin layer is best measured by $T_f$ (blue area in Fig. 2.12).

![Figure 2.12. Temperature gradient model of the catalyst bed.](image)

Due to the short penetration depth of light, the nonthermal reaction is restricted to the top surface whereas thermal reaction can occur throughout the catalyst. Using measured $T_f$ and $T_2$ temperatures, an equivalent temperature, $T_e$ can be calculated. This figure is adapted with permission from Ref 105.
Of course, thermal reactions can occur throughout the catalyst bed and only depend on the temperature of catalyst, regardless the source of heat (red area in Fig. 2.12). This is even true for photothermal heating because the thermal conductivities of the catalyst and flowing gases transport surface heating throughout. Note that thermal and nonthermal reactions are defined by the driving force of reaction but not the location in the catalyst bed. Moreover, the local temperature within the catalyst generally increases with increasing illumination but decreases with increasing gas flow and may further increase or decrease depending on how exothermic or endothermic the reaction is. Consequently, the temperature profile in the catalyst evolves in a complex, dynamical manner as a function of many factors.

2.3.4 Calculating an equivalent temperature, $T_e$

To capture the dynamic thermal profile, we propose a model with a vertical temperature gradient within the catalyst bed. Under steady state conditions, a linear vertical temperature gradient approximation captures the excellent thermal conduction throughout both the catalyst bed and the gaseous reaction mixture, while the uniform illumination of the catalyst requires no horizontal gradient. Since the relationship between the thermal reaction rate and the reaction temperature follows an Arrhenius equation under conditions of low reactant conversion (< 10%), an equivalent temperature $T_e$, defined through the relationship:

$$e^{\frac{E_R}{kT_e}} = \frac{1}{T_2-T_1} \int_{T_1}^{T_2} e^{\frac{E_R}{kT}} dT,$$

(2.5)
conveniently describes the overall reactivity of thermal reactions in a catalyst bed with temperature gradients in both dark and light conditions. Due to the interdependent relationship of $T_e$ and the apparent activation energy $E_a$, the equation is solved by an iterative method using the measured $T_1$, $T_2$, and dark thermal reaction rate.

### 2.3.4.1 Iterative calculation of the equivalent temperature

The top- and bottom-surface temperatures and thermal reaction rate of a Rh-s/TiO$_2$ catalyst in dark thermal conditions are listed in the table below:

<table>
<thead>
<tr>
<th>$T_1/\degree$C</th>
<th>$T_2/\degree$C</th>
<th>$R_i$/μmol g$^{-1}$ s$^{-1}$</th>
<th>s.d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>344</td>
<td>216.2</td>
<td>1.1</td>
</tr>
<tr>
<td>300</td>
<td>323</td>
<td>119.1</td>
<td>1.5</td>
</tr>
<tr>
<td>275</td>
<td>299</td>
<td>59.7</td>
<td>0.2</td>
</tr>
<tr>
<td>250</td>
<td>272</td>
<td>26.0</td>
<td>0.1</td>
</tr>
<tr>
<td>225</td>
<td>245</td>
<td>10.9</td>
<td>0.1</td>
</tr>
<tr>
<td>200</td>
<td>217</td>
<td>3.97</td>
<td>0.07</td>
</tr>
<tr>
<td>175</td>
<td>190</td>
<td>1.33</td>
<td>0.06</td>
</tr>
<tr>
<td>150</td>
<td>163</td>
<td>0.38</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Under constant partial pressures of reactants, the relationship between reaction rate ($r$ in μmol g$^{-1}$ s$^{-1}$) and temperature ($T$ in K) can be described by Arrhenius equation:

$$\ln(r) = \frac{-E_a}{R} \left(\frac{1}{T}\right) + \ln(A),$$

(2.6)

The apparent activation energy, $E_a$, can be obtained by linear fitting of ln($r$) to 1/T with least square method. Using $T_1$ as T, $E_a$ is calculated to be 76.8±1.3 kJ/mol. Using $T_2$ as T, $E_a$ is calculated to be 78.0±1.3 kJ/mol. The difference in activation energies is due
to the different top- and bottom-surface temperatures of catalyst bed. As a result, an equivalent temperature, $T_e$, should be used to consider the temperature gradient that exists within the catalyst bed.

Due to the recursive nature of the $T_e$ calculation, an initial $E_a$ is used and an iterative method determines the real $E_a$.

Iteration 1: Using the input $E_a$ (76.8±1.3 kJ/mol) calculated with $T_i$, the following equivalent temperatures are obtained:

<table>
<thead>
<tr>
<th>$T_e$/°C</th>
<th>$T_1$/°C</th>
<th>$T_2$/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>334.8294</td>
<td>325</td>
<td>344</td>
</tr>
<tr>
<td>312.0236</td>
<td>300</td>
<td>323</td>
</tr>
<tr>
<td>287.6242</td>
<td>275</td>
<td>299</td>
</tr>
<tr>
<td>261.5805</td>
<td>250</td>
<td>272</td>
</tr>
<tr>
<td>235.5335</td>
<td>225</td>
<td>245</td>
</tr>
<tr>
<td>208.9320</td>
<td>200</td>
<td>217</td>
</tr>
<tr>
<td>182.8783</td>
<td>175</td>
<td>190</td>
</tr>
<tr>
<td>156.8216</td>
<td>150</td>
<td>163</td>
</tr>
</tbody>
</table>

$E_a = 77.4±0.1$ kJ/mol

Iteration 2: Input $E_a = 77.4±0.1$ kJ/mol
Table 2.3. Second iteration of $T_e$ and $E_a$ calculations.

<table>
<thead>
<tr>
<th>$T_e/°C$</th>
<th>$T_1/°C$</th>
<th>$T_2/°C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>334.8326</td>
<td>325</td>
<td>344</td>
</tr>
<tr>
<td>312.0286</td>
<td>300</td>
<td>323</td>
</tr>
<tr>
<td>287.6301</td>
<td>275</td>
<td>299</td>
</tr>
<tr>
<td>261.5859</td>
<td>250</td>
<td>272</td>
</tr>
<tr>
<td>235.5384</td>
<td>225</td>
<td>245</td>
</tr>
<tr>
<td>208.9361</td>
<td>200</td>
<td>217</td>
</tr>
<tr>
<td>182.8818</td>
<td>175</td>
<td>190</td>
</tr>
<tr>
<td>156.8246</td>
<td>150</td>
<td>163</td>
</tr>
</tbody>
</table>

$E_a = 77.4 ± 0.1 \text{ kJ/mol}$

Both $E_a$ and $T_e$ converge and the calculation is complete.

Notice that within each iteration, the calculated $T_e$ remained insensitive to minor changes in the value of activation energy used. Once $E_a$ is obtained, the total thermal contribution from the LED, the heater, and the exothermic reaction itself is captured by measuring the new $T_1$ and $T_2$ values upon illumination, from which the new $T_e$ and thermal reaction rate may be calculated. In this manner the effective thermal reaction rate ($R_t$) may be characterized and subtracted from the total measured reaction rate ($R_{tot}$) so that the nonthermal reaction rate ($R_{nt}$) may be confidently known and explored.

2.3.5 **Apparent quantum efficiency**

Since nonthermal reactions are limited to the top layer of catalyst bed, reaction rates normalized to the total weight of catalyst bed do not properly represent the intrinsic nonthermal catalytic activity, especially comparing the performance of different catalysts.
Instead, we introduce an apparent quantum efficiency (AQE), defined as the ratio of the deduced nonthermal rate to the photon flux delivered to catalyst.

\[
AQE = \frac{R_{\text{tot}} - R_t}{\text{photon flux}} = \frac{R_{nt}}{\text{photon flux}}.
\] (2.7)

The AQE, which may be used to evaluate the efficiency of plasmonic photocatalysis, does not involve and should be independent of the total weight (thickness) of catalyst. We confirm this expectation through measurements and calculations of nonthermal AQE using thick (~3 mm thickness) and thin (~1 mm thickness) layers of Rh-s/TiO₂ catalyst (Fig. 2.13).

<table>
<thead>
<tr>
<th>Top surface temperature (°C)</th>
<th>AQE at 0.95 W cm⁻² (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thick layer</td>
</tr>
<tr>
<td>300</td>
<td>19.5±0.8</td>
</tr>
<tr>
<td>250</td>
<td>5.6±0.2</td>
</tr>
</tbody>
</table>

Figure 2.13. Calculated AQE from a ~3 mm and a ~1 mm thick Rh-s/TiO₂ catalyst for \( T_1 = 300 \) °C and 250 °C for \( I_n = 0.95 \) W cm⁻². The reactions are carried out with 50 sccm CO₂, 150 sccm H₂, and 50 sccm Ar. This figure is adapted with permission from Ref 105.

The fact that they are the same to within experimental uncertainty validates the ability of our model to ascertain the effective thermal reaction rate and extract the real contribution from nonthermal reactions. To maintain a low conversion of reactants and minimize the temperature gradient in the catalyst bed, a thin layer (~1 mm) of catalyst is used in the following experiments.
2.3.6 Illuminated conditions

2.3.6.1 Light-intensity dependent

To explore the mechanism for nonthermal contribution, we begin by investigating the dependence of $R_{nt}$ on light intensity with 50 sccm CO$_2$, 150 sccm H$_2$, and 50 sccm Ar. These experiments were carried out by fixing not $T_c$ but the top-surface temperature $T_1 = 250$ °C, since $T_l$ describes the temperature where nonthermal reaction occurs. As $I_{uv}$ increased, both $T_2$ and $T_c$ decreased as photothermal heating of the top surface caused the thermostat to reduce $T_c$ to maintain $T_1$ (Fig. 2.14a). The resulting $T_e$ decreased at first, explaining why $R_t$ and the total reaction rate actually slowed as $I_{uv}$ increased (Fig. 2.14b).

Figure 2.14. Light-intensity dependent temperatures and reaction rates.
(a) Measured $T_1$, $T_2$, $T_e$, and $T_c$ of a ~1 mm thick of Rh-s/TiO$_2$ catalyst with $T_1 = 250$ °C as a function of $I_{uv}$. (b) Total, effective thermal, and nonthermal reaction rates at $T_1 = 250$ °C as a function of $I_{uv}$. The nonthermal reaction rate is the difference between the total and effective thermal reaction rates. This figure is adapted with permission from Ref 105.

However, as $I_{uv}$ grew even higher, the total reaction rate began to increase, even though $T_e$ and $R_t$ continued to drop. It became increasingly apparent that $R_{nt}$, calculated as the difference between the measured total reaction rate and the deduced $R_t$, had begun
to make a larger contribution as the reaction evolved from a thermal-dominated to nonthermal-dominated mechanism. Indeed, the $R_{nt}$ exhibited a super-linear dependence on $I_{uv}$, a signature consistent with hot-electron-driven reactions that are the likely nonthermal mechanism in the present system.$^{47,126,127}$ Moreover, the AQE calculated from this nonthermal mechanism was a much more physically reasonable $\sim 6\%$ and relatively independent of $I_{uv}$ in the low light intensity regime, a further indication that the thermal effects have been correctly accounted and the remaining nonthermal mechanism is caused by the plasmonic generation and transfer of hot electrons.

2.3.6.2 Unheated-light only

Although only a portion of photons converts into hot electrons to drive reactions, all light energy absorbed by the catalysts eventually turns into heat through electron-phonon scattering. Therefore, under unheated, light only conditions, the catalyst can be heated through photothermal effects. Considering the measured $T_1$ and $T_2$, the $T_e$ can be calculated for each light intensity. However, at low temperatures, the thermal reaction rates are negligible, indicating that most of the reaction rate can be attributed to nonthermal effects. As shown in Figure 2.15, light-induced CO$_2$ methanation begins at an equivalent temperature of $\sim 75$ °C, far less than the $\sim 130$ °C needed under dark thermal conditions.
Figure 2.15. Total reaction rates from unheated, light only and dark thermal conditions. The dark thermal reaction rate is plotted as a function of $T_e$ whereas the unheated, light only reaction rate is plotted as a function of both $T_e$ and the corresponding light intensity. This figure is adapted with permission from Ref 105.

Further understanding of the nonthermal reaction mechanism may be obtained under blue illumination, which cannot be absorbed by the TiO$_2$ support but still can be absorbed by the Rh nanoparticles. This indicates that the Rh nanoparticles, not the TiO$_2$ support, are responsible for the nonthermal photo-induced reaction and provide further evidence of mediation by hot electrons.

There are two cases regarding photothermal effects that may result in an underestimation of $R_t$ under illumination and one may argue that the residual $R_{ni}$ is due to this underestimation of $R_t$: 1. $T_i$ only describes the temperature of the TiO$_2$ support, whereas illuminated Rh nanoparticles are hotter than the TiO$_2$ support; 2. $T_i$ is lower than
the temperature at the very top surface of the catalyst bed since the thermocouple tip is covered by catalyst to avoid direct photo-heating of thermocouple. In the first case, using established calculation methods, the temperature difference between illuminated Rh nanoparticles and TiO$_2$ support is estimated to be much smaller than 0.1 °C which is negligible in the calculation of R$_t$. As for the second case, a temperature difference between $T_I$ and the very top surface should respond linearly to light intensity as shown by trends of $T_2$ with constant $T_I$ (Fig. 2.14a). This would result in an exponential dependence of R$_{nt}$ on light intensity following Arrhenius equation. However, this deduction is inconsistent with the observed linear to super-linear dependence of R$_{nt}$ on light intensity (Fig. 2.14b). Therefore, the majority of the calculated residual, R$_{nt}$ cannot be due to an underestimation of R$_t$. In addition, the consistent AQE with thick and thin catalyst beds further proves the appropriate subtraction of R$_t$ with our proposed model.

2.3.7 Effects of support

Given that support materials offer much more than passive mechanical and thermal stabilizations of the metal nanoparticles in catalytic processes, we considered the effect of catalyst supports on the thermal and nonthermal reaction rate by comparing the activities of larger Rh nanocubes (35 nm edges) on Al$_2$O$_3$ and TiO$_2$ supports (Rh-c/Al$_2$O$_3$ and Rh-c/TiO$_2$) with similar Rh mass loadings. Consistent with previous reports, the TiO$_2$-supported Rh catalyst exhibited much higher thermocatalytic activity and slightly lower activation energies than the Al$_2$O$_3$-supported catalyst for both thermal and nonthermal reactions (Fig. 2.16).
Figure 2.16. Dark thermal reaction rates as a function of $T_e$ and calculated apparent activation energies for Rh-s/TiO$_2$, Rh-c/TiO$_2$ and Rh-c/Al$_2$O$_3$.
This figure is adapted with permission from Ref 105.

It is important to note that the reactivity comes almost entirely from the metal nanoparticles: control experiments on pure Al$_2$O$_3$ supports did not yield any detectable products under both dark and light conditions, while TiO$_2$ only showed a small response to UV light with CO as the product ($<0.01$ μmol g$^{-1}$ s$^{-1}$). Moreover, the Rh-c/Al$_2$O$_3$ catalyst did not select for CH$_4$ under thermal conditions as effectively as either TiO$_2$-supported catalyst. This has been attributed to highly active sites at the interface between Rh and reducible TiO$_2$; in particular, the interaction between the O atom in CHO intermediates and the reduced Ti$^{3+}$ centers can weaken the C-O bond and facilitate the production of CH$_4$. It was recently demonstrated that nonthermal plasmon-
enhanced hot electron effects dramatically improve the selectivity of the Rh-c/Al₂O₃ catalyst towards CH₄, but Figure 2.17 shows that both TiO₂-supported Rh catalysts exhibit higher nonthermal activities than the Al₂O₃ supported catalyst. This suggests that the benefits of highly active sites at Rh-TiO₂ interface surpass the drawback of trapping hot electrons in TiO₂ for these plasmon-enhanced catalysts. As expected, Eₐ of the nonthermal reaction is always lower than Eₐ of the thermal reaction for all three catalysts, indicating that the nonthermal mechanism, perhaps hot-electron transfer to the critical intermediate at the RDS, lowers Eₐ beyond the thermal Eₐ. Another possible contribution to nonthermal effects is photo-modification at the Rh-TiO₂ interface, which needs to be investigated in the future.

Figure 2.17. Nonthermal AQE and calculated apparent activation energies for Rh-s/TiO₂, Rh-c/TiO₂ and Rh-c/Al₂O₃ as a function of T₁ under 2.73 W cm⁻² UV illumination. This figure is adapted with permission from Ref 105.
2.3.8 Reaction order of thermal and nonthermal reactions

Regarding the CO₂ and H₂ reaction orders, the different thermal conductivities of the reactant gases (33.5 and 272 mW m⁻¹ K⁻¹ at 227 °C for CO₂ and H₂, respectively) produce temperature gradients within the catalyst bed that evolve as the partial pressures are varied. To extract the reaction order, the results are plotted in double logarithmic scales and fitted with

\[ R = k p_{CO₂}^x p_{H₂}^y, \]

where \( p_{CO₂} \) and \( p_{H₂} \) are the partial pressures of CO₂ and H₂ with reaction orders \( x \) and \( y \), respectively. Positive reaction orders indicate the reaction is starved for that reactant, accelerating as additional gas is provided, while negative reaction orders indicate the reaction quenches as additional reactant is added.

2.3.8.1 Thermal reaction order

Under dark thermal conditions, the \( T_l \) is set at 200, 250, and 300 °C (Fig. 2.18a and b). Due to the external heating from the bottom and flowing gases through the top, the measured \( T_2 \) is consistently higher than \( T_l \). For varied CO₂ and H₂ partial pressures, the thermal profile remains stable, replicating identical \( T_l \) and \( T_2 \) temperatures. Using these measured temperatures, the \( T_e \) is determined to be 208, 261, and 313 °C. Thermal reactions respectively exhibit reaction orders of \( x = 0.14 \) and \( y = 0.37 \) for CO₂ and H₂ at \( T_e = 313 \) °C (Fig. 2.18c and d), values close to previous reports on supported Rh catalysts. In both cases, the thermal reaction orders for CO₂ and H₂ have a dependence on \( T_e \). Positive slopes indicate that thermal reactions accelerate with increasing \( p_{CO₂} \) and
pH₂, a consequence of the moderate binding strength of the associated intermediates to the catalyst surface, with H₂ and H adsorbing less readily than CO₂ or CO.\(^\text{129}\)

**Figure 2.18. Dark thermal reaction order for CO₂ and H₂.**
Measured \(T_1\), \(T_2\) and calculated \(T_e\) for varied (a) CO₂ and (b) H₂ partial pressures. Measured total reaction rates at \(T_e = 208, 261, 313 \, ^\circ\text{C}\) for varied (c) CO₂ and (d) H₂ partial pressures. Corresponding reaction orders are calculated.

**2.3.8.2 Nonthermal reaction order**

Nonthermal reaction orders are obtained by comparing the extracted nonthermal reaction rate for a constant \(T_I\) temperature and light intensity at varied CO₂ and H₂ partial...
pressures. The calculated $T_e$ from measured $T_1$ and $T_2$ temperatures (Fig. 2.19a and c) can be used to determine an effective thermal reaction rate. Then the nonthermal reaction rate can be extracted by subtracting the effective thermal rate from the total measured rate as described previously (Fig. 2.19b and d).

![Figure 2.19](image)

**Figure 2.19.** Measured temperatures and extracted nonthermal reaction rates for varied CO$_2$ and H$_2$ partial pressures. $T_1$ is set at 250 °C and measured $T_2$ for UV and blue illumination is plotted as a function of (a) CO$_2$ and (c) H$_2$ partial pressures. Using calculated $T_e$, the effective thermal reaction rate is determined for varied (b) CO$_2$ and (d) H$_2$ partial pressures. The nonthermal reaction rate is the residual rate after the effective thermal rate is subtracted from the total measured rate and is represented as the yellow shaded region.
Under moderate UV and blue illumination, the nonthermal CO$_2$ reaction order for $T_i = 250 \, ^\circ C$ is $\sim 0.06$ and remains similar to the thermal reaction order at $T_e = 261\, ^\circ C$ within experimental uncertainty (Fig. 2.20). This suggests that the surface coverage of CO$_2$ or CO has minimal effect on the efficiency of nonthermal reactions. However, blue illumination at 3.55 W cm$^{-2}$ produces a CO$_2$ reaction order of 0.12, close to the reaction order measured at a higher $T_e$ of 313 $^\circ C$. This suggests that the nonthermal CO$_2$ reaction order may have a dependence on light intensity.

Figure 2.20. Nonthermal CO$_2$ reaction order.  
The extracted nonthermal reaction rate is converted to AQE and plotted as a function of CO$_2$ partial pressures. The nonthermal CO$_2$ reaction order is calculated from the slopes of the double-log graph.

In contrast, the nonthermal H$_2$ reaction order is significantly different from the thermal H$_2$ reaction order (Fig. 2.21). Under UV and blue illumination, the calculated
nonthermal reaction orders are all negative with 3.55 W cm$^2$ blue light producing the largest negative H$_2$ reaction order of -1.24.

![Figure 2.21. Nonthermal H$_2$ reaction order.](image)

The extracted nonthermal reaction rate is converted to AQE and plotted as a function of H$_2$ partial pressures. The nonthermal H$_2$ reaction order is calculated from the slopes of the double-log graph.

Because of the high thermal conductivity of H$_2$, it might be argued that increasing p$_{H2}$ increasingly cools the catalyst which slowed the reaction. However, if our proposed methodology has completely subtracted all such thermal contributions, the change from a slightly positive reaction order for thermal reactions to a strongly negative reaction order for nonthermal reactions indicates that hydrogen has a profound effect on the nonthermal contribution to the reaction. Since hydrogen surface coverage depends on p$_{H2}$, surface hydrogen appears to poison the nonthermal reaction but not the thermal reaction.
Why does the addition of hydrogen quench the nonthermal reaction? Consider that \textit{in situ} infrared measurements under working CO\textsubscript{2} methanation conditions indicate the dominant surface intermediates on Rh catalysts are CO and H.\textsuperscript{94,96} Assuming CH-O dissociation is the RDS, the reaction order may be deduced from the rate equation

\begin{equation}
R = \frac{(K_1 K_3 K_5 k_6/2)^{1/2} K_2^{3/4}}{1 + K_2^{1/2} P_{H_2}^{1/2} + (K_2 K_2^{1/2} K_5 k_6/2 K_3 k_4)^{1/2} P_{CO_2}^{1/2} P_{H_2}^{3/4}} P_{CO_2}^{1/2} P_{H_2}^{3/4}, \quad (2.9)
\end{equation}

where \( K_2^{1/2} P_{H_2}^{1/2} \) and \( (K_1 K_2^{1/2} K_5 k_6/2 K_3 k_4)^{1/2} P_{CO_2}^{1/2} P_{H_2}^{3/4} \) are proportional to the surface coverage of H and CO, respectively. Thus, the most negative reaction order possible for H\textsubscript{2} is only -0.25, which occurs when the surface is saturated with hydrogen. The surface is not saturated with hydrogen for positive reaction orders, such as the thermal reaction with \( y = 0.37 \). Rate equations derived for other possible mechanisms (through CH\textsubscript{2}O or CO dissociation)\textsuperscript{95,96,130} and different assumptions about the RDS can only produce a H\textsubscript{2} reaction order for a hydrogen-rich surface as negative as -0.5. Thus, the rate equations alone cannot explain experimentally observed nonthermal reaction orders as negative as -1.24, so another possibility must be considered. One clue comes from the observation that the H\textsubscript{2} reaction order becomes more negative as illumination intensity increases, which suggests a change in surface coverage with increasing light intensity.

Assuming the nonthermal reactions are caused by transfer of plasmonically-excited hot electrons to the anti-bonding orbital of the critical CH-O intermediate, we use density functional theory (DFT) calculations to explore how its electron-accepting capability may be affected by the dominant surface intermediates (H and CO). We
calculated the local density of states (LDOS) for two CHO intermediates adsorbed on a Rh(100) facet separated in turn by a bare Rh surface, two CO molecules, and two H atoms, all optimized to their most stable configurations. When C-O anti-bonding orbitals accept hot electrons, they activate the CHO intermediate to accelerate CH₄ production. In all cases, obvious peaks at ~2.3 eV above the Fermi level in the LDOS plot are observed (Fig. 2.22a), indicating the anti-bonding bands of the C-O bond in CHO intermediates. The insertion of CO molecules in the space between CHO adsorbates only slightly lowers the LDOS associated with the C-O anti-bonding orbitals, as shown by a ~15% decrease in the LDOS of the C(pz) orbitals.

![Figure 2.22. DFT calculations for the nonthermal reaction.](image)

(a) LDOS of C-O anti-bonding bands (solid lines for C(pz) orbitals, dashed lines for O(pz) orbitals) of two CHO adsorbates on a Rh(100) facet separated by bare Rh surface (black), CO molecules (red), and H atoms (blue) in between. The obvious decrease of π* anti-bonding bands at ~2.3 eV (above the Fermi level) with the insertion of H atoms explains the negative reaction order on H₂ of nonthermal reactions. (b) Top view of the distribution of a C-O π* anti-bonding orbital consisting of two CHO adsorbates separated by two H atoms. The majority of probability density locates evenly on the two CHO adsorbates, indicating the delocalization of anti-bonding orbitals among them. Part of probability density is found on H atoms and Rh atoms interacting with the CHO adsorbates. This figure is adapted with permission from Ref 105.
By contrast, inserting atomic hydrogen significantly decreases the LDOS and a decrease of ~50% in the LDOS of the C(pz) orbitals is observed, thereby reducing the ability of CHO adsorbates to accept hot electrons from the Rh nanoparticles. Implicitly, these calculations reveal that C-O anti-bonding orbitals can delocalize and be distributed among these two CHO adsorbates, regardless whether they are separated by the bare Rh surface or other adsorbates (Fig. 2.22b). This implies that some plasmonically generated hot electrons transferred from the Rh nanoparticle may simultaneously weaken the C-O bonds in nearly proximal CHO intermediates and induce the formation of multiple product CH₄ molecules. It has also been proposed after inducing reactions, hot electrons may dissipate their excess energy by re-emission of photons, which can be absorbed again to increase the efficiency of plasmon-enhanced catalysis. The delocalization of hot electrons among two or more critical intermediates helps explain the high nonthermal AQE, while the sensitivity of the LDOS on proximal atomic hydrogen may explain the negative reaction order for pH₂.

Alternatively, we can examine the effective thermal reaction order calculated from each condition to determine the validity of the extracted nonthermal reaction order. For CO₂ and H₂ reaction order studies, the partial pressure of one gas is held constant while the one of interest is varied. To maintain a constant total flow rate of 250 sccm, additional Ar gas is added to the mixture. For varied CO₂ partial pressures, the Tₑ remains stable for all illuminated conditions (Fig. 2.23a). Therefore, we can use the effective reaction rate to calculate the reaction order for the thermal portion. Here we see that the calculated effective thermal reaction orders fall on the linear fit of the dark
thermal reaction order as a function of $T_e$ (Fig. 2.23b). This indicates that the extracted nonthermal reaction rate is valid.

**Figure 2.23. CO$_2$ reaction order of the calculated thermal contribution.**

(a) $T_e$ for each light intensity is calculated from measured $T_1$ and $T_2$ temperatures and plotted as a function of CO$_2$ partial pressure. (b) Reaction order of the thermal portion is plotted as a function of $T_e$ and compared with dark thermal reaction orders.

For varied H$_2$ partial pressures, the $T_e$ increases for increasing H$_2$ (Fig. 2.24a). At decreased H$_2$ partial pressures, Ar is used to maintain a constant total flow rate of 250 sccm. Our use of powdered catalysts means that the thermal conductivity of the gas mixture will have a large effect on the thermal gradient within the catalyst. The thermal conductivity of a gas mixture can be derived from knowledge of the pure component conductivities, heat capacity, boiling points, and molecular weights.$^{132-134}$ However, H$_2$ and Ar have vastly different thermal conductivities of 272 and 26.5 mW m$^{-1}$ K$^{-1}$ at 227 $^\circ$C, respectively.$^{118}$ Therefore, the thermal conductivity of the overall gas mixture varies greatly with H$_2$ partial pressures for these experimental results.
Determining a reaction order from reaction rates with slightly different $T_e$ may result in huge errors as shown in Figure 2.24b. Most notably, the calculated reaction orders for the thermal portion of the illuminated catalyst is very different from the measured dark thermal reaction orders. Although the $T_e$ for each light intensity only varies by less than five degrees, the magnitude of the thermal gradient is quite different. In calculating the effective thermal rate, only the equivalent temperature is considered and factors relating to the magnitude of the thermal gradient are overlooked which may possibly lead to over or under estimations in the extracted nonthermal reaction rate.

![Figure 2.24. H\textsubscript{2} reaction order of the calculated thermal contribution.](image)

(a) $T_e$ for each light intensity is calculated from measured $T_1$ and $T_2$ temperatures and plotted as a function of H\textsubscript{2} partial pressure. (b) Reaction order of the thermal portion is plotted as a function of $T_e$ and compared with dark thermal reaction orders.

As a result, the overall thermal conductivity of the gas mixture must be carefully considered for future nonthermal reaction order studies and an appropriate inert gas must be used to maintain the total flow rate. Of inert gases, helium (He) has a thermal conductivity of 221.4 mW m\textsuperscript{-1} K\textsuperscript{-1}, closest to that of H\textsubscript{2}.\textsuperscript{118} Using He instead of Ar will
allow similar thermal profiles be produced for varied H₂ partial pressures. Only under these conditions may the real nonthermal H₂ reaction order be determined.

2.4 Conclusion and outlook

In conclusion, we introduce a methodology to distinguish the thermal and nonthermal contributions from an illuminated, plasmon-enhanced catalyst composed of Rh nanoparticles on a TiO₂ support. The model extracts the effective thermal and nonthermal reaction rates under illumination by simultaneously measuring the total reaction rate and the top- and bottom-surface temperatures of the catalyst bed. Unlike the thermal reaction, the nonthermal reaction rate is quenched with increasing hydrogen partial pressure. DFT calculations indicate that nearby hydrogen inhibits the ability of the critical CHO adsorbates to accept hot electrons which results in the strongly negative H₂ reaction order. In contrast to traditional photocatalysis, heat and light work synergistically in these reactions: the higher the temperature, the higher the efficiency in plasmonic photocatalysis. One may envision that the full solar spectrum can be used to its full potential, with a portion of the spectrum providing photoheating while another promoting nonthermal reaction.
Chapter 3: Light-Induced Thermal Gradients in Ruthenium Catalysts Significantly Enhance Ammonia Production

The content of this chapter is adapted from our publication (Nano Letters, 2019, 19, 3, 1706-1711).\textsuperscript{135} We acknowledge our coauthors, Dr. Henry O. Everitt and Dr. Xiao Zhang, for helpful discussions about experimental design.

3.1 Introduction

Although photocatalysts for solar-powered synthesis or decomposition of chemical compounds have shown great promise in the laboratory, the efficiency of these catalysts has long been hampered by poor light penetration that confines chemical reactivity to the illuminated surface regions. Consequently, it is widely perceived that photocatalysts will never compete with traditional thermal catalysts for industrial-scale molecular synthesis, even though tremendous resources are being expended to produce such “green” solar-based alternative technologies.\textsuperscript{136-138}

When thin photocatalysts are subjected to high gas flow rates and are illuminated by low duty cycle, short-pulsed lasers, photothermal heating is minimized and isothermal conditions may be assumed. Such conditions facilitate demonstrations of nonthermal plasmonic effects such as hot carrier generation and transfer and/or enhanced local fields.\textsuperscript{6,7,79} Although the effects of hot-carrier driven processes may be identified through certain signatures, such as a super-linear dependence of photocatalytic reaction rates on light intensity,\textsuperscript{3,139} the effects from photothermal heating are subtle and often inadequately accounted in investigations of plasmonic photocatalysis. Moreover, these demonstrations do not easily translate to the motivating case of solar-activated
photocatalysis because of the broad-banded, continuous wave nature of solar illumination and its limited penetration depth.

Here, using a plasmonic photocatalyst much thicker than the light penetration depth, we report enhanced production of ammonia using a conventional ruthenium (Ru)-based catalyst. Ruthenium, a well-known thermal catalyst for ammonia (NH₃) synthesis,¹⁴₀,¹⁴¹ is also a plasmonic metal capable of absorbing light throughout the ultraviolet-visible-near infrared (UV-vis-NIR) region.⁸⁹ While the weak, broad plasmon resonance of Ru nanoparticles limits hot carrier generation, it facilitates plasmonic photothermal heating when illuminated by broad-band sources such as natural sunlight. Plasmonic photocatalytic ammonia synthesis and hot carrier driven processes have already begun to be explored in both solution and gas phases.¹⁴²⁻¹⁴⁴ Here we demonstrate how intense photothermal heating of these plasmonic nanoparticles from illumination of the surface produces a beneficial non-isothermal gradient in a thick photocatalyst. We hypothesize that the rate-limiting nitrogen scission step is accelerated in the hot surface region while the NH₃ products are preserved in the cooler lower regions. Through a series of experiments, we demonstrate the potential of these thick, non-isothermal plasmonic photocatalysts for significantly enhancing solar ammonia reaction rates and conversion yields beyond what is possible under dark conditions or isothermal illumination. We confirm that the effects are purely thermal, can operate by both broad-band and narrow-band illumination at atmospheric pressure without applying additional heat, and can be readily scaled up toward high volume or solar-based production.
3.2 Experimental methods

3.2.1 Synthesis of ruthenium catalysts

The Cs-promoted ruthenium catalyst, Ru-Cs/MgO, with a nominal Ru loading of 2.5 wt% was prepared following a published co-precipitation method.\textsuperscript{145} 19 mg ruthenium(III) chloride hydrate (RuCl$_3$ $\cdot$ xH$_2$O, ReagentPlus, Aldrich) and 1.34 g magnesium nitrate hexahydrate (Mg(NO$_3$)$_2$ 6H$_2$O, ACS, Sigma) were dissolved in 5 mL ethylene glycol (EG, J.T. Baker) in a clean 20 ml glass scintillation vial and stirred in an oil bath at 110 °C for 2 h. The black reaction mixture was then cooled and a solution of potassium hydroxide (KOH, ACS, Alfa Aesar) with stoichiometric molar ratio was added to precipitate the Ru/Mg(OH)$_2$. The product is aged for 10 min and washed by DI-H$_2$O for four times to remove K$^+$ and Cl$^-$ ions. The solid was dried at 120 °C for 5 h. A wet impregnation method is performed with an ethanol solution of cesium carbonate (Cs$_2$CO$_3$, Alfa Aesar) to produce a Cs-promoted sample with a molar ratio of Ru:Cs = 1:2. The dried promoted sample is then calcined in air at 450 °C for 2 h and reduced under H$_2$ at 450 °C for another 2 h.

3.2.2 Reactor setup and catalytic reactions

The photocatalytic reaction was carried out on a custom-built gaseous reaction system as described in detail in Chapter 2. Approximately 20 mg of Ru photocatalysts was loaded in the reactor to fill a 3-mm height and 6-mm diameter catalyst cup and ensure complete absorption of light for the catalytic measurements. H$_2$ (UHP), N$_2$ (Research grade), and Ar (UHP) were obtained from Airgas. The Ru photocatalysts were first reduced under 60 standard cubic centimeters per minute (sccm) H$_2$ and 40 sccm Ar
at 350 °C for 2 h, and then the gas flow was switched to a mixture N₂, H₂, and Ar with desired ratio of 1:3:1 for N₂:H₂:Ar and a total flow rate of 75 sccm.

3.2.2.1 Improved mesh cup design

The standard mesh holder is flat, circular and sits on a small ~0.6 mm ledge. The structural integrity of the mesh holder is severely compromised when thermocouples are inserted through a hole in the center. When the amount of catalyst loaded in the sample cup exceeds a height of 1 mm, the simple circular mesh is unable to sustain the mass. Under flowing gas conditions, copious catalyst mass along with position of inserted thermocouples may cause the mesh holder to slightly tilt. Over time, catalyst may fall through the side cracks of the mesh holder. To address these issues, a mesh cup design with interlocking panels is implemented as shown in Figure 3.1. First, a 12 mm circle is cut from 635 stainless steel mesh (20 micron opening). Then, 3 mm cuts are made along the outer edge to form evenly spaced panels attached to an inner circle with a diameter of 6 mm to match the size of the catalyst cup. Each panel is folded at 90 ° and interlocked with one another to form a self-supported mesh cup. Rather than only supporting the bottom of the catalyst, this design envelopes the sides as well.
Figure 3.1. Cup-style mesh catalyst holder.
(a) Schematic representation of cup-style mesh. (b) mesh styles from left to right: flat, cup template, folded cup-style mesh. (c) Photograph of cup-style mesh catalyst holder in sample cup.

As a proof of concept, a large-scale model was made using a combination of sand and thin paper towels. Compared to a traditional flat mesh design, the mesh cup design sustained over ten times the amount of weight. This cup style mesh catalyst holder enables testing with increased catalyst mass and higher flow rates. Additionally, the side panels of cup-style mesh holder allow for easier removal of the catalyst sample between experiments.

3.2.2.2 Analysis of effluent gas

The gaseous product was monitored by an online quadrupole mass spectrometer (Hiden, HPR-20) equipped with a Faraday cup and Secondary Electron Multiplier (SEM) detector at m/z = 2 (H₂), 17 (NH₃), and 28 (N₂) in real time. The filament setting was changed to 18 V and 100 μA to avoid interference of H₂O with NH₃. For most cases, a
filament setting of 70 V is used for electron ionization in the mass spectrometer. The ionization process produces either a molecular ion \( M^+ \), a radical cation with the same molecular weight and elemental composition, or a fragment ion. Decreasing the electron energy to 18 V reduces fragmentation of all analytes. The detection limit of the mass spectrometer is \(~0.001\%\) conversion of \( \text{N}_2 \). For each temperature and light intensity condition, at least 40 min elapsed before reaching steady state, and ten sequential measurements were made to ascertain the steady-state concentration of each gas and the associated reaction rates and uncertainties. All reactions were operated under atmospheric pressure. Mass spectrometer signals were calibrated using a calibration gas of 100 ppm \( \text{NH}_3 \) in \( \text{N}_2 \) (Gasco). The reaction rate was calculated according to the following equation:

\[
r (\mu\text{mol g}^{-1}\text{h}^{-1}) = \frac{\text{NH}_3\text{ratio} f_{\text{N}_2} (\text{sccm}) \times 60 (\text{min h}^{-1}) 	imes 10^6 (\mu\text{mol mol}^{-1})}{22400 (\text{ml mol}^{-1}) m_{\text{catalyst}}(g)}
\]  

(3.1)

where \( f \) is the flow rate of the feeding \( \text{N}_2 \).

Production of \( \text{NH}_3 \) was also unambiguously confirmed using rotational spectroscopy of a \( J = 0 \rightarrow 1 \) absorption feature near 572.498 GHz from collected gas samples for various reaction conditions\(^{146}\). Water was also detected as a contaminant from the \( \text{H}_2 \) source, but we confirmed that the \( \text{NH}_3 \) detected by the mass spectrometer was not obfuscated by monitoring different mass-to-charge ratios under reduced voltage settings.

### 3.2.3 Material characterization

Transmission electron microscopy (TEM) images were collected by a FEI Tecnai G\(^2\) Twin operating at 200 kV. The TEM samples were prepared by dispersing the
photocatalysts in ethanol with sonication and depositing on a copper grid coated with a carbon film (Ted Pella, 01813). Diffuse reflectance ultraviolet-visible extinction spectra were obtained on an Agilent Cary 5000 equipped with an external diffuse reflectance accessory (DRA-2500). The composition of the photocatalysts was measured by a Kratos Analytical Axis Ultra X-Ray Photoelectron Spectrometer (XPS).

3.3 Results and discussion

3.3.1 Ru-based catalysts

Typical kinetic studies of plasmon-enhanced reactions favor the use of thin (≪ 1 mm) photocatalysts so all plasmonic nanoparticles are illuminated and their nonthermal effects may be elucidated. For less active catalysts and/or more difficult chemical reactions, such as the energy demanding NH$_3$ synthesis reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$, an increased amount of catalyst is required to produce measurable catalytic activity. Therefore, our investigation of NH$_3$ synthesis uses a commonly studied cesium-promoted, magnesium oxide-supported, ruthenium (Ru-Cs/MgO) catalyst\textsuperscript{140,145,147-149} (Fig. 3.2), for which the light penetration depth is less than 100 µm.\textsuperscript{68,79,105,150} Reactant gases flow through this loosely-packed, 3 mm-thick powdered catalyst in the reactor, and all experiments are operated below diffusion limits.
Figure 3.2. Morphology and size distribution of Ru-Cs/MgO.
(a) TEM image (b) Size distribution of Ru nanoparticles in the Ru-Cs/MgO photocatalyst. More than 100 nanoparticles were measured to obtain the size distribution. This figure is adapted with permission from Ref 135.

It has been well established that basic supports (MgO), and alkali promoters (Cs) assist in NH₃ synthesis via electron transfer to Ru.¹⁴⁰,¹⁴¹,¹⁴⁵,¹⁵¹,¹⁵² The electron-rich surface of the Ru metal is more active for N₂ dissociative chemisorption, which is the RDS in NH₃ synthesis. Under reaction conditions, alkali hydroxides act as a stable promoter against poisons and improve the Ru dispersion.¹⁵²,¹⁵³ In our catalyst preparation, Ru/Mg(OH)₂ is promoted with Cs via wet impregnation of Cs₂CO₃. After the solvent is evaporated, it is ground into a fine powder and reduced at 450 °C for 2 h under hydrogen. Based on the XPS survey scan of Ru-Cs/MgO, the presence of Ru, Cs, and MgO can be confirmed (Fig. 3.3a). However, the primary Ru 3d region at ~280 eV overlaps with the C 1s region at ~284.8 eV. Congruent with previous reports,¹⁴⁸,¹⁴⁹ Cs peaks are not present in the XRD spectra (Fig. 3.3b), which indicates that the Cs does not
form a crystalline phase and is most likely present as a thin amorphous layer that partly covers the surface of Ru crystallites. Using XRD, Ru(0) metal can be confirmed (Fig. 3.3b). The sample prior to calcination and reduction is denoted “Ru-Cs/Mg(OH)$_2$” and contains both metallic Ru and RuO$_2$ along with Mg(OH)$_2$ peaks. After treatment at 450 °C under an H$_2$ atmosphere, the Ru-Cs/MgO sample only contains metallic Ru peaks and MgO peaks.

![Figure 3.3. XPS and XRD characterization of Ru-Cs/MgO.](image)

(a) XPS survey scan. (b) XRD of Ru-Cs/MgO (post calcination & reduction in H$_2$) and Ru-Cs/Mg(OH)$_2$ (pre calcination). * indicates metallic Ru(0), ** indicates RuO$_2$. This figure is adapted with permission from Ref 135.

The optical properties of Ru-Cs/MgO were measured by diffuse-reflectance UV-vis spectroscopy as shown in Figure 3.4. Pure MgO support did not show any absorption in the measured 270-800 nm wavelength range due to its large band gap. The absorption of light by Ru-Cs/MgO in the UV-vis-NIR regions can be attributed to the properties of Ru nanoparticles.
Figure 3.4. Ru-Cs/MgO absorption spectrum and emission spectra of light sources.
The normalized optical spectra of Ru-Cs/MgO (black line) is measured by diffuse reflectance in an integrating sphere. This figure is adapted with permission from Ref 135.

3.3.2 Thick vs. thin thermocouples

Initially, our setup used inserted thermocouples with sheath diameter of 0.5 mm. Here, we compare the influence of the sheath diameter on the measured temperatures to improve the depiction of the thermal profile under reaction conditions. It has been shown that decreasing the thickness of the sheath diameter increases the accuracy of the measured temperature.\textsuperscript{154} Thermocouples with a sheath diameter of 0.25 and 0.5 mm are denoted as thin and thick, respectively. Each data point corresponds to the average of three sets of experiments under the identical conditions. In all cases, ~20 mg of Ru-Cs/MgO catalyst is loaded into the sample cup and the tip of the \( T_i \) thermocouple is covered with a very small amount of catalyst to prevent direct illumination of the thermocouple.
Using the measured $T_1$ and $T_2$, a $T_e$ is calculated for each condition as described in detail in Chapter 2. For identical catalyst mass under the same dark thermal conditions, the production rate should remain unchanged as a function of temperature. However, it is evident that at higher $T_e$, the differences between measured NH$_3$ synthesis rates deviate for the $T_e$ calculated from thin and thick thermocouples as shown in Figure 3.5. This indicates that one of the temperatures may be wrong.

![Dark Thermal](image)

**Figure 3.5.** Measured dark thermal NH$_3$ synthesis rates as a function of $T_e$ for inserted thermocouples of varied sheath diameter.

Taking a closer look at the measured temperatures, for each set $T_2$, $T_1$ measured by the thin thermocouple is lower than that of the thick thermocouple (Fig. 3.6a). The resulting thermal gradients calculated from measured $T_1$ and $T_2$ temperatures are shown in Figure 3.6b for both thermocouples. At $T_2 = 350$ °C, thin thermocouples indicate a thermal gradient of ~60 °C whereas thick thermocouples show a gradient that is half its size of ~30 °C.
Figure 3.6. Measured temperatures from thick and thin thermocouples under dark thermal conditions.
(a) Measured $T_1$ as a function of $T_2$. (c) Thermal gradient as a function of $T_2$.

Under unheated, blue light only experiments, the influence of the thermocouples thickness is amplified. As shown in Figure 3.7a, under light only conditions, the measured NH$_3$ synthesis rates are plotted as a function of light intensity. The reaction rates are nearly identical indicating that the conditions are identical. Figure 3.7b shows measured temperatures from inserted thermocouples under various conditions. Without any catalyst in the sample cup, the thick and thin thermocouples measure identical temperatures. Direct illumination of the thermocouple tip raises the measured temperature up to $\sim$130 °C at the maximum intensity of blue light (4.7 W cm$^{-2}$). With the catalyst loaded into the sample cup, measured $T_2$ temperatures are identical. Both $T_1$ temperatures exceed the measured $T_1$ temperature of the bare thermocouple without catalyst. The increased temperature is due to the exothermic heating from the NH$_3$ synthesis reaction. At the maximum intensity of blue light, thick and thin thermocouples
measure a $T_1$ of $\sim$190 and $\sim$311 °C, respectively. Using these measured $T_1$ and $T_2$, the corresponding $T_e$ can be calculated.

![Figure 3.7](image.png)

**Figure 3.7. Comparison of thick and thin thermocouples under unheated blue light only conditions.** Measured (a) NH$_3$ synthesis rate and (b) $T_1$, $T_2$ temperatures as a function of $I_{\text{blue}}$ for thick and thin thermocouples.

Figure 3.8 shows a plot of the NH$_3$ synthesis rates as a function of the equivalent temperature. As discussed in Chapter 2, the measured reaction rate for illuminated conditions always comprise of a thermal and nonthermal component. In consideration of that the dark thermal NH$_3$ synthesis does not initiate until a $T_e$ of $\sim$250 °C, the thermal component is negligible for temperatures lower than this threshold. For thick and thin thermocouples, the $T_e$ at 4.7 W cm$^{-2}$ blue illumination is 161 and 261 °C, respectively. At this $T_e$ range, the thermal contribution is minimal and most of the measured total reaction rate should be due to nonthermal effects. However, any errors in the measured $T_1$ will drastically affect the calculated $T_e$ and could lead to over or underestimations of the thermal contribution.
Figure 3.8. NH₃ synthesis rates as a function of $T_e$ for various conditions.
Total NH₃ synthesis rates are measured under dark thermal and unheated blue illumination conditions with varied thermocouple sheath diameter. Thin thermocouples are used to calculate the $T_e$ for the dark thermal data presented.

In comparison to the dark thermal reaction rate, experiments using thin thermocouples still suggests that there are nonthermal effects present due to a decreased $T_e$ initiation temperature of ~200 °C (Fig. 3.8). One might also suggest that the position of the $T_l$ could be different between the thick and thin samples. However, the amount of catalyst covering the tip is controlled and replicated for each set of experiment, such that the error between batches of experiments measure the same temperature within 3 °C. Changing from thick to thin thermocouples increases the accuracy of the measured top surface temperature, shifting the reaction rates to the right as a result of higher calculated $T_e$. Consequently, thinner thermocouples should be used to properly account for the contribution from thermal effects on the total reaction rate measured. Indeed, ultra-thin
thermocouples with sheath diameter <0.25 mm may indicate an even higher $T_i$ temperature and shift the reaction rate under blue illumination further to the right. The use of ultra-thin thermocouples in our setup was attempted but unsuccessful as they were easily broken and too flimsy to maintain a stable position within the catalyst.

![Diagram of thermal profile](image)

**Figure 3.9. Representation of thermal profile for dark thermal vs. unheated light only conditions.**

Regardless of the accuracy of the thermocouples, another crucial factor can explain the differences between reaction rates under dark thermal and light only conditions (Fig. 3.9). In all conditions, the gas flows through the catalyst from the top to the bottom. Since the gas is not preheated, room temperature gas adds a cooling effect. Under dark conditions, a heating block underneath the catalyst bed contributed thermal energy to maintain the desired set point temperature. Using $T_i$ as a setpoint, an illumination-dependent thermal gradient ($\nabla T = T_2 - T_i$) is created within the catalyst bed: in dark conditions the flowing gas cools the surface and produces a positive gradient (increasing temperature with depth), but upon illumination this evolves to a negative gradient as photoheating of the surface reduces the external heating required to maintain
We thereby create non-isothermal conditions, in contrast with previous investigations of plasmonic photocatalysis that operated under isothermal conditions.\textsuperscript{141,142,145,151,155}

### 3.3.3 Thermal gradients in ruthenium catalysts

Using a catalyst only ~0.9 mm thick, similar to that of previous investigations,\textsuperscript{142} we observe $T_2 - T_1$ as large as -80 °C for maximum blue illumination (4.7 W cm$^{-2}$) and 30 °C under dark thermal conditions. This indicates that a single temperature measurement is inadequate even for many “thin” layer catalyst studies. Figure 3.10a illustrates the relationship between the thermal gradient and the equivalent temperature for dark conditions (positive gradient, red) and for illumination using a white light emitting diode (LED) that mimicked concentrated solar illumination of 27 sols (negative gradient, green).

**Figure 3.10. NH$_3$ synthesis under dark thermal and heated white light illumination.**

(a) Measured thermal gradients and (b) Measured NH$_3$ synthesis rates under as a function of equivalent temperature under dark thermal and heated white light illumination. Circled data point indicates the light-only condition with no external heating applied. This figure is adapted with permission from Ref 135.
Using this white LED, we examined the potential of this catalyst for solar-driven \text{NH}_3\ synthesis. Under combined light and heat, the \text{NH}_3\ production rate is consistently higher than dark thermal conditions at the same \(T_e\); indeed, it is almost 100 times greater for the most energy-efficient scenario when no external heat is applied (Fig. 3.10a). Illumination significantly improves catalytic activity over dark conditions for the same equivalent temperature and the same absolute magnitude of the thermal gradient. In fact, the illuminated catalyst with no additional heating produces more than 100 µmol g\(^{-1}\) h\(^{-1}\) of ammonia, a rate not achieved for the unilluminated catalyst until heated to an equivalent temperature of almost 300 °C (Fig. 3.10b, circled green data point).

This enhancement is surprising: the catalyst was optimized for dark thermal conditions so that for \(T_e = 333\) °C and \(\nabla T = +58\) °C, the measured \text{NH}_3\ synthesis rate was 1530 µmol g\(^{-1}\) h\(^{-1}\) (Fig. 3.11). However, at the same equivalent temperature, illumination from a blue LED (455 nm) at 2.0 and 4.7 W cm\(^{-2}\) increased the \text{NH}_3\ synthesis rates 36\% (2088 µmol g\(^{-1}\) h\(^{-1}\), \(\nabla T = -39\) °C) and 192\% (4464 µmol g\(^{-1}\) h\(^{-1}\), \(\nabla T = -184\) °C), respectively. Clearly the strong negative thermal gradient created by illumination significantly improved the catalytic activity of the Ru-Cs/MgO catalyst.
Figure 3.11. \( \text{NH}_3 \) synthesis rates under dark and illuminated conditions. *Blue LED illumination of 4.7 W cm\(^{-2}\) raises the “unheated” equivalent temperature of the catalyst bed from 25 °C to 261 °C. This figure is adapted with permission from Ref 135.

For a “room temperature” test of plasmonic photothermal heating efficacy within the Ru-Cs/MgO catalyst, we conducted light-only \( \text{NH}_3 \) synthesis experiments without applying any external heating. At room temperature, atmospheric pressure, and dark conditions, \( \text{NH}_3 \) synthesis rates are unmeasurably slow. However, \( \text{NH}_3 \) is copiously produced with blue illumination as the sole energy source (Fig. 3.12a). At 4.7 W cm\(^{-2}\) of blue illumination, the maximum intensity of our blue LED, \( T_1 \) and \( T_2 \) climb above room temperature to 311 °C and 88 °C, respectively, so \( T_e = 261 \, ^\circ C \), \( \nabla T = -223 \, ^\circ C \), and the reaction rate reaches 858 \( \mu \text{mol g}^{-1} \text{ h}^{-1} \) (Fig. 3.12b).
Figure 3.12. Light-only NH$_3$ synthesis rates and measured temperatures.
(a) Measured unheated, light only NH$_3$ synthesis rates and calculated effective thermal rates as a function of blue light intensity, $I_{\text{blue}}$. (b) Measured $T_1$, $T_2$ and calculated $T_e$ temperatures as a function of $I_{\text{blue}}$. This figure is adapted with permission from Ref 135.

3.3.4 Light-induced thermal gradients

It is well known that thermal gradients play an important role in chemical reactions, from catalyst synthesis$^{156,157}$ to reaction engineering.$^{158}$ However, previous investigations of plasmonic photocatalysis typically do not measure the vertical temperature profile of the catalyst bed and claim negligible plasmonic photothermal heating.$^{31,37,38}$ While the temperature of solutions is well equilibrated in liquid reaction systems,$^{37,159,160}$ thermal gradients can be quite severe within thicker illuminated solid state catalysts for gaseous reaction systems.$^{106}$ Inside a porous catalyst bed, thermal gradients are inevitable due to a combination of illumination, external heating, gas flow, and reaction energetics.
Figure 3.13. Experimental reaction quotient and N\textsubscript{2} conversion.
Experimental reaction quotient, $Q_P$, for dark heated, combined blue light and heated conditions, and calculated isothermal equilibrium constant, $K_{iso}$, as a function of equivalent temperature, $T_e$. The inset plots theoretical isothermal and experimental N\textsubscript{2} conversion under 4.7 W cm\textsuperscript{-2} blue illumination as a function of $T_e$. This figure is adapted with permission from Ref 135.

The effect of the gradient is also seen in how it affects the relationship between the isothermal equilibrium constant ($K_{iso}$) and the calculated reaction quotient ($Q_P$) (Fig. 3.13). For the NH\textsubscript{3} synthesis reaction, the equilibrium constant can be calculated for each temperature and pressure.\textsuperscript{161} At each condition, the extent of the reaction, $\xi$, can be solved to calculate the maximum possible conversion under isothermal conditions:
where \( P \) represents the sum of partial pressures of nitrogen and hydrogen in the feedstock.

Under experimental conditions, the reaction quotient, \( Q_p \), is calculated according to the following equation:

\[
Q_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3}
\]  

(3.2)

where \( P_i \) represents the partial pressure of component \( i \).

In a simplified view, the equilibrium constant of a reaction is a function of pressure, temperature, and feed composition, and reactions under isothermal conditions are limited by this curve \( Q_p \leq K_{iso} \).\(^{162}\) However, non-isothermal conditions augmented by light illumination show an apparently unphysical \( Q_p > K_{iso} \) for a given \( T_e > 450 \degree C \) (Fig. 3.13). For example, at \( T_e = 500 \degree C \), the measured \( \text{N}_2 \) conversion under 4.7 W cm\(^{-2} \) of blue illumination is nearly 50\% larger than the calculated equilibrium conversion (Fig. 3.13, inset). Anisotropic temperature profiles formed within the catalyst bed through microwave heating or traditional heating blocks have been shown to act as a thermodynamic pump to shift the global equilibrium.\(^{158,163}\) In a similar manner, illumination-augmented gradients within the catalyst cause significant deviations from isothermal conditions, with total conversions that appear to exceed thermodynamic limits if the effect of a non-isothermal gradient is ignored. Simply stated, light-induced non-isothermal negative gradients resolve conflicting requirements for catalysis: the hotter \( T_i \)
temperature allows for increased catalytic activities while the cooler $T_2$ temperature maintains higher conversion yields.

### 3.3.5 Intensity dependent studies

Consider next the dependence of thermal gradients on illumination wavelength and intensity. Examination of the intensity-dependent reaction rate for our four light sources suggests that the catalyst has a dependence on wavelength (Fig. 3.14a). At first glance this would appear to contradict the predicted behavior from the broad absorption of Ru nanoparticles in the catalyst.$^{89,142}$ But we find that UV and visible LEDs of the same intensity produced similar heating regardless of wavelength. For the equivalent temperature of 325 °C, the dependence of $T_1$ and $T_2$ on illumination intensity for each LED is shown in Figure 3.14b. Only in the NIR were deviations observed, where the illuminated reaction was only half as efficient at similar light intensities. The lower absorption of NIR light by the catalyst allowed it to penetrate deeper$^{105}$; consequently, the same intensity of light effectively heated a larger portion of the catalyst, and the overall thermal gradient shrank. Thus, the smaller $\nabla T$ produced by NIR illumination reduced the production rate.
Figure 3.14. NH₃ synthesis and light-induced thermal gradients for \( T_e = 325 ^\circ C \).
(a) Measured \( T_1 \) and \( T_2 \) temperatures of the catalyst and (b) Measured NH₃ synthesis rates as a function of light intensity for using UV, blue, and white LEDs and the NIR laser. UV and white LEDs have a maximum intensity of 2.73 and 2.84 W cm⁻², respectively. This figure is adapted with permission from Ref 135.

So not only does \( T_e \) determine reaction rates, the size and sign of \( \nabla T \) are critically important. For an instructive example, consider NH₃ synthesis rates for a given \( T_e \), with light and dark conditions chosen to produce gradients with equal amplitude but opposite in sign (\( \nabla T = \pm 50 ^\circ C \) for \( T_e = 280 ^\circ C \), \( \nabla T = \pm 60 ^\circ C \) for \( T_e = 325 ^\circ C \)). As can be seen in Figure 3.15, the NH₃ synthesis rate has no significant dependence on illumination wavelength for identical equivalent temperatures and thermal gradients, but it has a strong dependence on the sign of \( \nabla T \).
Figure 3.15. Wavelength dependence of NH$_3$ synthesis for $T_e = 280$ and 325 °C. Measured NH$_3$ synthesis rates from dark thermal conditions are compared with illuminated conditions, for the light intensities specified in Table 3.1. This figure is adapted with permission from Ref 135.

Table 3.1. Light Intensity and Gradient in Wavelength Dependence Studies

<table>
<thead>
<tr>
<th>Equivalent Temperature (°C)</th>
<th>Wavelength (nm)</th>
<th>Light Intensity (W cm$^{-2}$)</th>
<th>Thermal Gradient, $T_2 - T_1$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_e = 280$ °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dark Thermal</td>
<td>0.0</td>
<td>365</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>385</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>405</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>455</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>525</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>550*</td>
<td>2.2</td>
<td>-50</td>
</tr>
<tr>
<td></td>
<td>805</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>$T_e = 325$ °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dark Thermal</td>
<td>0.0</td>
<td>365</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>455</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>550*</td>
<td>2.0</td>
<td>-60</td>
</tr>
<tr>
<td></td>
<td>805</td>
<td>4.1</td>
<td></td>
</tr>
</tbody>
</table>

*Average wavelength of the white LED
More importantly, as illumination intensity increases and thermal gradients evolve from positive to negative, the reaction rate first slightly decreases to a minimum then significantly accelerates (Fig. 3.16), regardless of the wavelength. The minimum occurs for isothermal conditions where the thermal gradient is zero ($T_i = T_2$).

![Figure 3.16. NH$_3$ synthesis rates as a function of the thermal gradient for $T_e = 325$ °C for various light sources.](image)

This figure is adapted with permission from Ref 135.
Figure 3.17. NH$_3$ synthesis rates vs. thermal gradients vs. equivalent temperatures.
3D plot of measured NH$_3$ synthesis rates as a function of thermal gradients at equivalent
temperatures of 275, 300, and 325 °C under blue illumination (light intensities and specific data
in Table 3.2). This figure is adapted with permission from Ref 135.

The same trend is seen at $T_e = 275$ and 300 °C, however, the NH$_3$ synthesis rates
are relatively lower (Fig. 3.17). This confirms that the reaction rates are dependent on
both the equivalent temperature and overall thermal gradient.
Table 3.2 Light intensity, gradient, and NH₃ synthesis rates.

<table>
<thead>
<tr>
<th>Equivalent Temperature, Tₑ (°C)</th>
<th>Thermal Gradient, Tₑ – T₁ (°C)</th>
<th>NH₃ Synthesis Rate, ( \text{µmol g}^{-1} \text{ h}^{-1} )</th>
<th>SD, ( \text{µmol g}^{-1} \text{ h}^{-1} )</th>
<th>Light Intensity, (W cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>275</td>
<td>-47</td>
<td>113.73</td>
<td>1.24</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>-58</td>
<td>240.99</td>
<td>0.65</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>-123</td>
<td>602.43</td>
<td>5.58</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>-170</td>
<td>1014.57</td>
<td>9.25</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>-214</td>
<td>1360.35</td>
<td>20.37</td>
<td>4.7</td>
</tr>
<tr>
<td>300</td>
<td>-54</td>
<td>276.86</td>
<td>10.21</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>-92</td>
<td>269.49</td>
<td>4.33</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>-16</td>
<td>280.90</td>
<td>3.23</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>-137</td>
<td>306.96</td>
<td>4.22</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>-170</td>
<td>400.35</td>
<td>8.89</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>-200</td>
<td>630.75</td>
<td>13.87</td>
<td>2.7</td>
</tr>
<tr>
<td>325</td>
<td>-59</td>
<td>1104.78</td>
<td>8.14</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>-10</td>
<td>970.49</td>
<td>7.15</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>-41</td>
<td>917.95</td>
<td>7.24</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>-28</td>
<td>889.45</td>
<td>4.98</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>-8</td>
<td>918.57</td>
<td>4.47</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>-45</td>
<td>1094.64</td>
<td>3.41</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>-125</td>
<td>1534.84</td>
<td>8.27</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>-157</td>
<td>2422.15</td>
<td>8.31</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>-185</td>
<td>3235.39</td>
<td>11.29</td>
<td>4.1</td>
</tr>
</tbody>
</table>

When a temperature gradient exists, molecules tend to move from regions of high temperature to low due to thermophoretic forces. Under a negative gradient, thermophoretic forces align with the flow of gases through the catalyst and improve yield as NH₃ products are drawn away from the hottest region to avoid the reverse decomposition reaction. We see different behaviors for a negative gradient than for a positive gradient, with a negative gradient being more effective at increasing reaction rates and product yields than a positive gradient of the same absolute value. Evidently, for \( \nabla T < 0 \) the rate-limiting nitrogen scission step is favored in the illuminated hot surface region while the NH₃ products are increasingly preserved in the cooler dark lower
regions. In summary, the increased NH$_3$ production for surface illumination confirms the merits of negative temperature gradients created by plasmonic photothermal heating.

### 3.3.6 Direct and indirect illumination

To ascertain whether any of these photo-enhancements might be caused by nonthermal effects such as hot electron transfer, we compared NH$_3$ synthesis using the same Ru-Cs/MgO catalyst under direct and indirect illumination. For the latter, we placed a thin layer (~1 mm) of Ti$_2$O$_3$, a black photothermal material that is inactive for ammonia synthesis, on top of the catalyst to absorb all the light and convert it into heat (Fig. 3.18).

![Figure 3.18. Direct and indirect illumination of Ru-Cs/MgO.](image)

Schematic for direct and indirect photothermal heating along with photographs of the Ru-Cs/MgO catalyst without and with a top layer of Ti$_2$O$_3$. This figure is adapted with permission from Ref 135.
As a control test, a ~0.5 mm thick sample of Ti$_2$O$_3$ powder was placed on a quartz substrate (Fig. 3.19a and b). Due to the strong broad absorption of Ti$_2$O$_3$,$^{165}$ no light passed through the sample. This indicates that a ~1 mm Ti$_2$O$_3$ will absorb all light to facilitate indirect illumination of the active catalyst. Under all conditions, negligible NH$_3$ is produced on a full catalyst cup of Ti$_2$O$_3$, confirming that it is inactive for the reaction (Fig. 3.19c). Due to the thermal gradient within the catalyst, the data is shown as a bar, capturing the range of temperatures from $T_1$ to $T_2$.

![Figure 3.19](image)

**Figure 3.19. NH$_3$ synthesis control experiments with Ti$_2$O$_3$.**
(a) Optical image of commercial Ti$_2$O$_3$ powder. (b) At a thickness of ~0.5 mm, the Ti$_2$O$_3$ can absorb all light illuminated from the top. (c) Measured NH$_3$ synthesis rates as a function of measured temperatures of the catalyst under dark thermal and illuminated conditions. There are negligible amounts of NH$_3$ produced on Ti$_2$O$_3$ under both dark thermal and illuminated conditions. This figure is adapted with permission from Ref 135.
In both cases, the positions of the \( T_1 \) and \( T_2 \) thermocouples within the Ru-Cs/MgO catalyst remained the same. As with the directly illuminated catalyst, photothermal heating of the light absorptive Ti\(_2\)O\(_3\) overlayer also produced negative gradients within the catalyst (Fig. 3.20).

**Figure 3.20. Effect of direct and indirect illumination on NH\(_3\) synthesis.**

\( T_e \) is set at 325 °C (a) Top- and bottom-surface temperatures of the Ru-Cs/MgO catalyst as a function of blue light intensity. (b) Measured NH\(_3\) synthesis rates as a function of the thermal gradient for direct and indirect illumination of Ru-Cs/MgO by the blue LED. This figure is adapted with permission from Ref 135.

This technique allows us to achieve identical \( T_1 \) and \( T_2 \) temperatures through both direct or indirect illumination so the effects of light may be compared. For the same equivalent temperature of 325 °C and illumination by the blue LED over the range of 0 – 4.7 W/cm\(^2\) (Fig. 3.20a), we observe similar rate enhancements for NH\(_3\) synthesis with both direct and indirect light illumination of the Ru-Cs/MgO catalyst for equivalent thermal gradients (Fig. 3.20b). This observation rules out significant contributions from nonthermal effects and from nanoparticles differentially heated in response to the temperature-dependence of the dielectric function.\(^ {76} \) We thereby confirm that the
negative gradient produced through photothermal heating of the top surface is the dominant factor responsible for the enhanced reaction rates and product yields under illumination.

3.4 Conclusion and outlook

Although nonthermal effects in light-driven reactions are deservedly drawing much attention in the literature, photothermal effects may prove even more beneficial because of the way illumination can tailor thermal profiles within a catalyst. For the purely photothermal plasmonic system investigated here, we demonstrated that thermal gradients can be precisely tuned by varying the light intensity, even without external heating, to enhance both the yield and the reaction rate in the ammonia synthesis reaction. The short penetration depth of light, previously considered a major weakness in photocatalysis, is ideal for creating the desired non-isothermal conditions. The presence of thermal gradients within a catalyst acts as a thermodynamic pump to shift the global equilibrium to improve catalytic activities and product yield simultaneously. Our demonstration of direct and indirect light illumination verifies that surface photothermal heating is the dominant factor for enhanced reaction rates. This strategy can be universally applied to enhance yield and reaction rates for other exothermic reactions under ambient conditions, thus simplifying reactor designs and reducing energy costs, especially for applications such as the solar production of ammonia at room temperature and atmospheric pressure.
Chapter 4: Confirming Nonthermal Plasmonic Effects Enhance Carbon Dioxide Methanation on Rh/TiO₂ Catalysts

4.1 Introduction

As discussed in Chapter 2, the plasmonic nonthermal reaction rate ($R_{nt}$) is typically derived from a simple subtraction of the dark thermal reaction rate ($R_t$) from the total light-enhanced rate ($R_{tot}$) at the same temperature: $^3,38,55,56,72,79,80$ However, thoroughly accounting for photothermal effects significantly complicates this subtraction, as illumination produces intertwined thermal and nonthermal contributions in these reactions. The development of tailored plasmonic nanostructures that promote hot carrier generation to diminish photothermal effects, or vice versa, offer only a partial solution to this issue.$^{56,60,62}$ One reason is that thermal gradients exist in catalysts under both dark and illuminated conditions.$^{105,106}$ In such cases, previous approaches that rely on a single temperature probe may lead to inaccurate conclusions about the extent of the nonthermal contribution. Furthermore, the difficulty in accurately measuring the temperature of illuminated metal nanoparticles has raised the question whether effects ascribed as nonthermal are actually thermal effects caused by superheated nanoparticles.$^{31,76,77,166,167}$ Consequently, temperatures recorded by thermocouples embedded within the catalyst cannot discern whether the surface nanoparticles are hotter than the support, further complicating the comparison between dark and illuminated conditions.

To account for thermal gradients and distinguish between thermal and nonthermal catalytic effects experimentally, it is first necessary to create controlled thermal profiles. When this is achieved, measured dark thermal reaction rates using purely external heating
can be used to characterize the equivalent effects of photothermal heating caused by illumination. Here, we demonstrate how direct and indirect illumination techniques introduced in Chapter 3 can be extended to a different system, CO\(_2\) methanation on Rh/TiO\(_2\), to accurately deduce the thermal and nonthermal contributions.

4.2 Experimental methods

4.2.1 Synthesis of Rh/TiO\(_2\) photocatalyst

Rh nanospheres are synthesized by previously established polyol methods. 25 mg polyvinylpyrrolidone (PVP, M.W. \(\approx 55,000\), Aldrich) was dissolved in 5.6 ml ethylene glycol (EG, J. T. Baker) in a 20 ml glass vial and stirred in an oil bath at 160 °C for 30 min. 12 mg rhodium(III) chloride hydrate (RhCl\(_3\)•xH\(_2\)O, 40% Rh, Pressure Chemical) was separately dissolved in 0.4 ml EG and quickly injected into the hot solution to initiate nanoparticle growth. The reaction mixture was stirred for another 30 min and then cooled to room temperature. The solution of Rh nanospheres was washed with deionized water/acetone until no Cl\(^-\) and Br\(^-\) was detected in the supernatant. The purified nanoparticles were dispersed in 20 ml ethanol and wet-impregnated onto \(~95\) mg oxide supports to achieve \(~5\) wt% Rh loading. The oxide support, titanium dioxide (TiO\(_2\), Degussa, P25, specific surface area 35~65 m\(^2\) g\(^{-1}\)), was activated in air at 500 °C for 5 h before impregnation. Upon evaporation of the solvent, the obtained solid was ground into a fine powder and calcined in air at 400 °C for 2 h.
4.2.2 Plasmonic photocatalytic measurements

The photocatalytic reaction was carried out in a custom-built gaseous reaction system as described in Chapter 2. For each experiment, approximately 20 mg of the prepared Rh photocatalyst was loaded in the reactor to fill a 6-mm diameter catalyst cup to achieve a sample thickness of ~2 mm and ensure complete absorption of light for the catalytic measurements. Previous reports indicate a light penetration depth less than 1 micron for this catalyst, even for illumination energies below the bandgap of the TiO₂ support.¹⁰⁵ For experiments under indirect illumination, approximately 40 mg of commercial titanium(III) oxide (Ti₂O₃, Aldrich) was loaded on top of the Rh photocatalyst for a thickness of ~1 mm to prevent direct illumination of the active catalyst. Ultra-high purity (UHP) H₂, CO₂, and Ar were obtained from Airgas. The Rh/TiO₂ photocatalysts were first reduced under 60 standard cubic centimeters per minute (sccm) H₂ and 40 sccm Ar at 350 °C for 2 h to remove any Rh oxidation, and then the gas flow was switched to a mixture of CO₂, H₂, and Ar with the desired ratio and a total flow rate of 200 sccm. The gaseous product was monitored by an online quadrupole mass spectrometer (Hiden, HPR-20) equipped with a Faraday cup and secondary electron multiplier (SEM) detector at m/z = 2 (H₂), 15 (CH₄), 18 (H₂O), 28 (CO), 40 (Ar) and 44 (CO₂) in real time with filament settings of 70 V and 250 μA. The detection limit of the mass spectrometer was ~0.001% conversion of CO₂. For each temperature and light intensity condition, at least 30 minutes elapsed before ten sequential measurements were made to ascertain the steady-state concentration of each gas and the associated reaction rates and uncertainties. All reactions were operated under atmospheric pressure.
4.2.3 Material characterization

Transmission electron microscopy (TEM) images were collected by an FEI Tecnai G^2^ Twin operating at 200 kV. The TEM samples were prepared by dispersing the Rh nanospheres and Rh photocatalysts in ethanol with sonication, then depositing on a copper grid coated with a carbon film (Ted Pella, 01813). Diffuse reflectance UV-vis extinction spectra were obtained on an Agilent Cary 5000 equipped with an external diffuse reflectance accessory (DRA-2500). The composition of the photocatalysts was measured by a Kratos Analytical Axis Ultra X-Ray Photoelectron Spectrometer (XPS).

4.3 Results and discussion

4.3.1 Rh/TiO\textsubscript{2} photocatalyst

The morphology of Rh was investigated using TEM as shown in Figure 4.1. The synthesized Rh nanospheres maintained their shape and size (Fig 4.1b) after being deposited on the TiO\textsubscript{2} support and after being subjected to dark thermal and light-assisted reaction conditions.

![Figure 4.1. Morphology and size distribution of Rh/TiO\textsubscript{2} catalyst. TEM images of (a) Rh spheres, (b) Rh/TiO\textsubscript{2} pre reaction (c) Rh/TiO\textsubscript{2} post reaction, scale bar 50 nm. (d) Size distribution of Rh NPs in the Rh/TiO2 photocatalyst](image-url)
While the localized surface plasmon (LSP) peak of the Rh nanospheres is in the deep ultraviolet (UV) region (>6 eV), the broad tail of its resonance extends well into the blue/violet spectral region.\textsuperscript{89,109}

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Optical characterization of Rh/TiO\textsubscript{2} and LED emission spectra. The normalized optical spectra of Rh/TiO\textsubscript{2}, Rh spheres, TiO\textsubscript{2} is measured by diffuse reflectance in an integrating sphere. Emission spectra of UV, Blue and White LEDs are overlaid in dotted lines.}
\end{figure}

In accordance with previous investigations of the reduction of CO\textsubscript{2} by H\textsubscript{2} on Rh/TiO\textsubscript{2}, when Rh is fully reduced to its metallic state (Fig. 4.3), the main product is CH\textsubscript{4} under both dark and illuminated conditions.\textsuperscript{105,168} The Rh loading is determined to be ~6 wt\% for Rh/TiO\textsubscript{2} catalysts.
Figure 4.3. XPS characterization of Rh/TiO$_2$.
(a) Survey scan of Rh/TiO$_2$, Rh weight loading is determined to be 6 wt%. Region scans for (b) Rh 3d, only metallic Rh present, indicating that the Rh is fully reduced, (c) Ti 2p, (d) O 1s. All peaks are calibrated to the C-C peak at 284.8 eV.

In Chapter 3, we introduced the cup style mesh out of necessity to enable increased Ru-Cs/MgO catalyst mass for NH$_3$ synthesis. Here, we compare the use of a flat mesh vs. cup mesh to support the catalyst within the sample cup. The sample cup is loaded with ~20 mg of Rh/TiO$_2$ for a thickness of ~2 mm. The remaining ~1 mm of headspace is saved for the Ti$_2$O$_3$ layer and indirect illumination studies. In all cases, the measured CH$_4$ production rates are identical for all $T_e$ under dark thermal conditions (Fig. 4.4a and b). However, the thermal gradients produced upon the addition of the Ti$_2$O$_3$ layer are quite different.
Figure 4.4. Dark thermal CO$_2$ methanation using flat vs. cup mesh catalyst holder. Measured CH$_4$ production rate of Rh/TiO$_2$ as a function of $T_e$ using the (a) flat mesh and (b) cup mesh setup. Measured $T_1$ and $T_2$ as a function of $T_e$ using the (a) flat mesh and (b) cup mesh setup.

For both the flat and cup mesh, with only Rh/TiO$_2$ loaded in the sample cup, there is a positive gradient for dark thermal conditions. For indirect illumination techniques to function, identical thermal gradients must be replicated. However, once we load Ti$_2$O$_3$ on top of the Rh/TiO$_2$, the thermal gradient is significantly reduced for the flat mesh case (Fig. 4.4c). This is due to the increased thermal contact between the copper sample cup, Ti$_2$O$_3$ and the Rh/TiO$_2$ catalyst, which complicates the thermal profile within the catalyst.
Instead of only having energy input to the top or bottom surface of the catalyst, the sides are also affected, creating different horizontal gradients. When a cup mesh is implemented, identical thermal gradients can be reproduced for each corresponding \( T_e \).

The side panels of the cup mesh isolate the catalyst from the sides of the copper sample cup therefore restricting thermal energy to only the top and bottom surface. This configuration better fulfills the assumptions made of a linear vertical gradient and negligible horizontal gradient for the measurement of \( T_1 \) and \( T_2 \) to represent the top and bottom surface temperature.

![Figure 4.5. CO\(_2\) methanation under dark thermal conditions.](image)

(a) Measured CH\(_4\) production rate and (b) \( T_1 \) and \( T_2 \) temperatures as a function of \( T_e \). The flow is CO\(_2\) 50 sccm, H\(_2\) 150 sccm, and Ar 100 sccm for a total 250 sccm.

For the same flow of reactant gases as in Chapter 2, a thick layer of Rh/TiO\(_2\) produced copious amounts of CH\(_4\) (Fig. 4.5a). For \( T_e > 300 \) °C, heat released from the exothermic reaction sufficiently heats up the top surface of the catalyst such that even under dark thermal conditions, \( T_1 \) can be higher than \( T_2 \). Under this high conversion regime, a gradient of up to -70 °C degrees is formed. In fact, along with the production of
CH$_4$, there was also a significant amount of water produced by the reaction. Condensation on the tubing and collected water within the tubing was observed (Fig. 4.6a). To prevent water from flowing into the mass spectrometer, the effluent gas inlet is tilted upwards (Fig. 4.6b).

![Figure 4.6. Modified gas analysis setup.](image)

(a) Under original flow conditions of CO$_2$ 50 sccm, H$_2$ 150 sccm, and Ar 100 sccm for a total 250 sccm, the catalyst is highly active to produce water and methane. (b) The gas sampling tube for the mass spectrometer is positioned at an incline to prevent water from flowing in.

Additionally, the concentration of CO$_2$ and H$_2$ is diluted to reduce the production of water. The ratio of CO$_2$ to H$_2$ is maintained at 1:3 whereas the flow of Ar is increased for a total flow rate of 200 sccm. Under dark thermal conditions, the CH$_4$ produced is comparable for both concentrations. All following experiments are operated under the diluted mixture with 20 sccm CO$_2$, 60 sccm H$_2$, and 120 sccm Ar for a total 200 sccm to examine plasmon induced CO$_2$ methanation under low conversion conditions.
Figure 4.7. Reduced concentration of reaction gas mixture.
To prevent excessive production of water, the ratio of CO$_2$ to H$_2$ is maintained at 1:3 and the total flow rate is reduced to 200 sccm.

4.3.2 Direct vs. indirect illumination

For plasmon-enhanced CO$_2$ methanation, the Rh/TiO$_2$ photocatalyst was directly illuminated from the top by a UV LED (Fig. 4.8). The observed CH$_4$ production rate includes thermal, photothermal, and nonthermal contributions. In the direct illumination case, only the top sub-micron depth contains nonthermal (likely hot-electron-driven) light effects, whereas the remaining portion of the catalyst beyond the penetration depth of light contains the thermal contribution produced by illumination and external heating.\textsuperscript{105}

The thermal profile of the catalyst is carefully monitored using a previously established multi-thermocouple setup, and an equivalent temperature ($T_e$) can be calculated from the measured central temperatures of the top ($T_1$) and bottom ($T_2$) surface.\textsuperscript{105,135}
Figure 4.8. Schematic representation of photocatalytic reactions under direct and indirect illumination. The $T_1$ and $T_2$ are maintained at the same position within the Rh/TiO$_2$ catalyst to ensure identical thermal gradients can be created and compared.

Using the measured dark thermal reaction rates, $R_{t,m}$, we have previously shown how to calculate the equivalent thermal reaction rate, $R_{t,c}$ assigned to each $T_e$. In our experimental setup, dark and light conditions typically have opposite thermal gradients ($\nabla T = T_2 - T_1 > 0$ for dark, $< 0$ for strong illumination) within the catalyst since external heat is applied at the bottom of the catalyst while light and flowing gases are applied to the top.

Given the wide range of thermal gradients that can produce a given value of $T_e$ and the possibility of superheated nanoparticles, it is imperative to compare light and dark conditions for catalysts of identical temperature profiles. This can be achieved through an indirect illumination technique (Fig. 4.8) in which a photothermal material that is inactive for the reaction, Ti$_2$O$_3$, is used to cover the Rh/TiO$_2$ photocatalyst to prevent direct illumination of the active catalyst while the measurement locations of $T_1$ and $T_2$ thermocouples remain unchanged. Upon illumination, the Ti$_2$O$_3$ absorbs all the
light and acts as a photothermal heater to achieve the same $T_1$, $T_2$, and temperature profile within the Rh/TiO$_2$ photocatalyst as would occur without the Ti$_2$O$_3$ overlayer. Because this overlayer is much thicker than the light penetration depth, the Rh nanoparticles in the underlying catalyst are not illuminated and must be at the same temperature as the support. For a full cup of Ti$_2$O$_3$, no CH$_4$ is produced under all light and dark conditions, indicating that it is inactive for the CO$_2$ methanation reaction and can be used as a photothermal material (Fig. 4.9).

![Graph showing methane production rate vs. temperature for Rh/TiO$_2$ and Ti$_2$O$_3$](image)

**Figure 4.9. Control tests for Ti$_2$O$_3$ under reaction conditions.** Commercial Ti$_2$O$_3$ does not produce any CH$_4$ under dark and illuminated conditions with gas flow of 20 sccm CO$_2$, 60 sccm H$_2$, and 120 sccm Ar.

Then, the measured dark thermal CH$_4$ production rate ($R_{t,m}$) of Rh/TiO$_2$ with identical thermal gradients for covered and uncovered catalysts is compared over a wide
range of $T_e$ temperatures. Identical reaction rates for both (Fig. 4.10a) further confirm that Ti$_2$O$_3$ is inactive for the reaction and successfully establish this technique as a method to obtain the appropriate thermal correspondence from the measured temperature profile.

**Figure 4.10. CO$_2$ methanation under dark thermal and illuminated conditions.**
(a) CH$_4$ production rates are shown as a function of $T_e$. For the uncovered Rh/TiO$_2$ catalyst, the measured rate under dark thermal conditions ($R_{m, \text{dark}}$, black squares) and under direct illumination of 2.73 W cm$^{-2}$ UV light with additional external heating ($R_{\text{ill}}$, orange triangles) are plotted. For the covered catalyst, the measured rate under dark thermal conditions ($R_{m, \text{dark}}$, red circles) is shown. The calculated thermal CH$_4$ production rate ($R_{\text{calc}}$, purple dashed lines) as a function of $T_e$ is also shown in the figure. (b) Corresponding measured $T_1$ and $T_2$ temperatures for dark thermal and illuminated conditions for covered and uncovered Rh/TiO$_2$. The flow is CO$_2$ 20 sccm, H$_2$ 60 sccm, and Ar 120 sccm for a total 200 sccm.

For a heated Rh/TiO$_2$ photocatalyst under direct light illumination, heat and light combine to enhance CH$_4$ production rates for $T_e < \sim 350$ °C (Fig. 4.10a). However, at higher temperatures, the measured total CH$_4$ production rate ($R_{\text{tot}}$) is lower than that of dark thermal conditions at the same $T_e$. For exothermic, reversible reactions such as CO$_2$ methanation, the optimal temperature is a compromise between kinetic and thermodynamic factors. Although the CH$_4$ production rate initially grows exponentially
with operating temperature, the reverse reaction of CH₄ reforming starts to become more favorable at higher temperatures. The effects of this reverse reaction cause the deviation seen in Figure 1b for $T_e > \sim 350$ °C, and the addition of illumination reduces the rate even more. It is also interesting to note that when $T_e > \sim 350$ °C, it is possible for $T_1 > T_2$ even under dark conditions due to the exothermic nature of this reaction (Fig. 4.10b). Self-heating of the catalyst renders the thermal profile to be near isothermal. As a result, the calculated thermal rate ($R_{t,c}$) becomes unreliable under high intensity illumination where nonisothermal conditions are amplified since $R_{t,c}$ does not consider the magnitude or direction of the thermal gradient and assumes near isothermal conditions.

4.3.3 Unheated, light only experiments

Without precise temperature profile measurements, plasmon-driven reactions conducted at room temperature may under- or over-estimate photothermal contributions to the observed reaction rate. For a given $T_e$, UV light-only conditions produce more CH₄ than dark thermal conditions (Fig. 4.11); however, these comparisons are incomplete as vastly different thermal gradients exist.
Figure 4.11. Unheated UV light only vs. dark thermal CO\textsubscript{2} methanation.
Measured CH\textsubscript{4} production rates for unheated UV light only conditions (orange triangles), and dark thermal conditions (black squares) as a function of $T_e$ on bare Rh/TiO\textsubscript{2} catalyst. The flow is CO\textsubscript{2} 20 sccm, H\textsubscript{2} 60 sccm, and Ar 120 sccm for a total 200 sccm.

For example, when UV light is the sole energy input source, $T_1$ and $T_2$ respectively rise to 282 and 94 °C, producing $T_e = 224$ °C and $\nabla T = -188$ °C for the maximum LED intensity of $I_{UV} = 2.73$ W cm\textsuperscript{-2} (Fig. 4.12a). Under dark thermal conditions for the same $T_e$, the (opposite sign) thermal gradient is only $\nabla T = +27$ °C. When compared with the measured thermal rates ($R_{t,m}$) obtained through the indirect illumination technique for identical $T_1$ and $T_2$ temperatures, the calculated thermal $R_{t,c}$ rate accurately reproduces $R_{t,m}$ at most light intensities (Fig. 4.12b).
Figure 4.12. Unheated, UV light only CO$_2$ methanation.
(a) Measured top surface ($T_1$), bottom surface ($T_2$) and calculated equivalent ($T_e$) temperatures as a function of UV light intensity. (b) Measured total CH$_4$ production rate ($R_{tot}$) for unheated, UV light only (orange triangles) is shown as a function of UV light intensity. Calculated ($R_{t,c}$) thermal CH$_4$ production rates are based on corresponding $T_e$ (purple dashes). Measured ($R_{t,m}$) thermal CH$_4$ production rate from indirectly illuminated Rh/TiO$_2$ for identical $T_1$ and $T_2$ temperatures (red circles). The yellow shaded region represents the nonthermal contribution.

Slight deviations occur at higher light intensities in which large light-induced negative gradients exist. In this regime, because $R_{t,c}$ only considers the $T_e$, it does not account for additional photothermal effects due to an elevated $T_f$. As a result, under nonisothermal conditions, indirect illumination that generates identical thermal profiles becomes a more reliable method to ascertain the total thermal contribution. It can be seen that for directly illuminated Rh/TiO$_2$ with $I_{UV} = 2.73$ W cm$^{-2}$, $R_{t,m}$ accounts for only 27.6% of the total measured CH$_4$ production rate $R_{tot}$. This indicates that while a portion of the total CH$_4$ production under unheated UV light conditions can be attributed to thermal effects, the majority is due to nonthermal effects from light.
4.3.4 Light intensity dependent studies

To understand the dependence of light intensity in plasmon-driven reactions, we maintain the top surface at a constant temperature \( T_I \) by varying the light intensity and external heating, then monitor the total \( \text{CH}_4 \) production rate and thermal profile as a function of \( I_{UV} \) and \( T_2 \) (Fig. 4.13). Under direct illumination, the measured total methane production rate of Rh/TiO\(_2\) shows a characteristic “U” shape due to evolving light intensities and temperatures. At the lowest intensities of light, maximal external heating is required (\( T_2 > T_I \)), and the reaction is almost completely thermal in nature. The reaction rate decreases with increasing \( I_{UV} \) as less external heating is required and \( T_2 \) decreases toward \( T_I \). As light intensities increase further and \( \nabla T \) changes sign, the surface becomes the hottest portion of the catalyst, and \( R_{\text{tot}} \) increases as photothermal and nonthermal effects begin to dominate the reaction. Figures 4.13 reveal that the shape of the “U” depends on \( T_I \) but that nonthermal effects become significant for \( I_{UV} > 0.5 \text{ W cm}^{-2} \) for all \( T_I \).
Figure 4.13. CO$_2$ methanation using direct vs. indirect illumination.
For top surface temperature $T_1$ = (a) 200, (b) 250, (c) 300, and (d) 350 °C, the CH$_4$ production rates are plotted as a function of UV light intensity and corresponding bottom surface ($T_2$) temperature. Under direct illumination, measured total rate $R_{tot}$ (orange triangles) and calculated $R_{t,c}$ (purple dashed lines) are shown. Under indirect illumination, measured CH$_4$ production rates, $R_{t,m}$, are plotted using UV (pink left triangles), white (green right triangles), and blue (navy hexagons) LEDs. The yellow shaded region represents the nonthermal contribution.

Using the methodology of indirect illumination to reproduce and characterize the light intensity-dependent photothermal gradient without superheating the nanoparticles,
the relative contributions of thermal and nonthermal effects may finally be discerned. From the thermal profile, the $T_e$ and corresponding $R_{t,c}$ can be calculated. Indirect illumination with various LEDs and light intensities can reproduce thermal profiles to reveal the thermal portion of the $R_{tot}$ rates produced in the directly illuminated scenarios. Since Ti$_2$O$_3$ is inactive for CO$_2$ methanation and acts solely as a light absorber, the measured CH$_4$ production rates are independent of light wavelength. For most light intensities, the measured and calculated thermal portions are in close agreement (Fig. 4.13). However, at high intensities where the gradient is increased, the measured thermal contribution becomes more reliable, and the nonthermal light contribution can be obtained from

$$R_{nt} = R_{tot} - R_{t,m}. \quad (4.1)$$

One might argue that this extracted rate still contains a combination of effects from nonthermal hot carriers and superheated nanoparticles. However, the temperature increase caused by plasmonic heating of metal nanoparticles above its environment is negligible on supports with high thermal conductivity.$^{31,37,80,173}$ Under direct illumination, any increases in the temperature of Rh nanoparticles quickly equilibrates with the temperature of TiO$_2$ support. Therefore, the measured $T_f$ is a reasonable representation of the surface temperature. In addition, our investigations of a purely photothermal system showed that the measured total production rate and corresponding thermal contribution are identical under direct and indirect illumination.$^{135}$ Therefore, we are confident that the experimental approach described here captures the majority of the thermal contribution from light and the extracted reaction rate is mainly due to nonthermal effects.
4.3.5 Extracted nonthermal light effects

Once the thermal contribution is appropriately accounted, the extracted nonthermal CH$_4$ production rate $R_{nt}$ can be plotted as a function of $I_{UV}$ (Fig. 4.14a). For $T_l = 200$ and 250 °C, $R_{nt}$ has a super linear dependence on $I_{UV}$, presumably due to a hot carrier mediated process.$^{3,12,139}$ However, for $T_l = 300$ °C, $R_{nt}$ is linear, and for $T_l = 350$ °C, $R_{nt}$ becomes sub linear at the highest light intensities as CH$_4$ reactivity suffers from diffusion limitations and effects of the reverse reaction of CH$_4$ reforming. Since the nonthermal reaction is limited to the thin sub-micron surface region penetrable by light, the nonthermal CH$_4$ production rate per unit catalyst mass is indeed several orders of magnitude higher than the typical thermal CH$_4$ production rate at the same temperature.$^{77}$ The use of direct and indirect illumination techniques thereby experimentally distinguishes between thermal and nonthermal effects and demonstrates that light is not simply another heat source.

An apparent quantum efficiency (AQE$_{nt}$) can also be calculated by comparing the nonthermal rate to the number of incident photons,

$$AQE_{nt} (\%) = \frac{R_{nt} \text{ molecules s}^{-1}}{I_{LED} (\pi a^2 / 2) \text{ photons s}^{-1}} \times 100\%,$$

(4.2)

where $a (= 3 \text{ mm})$ is the radius of the illuminated catalyst. As observed in our previous investigations,$^{105}$ the near linearity of $R_{nt}$ with $I_{UV}$ means AQE$_{nt}$ is fairly independent of $I_{UV}$ (Fig. 4.14b).
Figure 4.14. Extracted nonthermal reaction.
(a) Nonthermal CH₄ production rate and (b) nonthermal apparent quantum efficiency, AQEn, as a function of UV light intensity (IUV) for varied top surface (T₁) temperatures.

Interestingly, the nonthermal rate and AQEn exhibit a strong dependence on top surface temperature, revealing the synergistic relationship between heat and light (Fig. 4.15). The AQEn ≈ 0% at T₁ ≈ 200 °C, the same initiation temperature for dark thermal conditions (Fig. 4.10a). It is no oxymoron that the nonthermal portion of the reaction depends on temperature, since the nonthermal part is not defined as an athermal contribution but as the part of the illuminated reaction rate that exceeds Rₜ,m. Several light-activated mechanisms may exhibit a temperature dependence. For example, it has been shown that illumination may reduce the activation barrier of the RDS so that at elevated temperatures, the increased relative population of adsorbate excited vibrational states requires less energy gain to overcome the activation barrier. 79,80,105
Figure 4.15. Nonthermal apparent quantum efficiency as a function of $T_1$ for varied $I_{UV}$.

Additionally, the probability of gaining a specific number of vibrational quanta increases when the molecule is initially in an excited vibrational state.\textsuperscript{3,12} Of course, this linear relationship between $R_{nt}$ and $T_1$ cannot continue indefinitely, lest AQE$_{nt}$ unphysically exceed 100%. Indeed, as $T_I$ increases toward $T_e \approx 350^\circ$C, AQE$_{nt}$ begins to deviate from the linear trend as the reverse reaction also becomes enhanced by the addition of light to heat.

4.3.6 Nonthermal apparent activation energy

Many demonstrations of plasmonic photocatalysis have shown a reduction in apparent activation energy under illumination.\textsuperscript{3,79,80,105} Here, using the extracted nonthermal reaction rate and the corresponding $T_I$ temperature, the apparent activation
energy is calculated under UV illumination at varied intensity as shown in Figure 4.16. Upon illumination, the apparent activation energy is significantly reduced, and further decreases are seen with increasing light intensity. Changes in the apparent activation energy are mostly attributed to a change in the RDS. Light contributes to these changes through the injection of hot carriers into anti-bonding orbitals of critical intermediates or through light-induced desorption of reaction intermediates. As a result, there may be a new RDS step for the nonthermal reaction. To verify possible changes in the RDS, future spectroscopic studies regarding the surface coverage of the catalyst under reaction conditions are needed.

![Graph showing apparent activation energy under UV light and dark thermal conditions](image)

**Figure 4.16. Dark thermal and light intensity dependent apparent activation energy.**
The apparent activation energy under UV light only is calculated using the extracted nonthermal reaction rate and corresponding $T_1$ temperatures.
It is well established that the apparent activation energy of a reaction will vary with the coverage of intermediates and that it increases in most cases with coverage for purely thermal reactions. While the overall thermal contribution from traditional heating and photothermal heating can be experimentally measured, the remaining nonthermal reaction from the overall reaction still has a temperature dependence. As a result, akin to thermal reactions, the apparent activation energy derived from the slope of the Arrhenius plot for the nonthermal reaction has three distinct regions. (1) In a low temperature region, coverage of adsorbates is high and constant, this results in a constant apparent activation energy. (2) In an intermediate temperature region, the adsorbates are destabilized by elevated temperature, and changes in coverage results in decreasing apparent activation energy. (3) Finally, at a high temperature region, coverage of adsorbates approach zero and results in a constant apparent activation energy. Thus, different processes limit the overall reaction at the different regions.
Figure 4.17. Arrhenius plot of nonthermal reaction rate as a function of $T_1$ temperature. Apparent activation energy for the nonthermal reaction for illumination with Blue and UV LEDs.

In addition, the nonthermal reaction produced under illumination of blue light was examined. The nonthermal apparent activation energy under blue illumination is only slightly reduced from that of the dark thermal reaction. With the LSP resonance of small Rh spheres residing in the deep UV, the reduced nonthermal effects from blue illumination is most likely related to the relative absorption of blue and UV light by the Rh/TiO$_2$ catalyst. Assumptions made from macroscopic data can lead to significant errors in the interpretation of the apparent activation energy as a catalytic reaction consists of
many elementary steps. Instead, micro-kinetic models must be developed for the nonthermal reaction.

4.4 Conclusion and outlook

In summary, we have designed a novel experimental technique to identify and characterize the nonthermal light effect in plasmonic photocatalysis. The thermal contribution of a directly illuminated catalyst can be captured through measurements of the reaction rate produced by indirectly illuminated catalysts with identical thermal profiles. Both $R_{nt}$ and $AQE_{nt}$ show a striking dependence on the top surface temperature for plasmon-enhanced CO$_2$ methanation on Rh/TiO$_2$. At low to moderate temperatures, light and heat work synergistically to accelerate CH$_4$ production. However, past a threshold temperature of $\sim$350 °C, heat begins to affect the light-driven reaction negatively as the reverse reaction of CH$_4$ reforming is also enhanced by illumination. A reduction in the apparent activation energy is observed under illumination, however, microkinetic models must be developed for the nonthermal reaction to understand this effect. Overall, this approach can be universally applied to plasmonic photocatalytic reactions to untangle the intertwined thermal and nonthermal effects and highlight the promise of light-driven reactions under mild conditions.
Chapter 5: Product Selectivity of Rh-c/Al₂O₃ for Carbon Dioxide Hydrogenation Revisited

5.1 Introduction

In thermally driven reactions, product selectivity requires the synthesis of nanostructures with well controlled geometries and compositions. Photon excitation of metal catalysts can induce chemical reactivity channels that cannot be accessed using thermal energy.⁴⁰,⁴⁸,¹²⁰,¹⁷⁵,¹⁷⁶ In parallel to these demonstrations, our own investigations of plasmonic photocatalysis stemmed from our discovery that plasmonic Rh nanoparticles are photocatalytic, simultaneously lowering activation energies and exhibiting strong product photo-selectivity, as illustrated through the CO₂ hydrogenation reaction.⁸⁰ Under illumination from blue or UV LEDs, the photocatalytic reactions on produced CH₄ with selectivity >98% over CO with a reaction rate twice that of the thermal catalytic reaction rate at 350 °C. Density functional theory (DFT) calculations indicated the photo-selectivity of the Rh photocatalyst can be attributed to the alignment of the hot electron distribution with the anti-bonding orbital of the critical reaction intermediate, CHO, which activates the CO₂ methanation pathway. Recently, there has been debate on whether photo-enhancements from demonstrations of hot carrier mediated processes can be in fact be attributed to thermal catalysis, driven by plasmonic photothermal heating.⁷⁶,⁷⁷ While enhanced reaction rates and reduced apparent activation energies may arise from errors in the consideration of the thermal contribution, plasmon-induced product selectivity remains to be a feature of plasmonic photocatalysis that cannot be simply explained using thermal effects. Armed with improved experimental
techniques, we revisit our investigations of CO$_2$ hydrogenation on Rh-c/Al$_2$O$_3$ catalysts for a comprehensive examination of the thermal contribution and assess the light-induced product selectivity in the nonthermal reaction.

5.2 Experimental methods

5.2.1 Synthesis of Rh-c/Al$_2$O$_3$

The Rh nanocubes were synthesized by a modified slow-injection polyol method. 54 mg potassium bromide (KBr, ACS, Acros) was dissolved in 2 mL ethylene glycol (EG, J. T. Baker) in a 20 mL glass vial and stirred in an oil bath at 160 °C for 1 h. 12 mg rhodium(III) chloride hydrate (RhCl$_3$·xH$_2$O, 38% Rh, Acros) and 25 mg polyvinylpyrrolidone (PVP, M.W. ≈ 55,000, Aldrich) were dissolved in 2 mL EG separately and injected into the hot reaction mixture by a two-channel syringe pump at a rate of 1 mL/h. The injection was paused for 15 min after adding 20 μL of the Rh precursor. After complete injection of the precursor, the reaction mixture was stirred for another 30 min and then cooled to room temperature. The suspension was washed with deionized water/acetone until no Cl$^-$ and Br$^-$ was detected in the supernatant. The solid was dispersed in 20 mL ethanol and impregnated on 90 mg Al$_2$O$_3$ nanoparticles to achieve a mass loading of ~5 wt% (Degussa, Alu Oxide C, specific surface area 85~115 m$^2$/g). The obtained solid was ground into powder and calcined in air at 400 °C for 2 h. The Rh nanocubes were well dispersed on the Al$_2$O$_3$ support and behaved as isolated nanoparticles.
5.2.2 Plasmonic photocatalytic measurements

The photocatalytic reaction was carried out in a custom-built gaseous reaction system as described in Chapter 2. For each experiment, approximately 12 mg of the prepared Rh photocatalyst was loaded in the reactor to fill a 6-mm diameter catalyst cup to achieve a sample thickness of ~2 mm and ensure complete absorption of light for the catalytic measurements. For experiments under indirect illumination, approximately 45 mg of commercial titanium(III) oxide (Ti$_2$O$_3$, Aldrich) was loaded on top of the Rh photocatalyst for a thickness of ~1 mm to prevent direct illumination of the active catalyst. Ultra-high purity (UHP) H$_2$, CO$_2$, and Ar were obtained from Airgas. The Rh-c/Al$_2$O$_3$ photocatalysts were first reduced under 60 standard cubic centimeters per minute (sccm) H$_2$ and 40 sccm Ar at 350 °C for 2 h to remove any Rh oxidation, and then the gas flow was switched to a mixture of CO$_2$, H$_2$, and Ar with the desired ratio of 1:3:1 and a total flow rate of 100 sccm. The gaseous product was monitored by an online quadrupole mass spectrometer (Hiden, HPR-20) equipped with a Faraday cup and secondary electron multiplier (SEM) detector at m/z = 2 (H$_2$), 15 (CH$_4$), 18 (H$_2$O), 28 (CO), 40 (Ar) and 44 (CO$_2$) in real time with filament settings of 18 V and 100 μA. The detection limit of the mass spectrometer was ~0.001% conversion of CO$_2$. For each temperature and light intensity condition, at least 30 minutes elapsed before ten sequential measurements were made to ascertain the steady-state concentration of each gas and the associated reaction rates and uncertainties. All reactions were operated under atmospheric pressure.
5.2.3 Adjusted mass spectrometer settings

Mass spectrometry is an analytical technique that ionizes chemical species and sorts the ions based on their mass-to-charge ratio (m/z). Masses and relative abundances of the ions in a mass spectrum can be used to determine the structure and elemental composition of the molecule. However, overlapping masses make it difficult to deduce quantitative data from mass spectrometer signals. In Figure 5.1, it is evident that several analytes of interest have coinciding peak signals. At a typical setting of 70 V, fragments of CO₂ can be found at m/z = 16 and 28, which overlaps the base peaks for CH₄ and CO, respectively. For CH₄, the signal at m/z = 15 is used instead as it does not overlap with any other possible signals. However, if the contribution from fragmented CO₂ to m/z = 28 is unaccounted for, then the “CO” signal is an overestimation of what is actually produced through the reaction.

Figure 5.1. Relative intensity of peaks for various compounds of interest.
As discussed in Chapter 3, decreasing the electron energy in the mass spectrometer settings reduced fragmentation of analytes and allowed signal distinction between water and NH₃. The choice in the electron energy is directly related to the analyte of interest. In our case, we do not want CO₂ to fragment into CO as it may affect calculations in product selectivity of the two main carbon products: CH₄ and CO. Based on a study of the ionization energy of CO₂, a minimum of 14 V is required to ionize CO₂ but ~19 V or higher results in its fragmentation into CO and O (Fig. 5.2). This indicates that our setting of 18 V will help to reduce overlapping signals and provide a quantitative measurement of CO produced.

<table>
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<th>Observed (volts)</th>
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<tr>
<td>CO₂→(CO₂⁺ + CO₂)→2CO + O₂⁺</td>
<td>19.3</td>
<td></td>
</tr>
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</table>

Figure 5.2. Theoretical energy needed for fragmentation of CO₂. This figure is adapted with permission from Ref 177.

Figure 5.3 shows comparisons of the CO and CH₄ raw signals for filament set at 70 and 18 V for varied reaction conditions. At 70 V, the raw CH₄ signal (m/z = 15) changes instantaneously with conditions, however, the noise for the raw CO signal (m/z = 28) is high and the background is not stable. Here, the CO signal is a combination of fragmentation from CO₂ and CO produced from the reaction. By decreasing the electron voltage to 18 V, the CO signal is noticeably cleaner and sensitive to changes in reaction conditions.
Figure 5.3. Raw signals from mass spectrometer for CH₄ and CO.
The filament is set at (a) 70 V, (b) 18 V and different light intensities and wavelengths are tested. Light intensity is tested from highest to lowest for each light source.
5.2.4 Material characterization

Transmission electron microscopy (TEM) images were collected by an FEI Tecnai G² Twin operating at 200 kV. The TEM samples were prepared by dispersing the Rh nanospheres and Rh photocatalysts in ethanol with sonication, then depositing on a Formavar/Cabon 200 mesh copper grid (Ted Pella, 01800-F). Diffuse reflectance UV-vis extinction spectra were obtained on an Agilent Cary 5000 equipped with an external diffuse reflectance accessory (DRA-2500). The composition of the photocatalysts was measured by a Kratos Analytical Axis Ultra X-Ray Photoelectron Spectrometer (XPS).

5.3 Results and discussion

5.3.1 Rh-c/Al₂O₃ catalyst

Rh nanocubes were synthesized via a previously reported slow-injection method. The LSP wavelength can be precisely tuned based on the size and the sharp corners of the synthesized Rh nanocubes can concentrate light and liberate hot carriers. For these experiments, Rh nanocubes with edge length of 37 nm on a porous Al₂O₃ support produced an LSP peak that overlapped our UV LED (365 nm) (Fig. 5.4a). The inset of Figure 5.4a shows a close-up view of the morphology of the Rh nanocubes indicating a concave cube shape with sharp corners. Figure 5.4b plots the strong absorption of the Rh photocatalysts in the UV region.
Figure 5.4. Characterization of Rh-c/Al₂O₃.
(a) TEM images of the Rh-c/Al₂O₃ catalyst, scale bar, 100 nm (inset: 25 nm). (b) UV-Vis extinction spectra of Rh/Al₂O₃ measured by diffuse reflectance in an integrating sphere.

The band structure of Rh\textsuperscript{124} indicates that the UV excitation avoids lower energy parasitic interband absorption and generates nearly free hot electrons with energies 2.5 above the Fermi level\textsuperscript{89,123}

5.3.2 Dark thermal: covered vs. uncovered

In contrast to our original investigation where the chamber temperature, $T_c$, was used to represent the catalyst temperature, here we employ our multi-thermocouple setup. As discussed throughout this dissertation, using the wrong temperature can lead to misconceptions regarding mechanisms for the reaction system. Under dark thermal conditions, the measured CH₄ and CO production rates are plotted as a function of the three measured temperatures (Fig. 5.5). The resultant curves differ based on the temperature used and the purple shaded region represents range of temperatures within
the catalyst. Depending on the temperature used, the calculated activation energy will also vary.

![Graphs showing CH₄ and CO production rates as a function of temperature](image)

**Figure 5.5. Production of CH₄ and CO as a function of measured temperatures.**
Under dark thermal conditions, the measured temperatures are \( T_c > T_2 > T_1 \) due to the location of the heating block by \( T_c \). Shaded purple region represents the temperatures found in the catalyst. The reactions are carried out with 20 sccm CO₂, 60 sccm H₂, and 20 sccm Ar.

Using the \( T_c \), the apparent activation energy for dark thermal conditions is calculated to be \( 83.3 \pm 2.3 \) and \( 86.6 \pm 1.8 \) kJ/mol for CH₄ and CO, respectively, consistent with previous reports on supported Rh catalysts.⁹¹,¹²⁸ As demonstrated in Chapter 3 and 4, the Rh-c/Al₂O₃ catalyst is covered with a layer of Ti₂O₃ for indirect illumination experiments. Under dark thermal conditions, covered vs. uncovered conditions show similar reaction rates for both CH₄ and CO at all \( T_c \) (Fig. 5.6a).
Figure 5.6. Dark thermal CO$_2$ hydrogenation. (a) The production rates for CH$_4$ and CO are plotted as a function of $T_e$ for covered and uncovered Rh-c/Al$_2$O$_3$ catalyst. (b) The CH$_4$ selectivity is calculated for covered and uncovered Rh-c/Al$_2$O$_3$ as a function of $T_e$. The reactions are carried out with 20 sccm CO$_2$, 60 sccm H$_2$, and 20 sccm Ar.

CH$_4$ production initiates around $T_e = \sim$200 °C like that of Rh/TiO$_2$ catalysts whereas CO production initiates slightly higher at $T_e = \sim$225 °C under thermal conditions. At increased temperatures, the production of CH$_4$ and CO increase at different rates as evidenced by the variation in calculated $E_a$. The low CH$_4$ selectivity for $T_e < 250$ °C can be explained by the difference in RDS for the two competing pathways for CO$_2$ hydrogenation.$^{80,90}$ For the RWGS to produce CO, the RDS is CO desorption whereas the RDS for CO$_2$ methanation involves the dissociation of CHO. In comparison, desorption of CO requires less energy input than the breaking of C-O bonds in CHO. However, once a threshold temperature for both RWGS and CO$_2$ methanation is surpassed, the CH$_4$ selectivity stabilizes around ~80% (Fig. 5.6b).
5.3.3 Light-induced product selectivity

Under direct UV illumination (2.73 W cm\(^{-2}\)), large negative gradients are produced within the ~2 mm thick Rh-c/Al\(_2\)O\(_3\) catalyst. For \(T_1\) set at temperatures from 225 to 325 °C, the corresponding measured \(T_2\) temperature is displayed in Table 5.1.

**Table 5.1.** Set \(T_1\) and Measured \(T_2\) temperatures produced from direct illumination of Rh-c/Al\(_2\)O\(_3\) with 2.73 W cm\(^{-2}\) UV light.

<table>
<thead>
<tr>
<th>(T_1) (°C)</th>
<th>(T_2) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>225</td>
<td>95.9 ± 1.3</td>
</tr>
<tr>
<td>250</td>
<td>130.8 ± 1.4</td>
</tr>
<tr>
<td>275</td>
<td>165.8 ± 1.3</td>
</tr>
<tr>
<td>300</td>
<td>199.8 ± 0.7</td>
</tr>
<tr>
<td>325</td>
<td>235.3 ± 0.5</td>
</tr>
</tbody>
</table>

Instead of using the thermal profile to calculate the \(T_e\) and determine the effective thermal contribution, indirect illumination of the Rh-c/Al\(_2\)O\(_3\) catalyst covered with Ti\(_2\)O\(_3\) is used to replicate identical thermal gradients. This ensures that effects of the magnitude and direction of the thermal gradient is also considered. In both direct and indirect, the \(T_1\) and \(T_2\) temperatures correspond to values in Table 5.1. Comparisons of covered vs. uncovered catalysts properly accounts the thermal contribution of the total measured reaction rate under direct illumination (Fig. 5.7). The residual reaction rates after subtraction of the thermal contribution, as represented by the yellow and green shaded regions, represent the nonthermal CH\(_4\) and CO production, respectively. Under direct
illumination, the CH₄ production rate is significantly enhanced compared to the CO production rate.

![Figure 5.7. Direct and indirect illumination of Rh-c/Al₂O₃.](image)

Measured CH₄ and CO production rates for covered and uncovered Rh-c/Al₂O₃ under illumination is shown as a function of T₁ temperature. The uncovered catalyst is illuminated with the maximum intensity of the UV LED at 2.73 W cm⁻². The thermal profile of the covered catalyst is set to match that of the directly illuminated catalyst. The yellow and green shaded region represents the nonthermal CH₄ and CO production, respectively.

When the total measured reaction rates for CH₄ and CO production are used, the calculated CH₄ product selectivity includes thermal, photothermal and nonthermal effects. After accounting for the thermal contribution from light and heat in directly illuminated catalysts, the extracted nonthermal rates for CH₄ and CO can be used to calculate the product selectivity in the nonthermal reaction (Fig. 5.8). The nonthermal
CH$_4$ selectivity is determined to be >90% for $T_1$ between 225 and 325 °C. The activation of a specific reaction intermediate using the absorption of specific photon energies by specific plasmonic metal nanostructures can specify product selectivity among competing reaction pathways. In accordance to previous DFT calculations, the distribution of hot carriers produced on the Rh photocatalyst align with the antibonding orbital of the critical reaction intermediate, CHO, which activates the CO$_2$ methanation pathway.$^{80}$

![Figure 5.8. CH$_4$ selectivity under illumination.](image)

The total CH$_4$ selectivity includes both thermal and nonthermal contributions. Indirect illumination of covered Rh-c/Al$_2$O$_3$ determines the thermal contribution and allows for the extraction of the nonthermal rate. Extracted nonthermal CH$_4$ and CO production is used to calculate the nonthermal product selectivity.
As discovered in Chapter 3, the magnitude and direction of the thermal gradient within the catalyst also influences the measured reaction rate. Therefore, directly comparing the enhanced nonthermal CH₄ selectivity with that of dark thermal conditions may not exclude effects from the thermal gradient. Instead, we must examine the product selectivity of catalysts with negative thermal gradients from the indirectly illuminated case. For indirectly illuminated Rh-c/Al₂O₃, the CH₄ selectivity increases with temperature under it plateaus at ~80% for T₁ > 275 °C. When this data is plotted as a function of Tₑ, it is identical to that of the dark thermal condition with positive thermal gradients. Moreover, unlike in the thermally driven process, the nonthermal reaction from direct illumination shows product selectivity that is relatively independent of temperature. This verifies that the light induced CH₄ product selectivity is most likely due to a nonthermal process such as hot carrier transfer rather than plasmonic photothermal heating.

To further investigate light induced selectivity, we perform intensity dependent studies. We monitor the rate of CH₄ and CO produced under direct and indirect illumination as a function of UV light intensity. For a top temperature set at 325 °C, the external heating block compensates for increasing light intensity and results in decreasing T₂ temperatures. The difference between direct and indirect illumination of Rh-c/Al₂O₃ represents the nonthermal production of CH₄ and CO as shown in Figure 5.9. At lower intensities, there is negligible CO produced whereas the CH₄ production rate is enhanced.
Figure 5.9. CO\textsubscript{2} hydrogenation using direct vs. indirect illumination.
For top surface temperature $T_1 = 325$ °C, the (a) CH\textsubscript{4} and (b) CO production rates are plotted as a function of UV light intensity and corresponding bottom surface ($T_2$) temperature. Under direct illumination, measured total rate $R_{\text{tot}}$ and calculated $R_{\text{c,t}}$ (purple dashed lines) are shown. Under indirect illumination, measured CH\textsubscript{4} and CO production rates, $R_{\text{m,t}}$, are plotted. The yellow and green shaded region represents the nonthermal contribution for CH\textsubscript{4} and CO, respectively.

The extracted nonthermal reaction rate is shown in Figure 5.10. The nonthermal production rate of CH\textsubscript{4} has a linear dependence whereas the nonthermal CO production rate appears to have an exponential dependence on the light intensity (Fig. 5.10a). The relationship between the reaction rate and light intensity has strong implications of the mechanism involved for photocatalysis. A linear to super-linear dependence is a unique characteristic of hot carrier mediated process.\textsuperscript{3} However, an exponential dependence is more common for thermally driven processes assuming that light intensity scales linearly with temperature. Subsequently, the AQE\textsubscript{nt} for CH\textsubscript{4} is relatively insensitive to the light intensity while the AQE\textsubscript{nt} for CO has increases with light intensity (Fig. 5.10b).
Figure 5.10. UV light intensity dependent reaction rate and AQE for $T_I = 325$ °C.
(a) The extracted (a) nonthermal production rate and (b) nonthermal AQE is for CH$_4$ and CO are plotted as a function of $I_{UV}$.

To further examine the nonthermal reaction, we also monitored the reaction rates under various light intensities for $T_I = 275$ and 300 °C (Fig. 5.11). The nonthermal CH$_4$ selectivity at various $T_I$ temperatures is near 100% for lower intensities which agrees with reported CH$_4$ selectivity on Rh/Al$_2$O$_3$ in a batch-type reaction system under irradiation with a 300 W Xenon lamp.$^{178}$ At $I_{UV} > 2$ W cm$^{-2}$, the nonthermal CH$_4$ selectivity starts to decrease to ~90%, in which light-induced desorption effects may be enhanced to increase CO production. Other possible explanations for the increase in CO production include light-induced morphological changes and/or changes in the RDS. This intensity dependent selectivity further highlights the potential of plasmonic photocatalysis.
Figure 5.11. Light intensity dependent nonthermal CH₄ selectivity for $T_1 = 275, 300, 325$ °C. The dark thermal condition is shown at 0 W cm⁻², here, while $T_1$ corresponds to 275, 300, 325 °C, the $T_e$ is slightly higher at ~300, 325, 350 °C.

5.3.4 Light intensity dependent activation energy

In kinetic studies, the measured reaction rate can be used to derive analytic expressions for the rate of reaction, activation energy and reaction orders. Changes in the slope of Arrhenius plots are traditionally interpreted as the signature of a change in the rate limiting step or the onset of diffusion phenomena. A characteristic feature of plasmonic photocatalysis is the reduction in apparent activation energy under illumination. The apparent activation energy for the production of CH₄ and CO can be determined using the measured rates and $T_e$ as the representative temperature for dark thermal conditions. In contrast, the Arrhenius plot for the nonthermal reaction
compares the reaction rates with respect to $T_1$. Analysis of the slopes in the nonthermal Arrhenius plot allows for the computation of the apparent activation energy at each light intensity. For the nonthermal reaction, we focus our attention to the apparent activation energy for the nonthermal CH$_4$ production (Fig. 5.12). An apparent activation energy for CO cannot be calculated due to negligible production for $I_{UV} < 2$ W cm$^{-2}$, and insufficient data points for $I_{UV} > 2$ W cm$^{-2}$.

![Diagram](image)

**Figure 5.12. Apparent activation energy for thermal and nonthermal CH$_4$ production.** The measured CH$_4$ production rate and corresponding $T_e$ is used to calculate a dark thermal apparent activation energy of $83.3 \pm 2.3$ kJ/mol. The extracted nonthermal reaction rate and $T_i$ is used to calculate a nonthermal apparent activation energy of $68.8 \pm 3.1$ kJ/mol under UV illumination.

For $I_{UV} < 2$ W cm$^{-2}$, the nonthermal apparent activation energy for CH$_4$ is $70.4 \pm 1.4$ kJ mol$^{-1}$. At higher intensities, this value drops, resulting in an overall nonthermal apparent activation energy of $68.8 \pm 3.1$ kJ mol$^{-1}$. This deviation at higher intensities
point to clues about changes in the RDS. Nevertheless, a key element of these analyses lies in the fact that they are “apparent” activation energies. Arrhenius expressions are valid for elementary reactions, but experimental data often involves several elementary steps. Therefore, what do changes in the “apparent” activation energy obtained by Arrhenius plots for a composite reaction reflect? The apparent activation energy consists of three different contributions: (1) $E_a$ of the RDS, (2) formation enthalpy of reactants in the RDS, (3) desorption enthalpy of intermediates on the surface times the number of sites used in the RDS. \(^{174}\) Contributions from (1) and (2) add to an effective activation barrier and are independent of reaction conditions. In contrast, the contribution from (3) is dependent on the coverage of sites and may depend strongly on the reaction conditions. Thus, \textit{in situ} spectroscopic techniques to investigate the surface coverage of reaction intermediates can reveal insight on the RDS and the effect of light on surface coverage.

\textbf{5.3.5 Catalyst stability}

To evaluate the effects of elevated temperatures and illumination on catalyst stability, the production rate of CH$_4$ and CO under dark thermal conditions are compared over time (Fig. 5.13). With $T_i = 300$ and 325 °C corresponds to a $T_e = 325.2$ and 352.6 °C respectively. The CO production rate is relatively stable whereas the CH$_4$ production rate significantly decreases over the course of a week. With continuous exposure to sequences of high temperatures and direct illumination, there is \textasciitilde8\% decrease in the measured CH$_4$ production rate. Once the catalyst is covered with a layer of Ti$_2$O$_3$, the CH$_4$ reaction rate stabilizes. This suggests that direct illumination of the catalyst is the main reason for declined photoactivity.\(^{66}\)
Figure 5.13. Catalyst stability under direct and indirect illumination.
The dark thermal condition with the $T_j$ set at 300 and 325 °C is tested over the course of a week when the catalyst is uncovered and covered.

Simulations of the near field intensity distribution for resonant illumination on the surface of a Rh nanocube show large enhancements of incident radiation intensity at edges and sharp corners. However, intense catalytic activity at corners and edges will reshape these nanoparticles and have a significant impact on the plasmonic properties. Indeed, in TEM images of the catalyst before and after a week of continuous testing (Fig. 5.14), the sharp corners of the originally concave Rh nanocubes are severely truncated.
In addition to tuning plasmonic and catalytic properties\textsuperscript{58,62,63,65} the synthesis of core shell structures may be implemented to increase catalyst stability. For metal-semiconductor core shell structures, metal nanoparticles influence photocatalytic behavior of semiconductor nanostructure either through Fermi level equilibration by accepting electrons or inducing LSP effects\textsuperscript{64} For example, a core shell heterostructure composed of Au/Al\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} demonstrated improved CO\textsubscript{2} reduction due to hot electron injection, charge separation and near field enhancement. The Al\textsubscript{2}O\textsubscript{3} interlayer exhibited a shielding effect on nearfield enhancement but ultrathin coating suppress surface charge recombination and improve photocatalytic activity\textsuperscript{64} Additionally, a semiconductor shell can protect the core from harsh conditions. It has been shown that a thin, conformal layer of crystalline TiO\textsubscript{2} preserves the morphology of gold nanostars and hot electrons from nanostar tips can be injected across defect free metal-TiO\textsubscript{2} interface\textsuperscript{180} Simulations of a
Rh nanocube located on Al₂O₃ show that a large concentration of plasmonically-excited carriers is produced at the interface between the particle and substrate. As a result, an ultrathin semiconductor shell on the Rh nanocube surface may preserve the morphology and improve photocatalytic activity.

5.4 Conclusion and outlook

Through direct and indirect illumination, the nonthermal production of CH₄ and CO from CO₂ and H₂ is quantified. After properly accounting for the thermal contribution, we confirm plasmon-enhanced CH₄ product selectivity in CO₂ hydrogenation on Rh-c/Al₂O₃ with a reduction in apparent activation energy. Over a week of continuous testing under elevated temperatures and intense illumination, the corners of the Rh nanocube are truncated which results in a severe decrease in catalytic activity of CH₄ production. An ultrathin semiconductor coating can be implemented to increase photocatalytic activity and maintain catalyst morphology. More importantly, in situ spectroscopic techniques to investigate the surface coverage of reaction intermediates can reveal insight on the RDS and the effect of light on surface coverage.
Chapter 6: Conclusions and Outlook

In this dissertation, mono-metallic photocatalysts with intrinsic plasmonic and catalytic properties are investigated for CO$_2$ hydrogenation and NH$_3$ synthesis. Through innovative theoretical and experimental techniques, we systematically evaluated thermal and nonthermal contributions, and how they may work together, to understand underlying mechanisms in plasmonic photocatalysis.

First, we developed a simplified model of the catalyst thermal profile and calculated the effective thermal reaction rate of an illuminated Rh/TiO$_2$ catalyst for CO$_2$ methanation. This allowed for the extraction of the nonthermal contribution from the total measured reaction rate. Identical nonthermal AQE of thick and thin layer catalysts confirmed that the thermal contributions can be approximated using this methodology. Unlike in thermal reactions, the nonthermal reaction rate is quenched by increasing H$_2$ as nearby hydrogen inhibits the ability of the critical CHO adsorbates to accept hot electrons. Significant enhancement of the reaction rate and reduced activation energies indicate that light and heat can work synergistically in plasmonic photocatalysis.

This approach was then applied to the investigation of traditional Ru-based catalysts with intrinsic plasmonic properties for photo-enhanced NH$_3$ synthesis from N$_2$ and H$_2$. While the weak, broad plasmon resonance of Ru nanoparticles limits hot carrier generation, it facilitates plasmonic photothermal heating when illuminated by broad-band sources such as natural sunlight. By varying the light intensity, large negative gradients are formed within the catalyst. This non-isothermal environment enhanced both the reaction rate and yield by balancing the conflicting requirements of kinetics and
thermodynamics, heralding the use of optically-controlled thermal gradients as a universal, scalable strategy for the catalysis of many exothermic chemical reactions. By comparing light and dark conditions with identical thermal gradients under direct and indirect illumination, we confirm that surface photothermal heating is the dominant factor for enhanced reaction rates in light driven NH$_3$ synthesis on the Ru-Cs/MgO catalyst.

The development of our indirect illumination technique allowed for an in-depth examination of the nonthermal CO$_2$ methanation reaction on the Rh/TiO$_2$ catalyst. The overall thermal and photothermal contribution of a directly illuminated catalyst was captured through measurements of the reaction rate produced by indirectly illuminated catalysts with identical thermal profiles. Interestingly, both the nonthermal rate and AQE show a striking dependence on the top surface temperature. At low to moderate temperatures, light and heat work synergistically to accelerate CH$_4$ production. However, past a threshold temperature of ~350 °C, heat begins to affect the light-driven reaction negatively as the reverse reaction of CH$_4$ reforming is also enhanced by illumination.

Finally, we revisited our investigation of CO$_2$ hydrogenation on Rh-c/Al$_2$O$_3$ with newly established experimental techniques to evaluate the light driven thermal and nonthermal reaction. After properly accounting for the thermal contribution, the photo-enhanced CH$_4$ selectivity in the nonthermal reaction is dominated by a hot carrier mediated process. Light-induced reshaping of the Rh nanocubes hinder the catalyst stability and highlight opportunities in catalyst design to preserve catalyst morphology under reaction conditions.
As the field of plasmonic photocatalysis continues to grow, it becomes increasingly important to develop a fundamental understanding of the underlying mechanisms to avoid misinterpretations of experimental results. Under illumination, the thermal contribution of the overall reaction definitively includes traditional heating and photothermal heating effects. In contrast, the nonthermal contribution remains to be an umbrella term used to represent plasmonic effects that cannot be achieved under thermal conditions. By carefully quantifying the thermal effects, our approach provides the first steps to understanding the nonthermal reaction in plasmonic photocatalysis. Moving forward, in situ techniques such as ultrafast spectroscopic studies are required to capture discrete adsorbates/products formed dynamically on the surface. These insights can aid the development of micro-kinetic models to understand the true meaning of changes in the apparent activation energy in plasmonic photocatalysis. Additionally, light-coupled environmental TEM can be used to explore the influence of particle structure on photocatalytic behavior at the sub-nanoparticle level in situ and in real-time.

The promise of plasmonic photocatalysis rests in its capability for precise control over product selectivity beyond what is possible under traditional thermal catalysis. Fulfilling this promise requires both experimental and theoretical efforts to identify desired structures and guide the rational design of plasmonic photocatalysts.
Appendix A: Bimetallic Au@Rh Nanostructures for Carbon Dioxide Hydrogenation

A.1 Introduction

Major constraints in current Rh-based photocatalysis include the rarity and high costs of Rh, low absorption of solar energy, inefficient generation of hot carriers, and fast decay of hot electrons (recombination). An effective strategy to overcome these limitations is through the incorporation of another metal to form bimetallic NPs. Possible bimetallic structures include alloy, core-shell and dendritic structures. It has been found that the properties of bimetallic NPs are dictated by their architecture and composition. Therefore, bimetallic catalysts have an extended range of tunable properties, allowing for improved rational design of heterogeneous catalysts. Core-shell NPs (denoted as core@shell) use the core as a support to allow for specific surface (shell) nanoarchitecture in terms of porosity and surface area. Kalisman et al. tailored the composition and morphology of Au@Pt bimetallic catalysts to achieve more than a fourfold increase in activity for the solar-driven photocatalytic splitting of water into hydrogen in comparison to that of pure Pt. Their investigations utilized CdSe@CdS nanorods decorated with different metal cocatalysts serving as reduction sites. In terms of relative efficiency, the Au@Pt decorated with Pt islands showed the best results due to increased surface area and activity sites (Fig. A.1). Plasmon-enhanced reactions can only take place when the reactants are adsorbed onto the catalyst surface, thus, the total surface area of the solid active phase has a substantial effect on the reaction rate.
CdSe@CdS nanorods are decorated with different metal cocatalysts serving as reduction sites: Au (yellow), Pt (red), Au@Pt core-shell and Au@Pt decorated with Pt islands. All measurements done under identical solution conditions and at equivalent concentrations. This figure is adapted with permission from Ref 182.

Compared to conventional spherical/compact Au@Pt NPs, the increased Pt surface area found in the branched structures of dendritic Au@Pt NPs showed improved catalytic activity for methanol oxidation. While a plethora of studies on Au@Pt and Au@Pd NPs exist, there is a lack of research performed on Rh-based bimetallic NPs. However, the similar chemical and physical properties of the platinum-group metals (Pt, Pd, Rh), suggest that findings from Pd or Pt-based bimetallic NPs may offer insight toward the design of Rh-based bimetallic NPs. Au has been a popular core choice due to its stability towards oxidation and facile synthesis of defined NPs of various shapes. Additionally, Au, Rh, Pd, Pt all have face-centered cubic (FCC) lattices with only slight lattice mismatch. Aside from unique nanostructure formation, there is an obvious economic motivation in the use of Au as a core substrate. According to the USGS, only
103 kg of Rh was mined in 2016.\textsuperscript{194} The cost of Rh peaked at $210 g\textsuperscript{-1}, approximately seven times that of Au.

The possibilities of bimetallic NPs using Au and Rh can be further deduced from their phase diagrams. Phase diagrams of alloys of Rh with Au predict no regions of stability below 2177 or 2139 K and 1.0 atm, respectively.\textsuperscript{195,196} While alloyed Au/Rh NPs cannot be synthesized, core@shell nanostructures circumvent this incompatibility. Currently, only Au@Rh bimetallic NPs with compact shells synthesized using a polyol method and microwave-assisted heating exist.\textsuperscript{197} Although Rh NPs are typically synthesized via polyol methods, there are many disadvantages in using such method. Primarily, polyol methods are troubled by irreproducible results in metal nanocrystal shapes. This is caused by the presence of trace amounts of impurities in commercial chemical reagents such as ethylene glycol.\textsuperscript{198} Additionally, compared to polyol synthesis, a water-based system provides a more environmentally sound route to the production of noble metal nanocrystals because it does not involve toxic organic solvents. Various reducing agents that are safe and easy to handle such as L-ascorbic acid and citric acid may be implemented. Finally, the simplicity and convenience of a water-based system provides great potential for large-scale production. Here, we demonstrate the overgrowth of Rh on Au NPs (Au@Rh) in a water-based system to create bimetallic nanostructures exhibiting a columnar Rh surface for increased light adsorption and tunable LSP resonance wavelength.
A.2 Experimental methods

A.2.1 Synthesis of bimetallic nanostructures

Au NPs were prepared following a previously reported two-step method\textsuperscript{199} and then used for the seeded overgrowth of Rh shells (Fig. A.2a). Briefly, \~{}3 nm Au seeds were synthesized using gold (III) chloride hydrate (HAuCl\textsubscript{4}) with sodium borohydride (NaBH\textsubscript{4}) as the reducing agent. These as-grown Au NPs were then used as seeds to grow larger Au cuboctahedrons in the presence of L-ascorbic acid (AA). Figure A.2c shows TEM images of Au cuboctahedrons with diameters of 18 ± 2.8 nm with LSPR peak located at 527 nm; consistent with previous reports on Au NPs with similar sizes.\textsuperscript{200}

Figure A.2. Synthesis of Au Nanoparticles.
(a) Two-step seeded synthesis of Au cuboctahedrons. (b) UV-Vis absorption spectrum shows a peak at 527 nm; Au cuboctahedron solution has a ruby red color. (c) TEM image of Au nanoparticles.
Following a modified procedure of Rh overgrowth on metallic nanocubes, Figure A.3 illustrates the iodide-mediated Rh island epigrowth on monodisperse Au cuboctahedrons. AA was used as the reducing agent in an aqueous solution of cetyltrimethylammonium bromide (CTAB), as-prepared Au cuboctahedrons, sodium iodide (NaI), and rhodium precursor salt (RhCl₃ x H₂O). Studies have shown that when the interaction between directing agents and the metals are too strong, the catalytic activity of the metal is reduced. Therefore, CTAB was chosen as the directing agent over the most widely used directing polymer polyvinylpyrrolidone (PVP). The weaker interaction between CTAB and Rh surface offers control of morphology while preserving catalytically active sites. Additionally, an excess amount of the AA reducing agent was used in the system to ensure a pseudo-first-order rate and to enable quick reduction of Rh(III) precursor ions into Rh(0) atoms.

![Diagram](attachment:image.png)

Figure A.3. Synthesis of Au@Rh.
Controlled Rh overgrowth on Au cuboctahedrons with the assistance of iodide adsorbate ions.

### A.2.2 Material characterization

Transmission electron microscopy (TEM) images were collected by an FEI Tecnai G² Twin operating at 200 kV. The TEM samples were prepared by dispersing the Rh nanospheres and Rh photocatalysts in ethanol with sonication, then depositing on a copper grid coated with a carbon film (Ted Pella, 01813). Diffuse reflectance UV-vis
extinction spectra were obtained on an Agilent Cary 5000 equipped with an external diffuse reflectance accessory (DRA-2500). The composition of the photocatalysts was measured by a Kratos Analytical Axis Ultra X-Ray Photoelectron Spectrometer (XPS).

A.2.3 Catalytic reactions

The catalytic reactions were carried out in a custom-built gaseous reaction system as described in Chapter 2. For each experiment, approximately 30 mg of the prepared Au@Rh/Al₂O₃ was loaded in the reactor to fill a 6-mm diameter catalyst cup to achieve a sample thickness of ~3 mm and ensure complete absorption of light for the catalytic measurements. The Au@Rh/Al₂O₃ photocatalysts were first reduced under 60 standard cubic centimeters per minute (sccm) H₂ and 40 sccm Ar at 350 °C for 2 h, and then the gas flow was switched to a mixture of CO₂, H₂, and Ar with the desired ratio and a total flow rate of 200 sccm. The gaseous product was monitored by an online quadrupole mass spectrometer (Hiden, HPR-20) equipped with a Faraday cup and secondary electron multiplier (SEM) detector at m/z = 2 (H₂), 15 (CH₄), 18 (H₂O), 28 (CO), 40 (Ar) and 44 (CO₂) in real time with filament settings of 70 V and 250 μA. The detection limit of the mass spectrometer was ~0.001% conversion of CO₂. For each temperature and light intensity condition, at least 30 minutes elapsed before ten sequential measurements were made to ascertain the steady-state concentration of each gas and the associated reaction rates and uncertainties. All reactions were operated under atmospheric pressure and use the chamber temperature, Tc as the set and measured temperature.
A.3 Results and discussion

A.3.1 Plasmonic properties

During the Rh overgrowth on Au reaction, a 500 µL aliquot of the reaction mixture was removed at 5-minute intervals and transferred to a clean vial for characterization. A time-dependent UV-vis spectrum gives more insight on the progression of the reaction. In Figure A.4a, the growing peak at 294.9 nm can be attributed to the Rh overgrowth. Figure A.4b shows a magnified view of the decreasing Au peak at 527 nm. This appearance of a UV peak from the Rh shell and disappearance of the Au peak suggests that LSPR effects are strongly dependent on the surface characteristics. Figure A.4c shows the color of the reaction mixture beginning as a light pink and changing to a light brown.

Figure A.4. Time-dependent iodide mediated Rh overgrowth on Au cuboctahedrons.
(a) Time-dependent UV-Vis spectrum shows the 294.9 nm Rh peak increasing over time. (b) Magnified view shows that the 527 nm Au peak decreases over time. (c) Reaction mixture starts as a light pink color and changes to a light yellow and finally a light brown color over the course of 30 minutes.
UV-vis spectra from the microwave-assisted polyol synthesis of Au@Rh with compact shells of varied thicknesses showed comparable results.\textsuperscript{197} Similarly, other studies have shown that thin coatings of Ag shell on Au nanocrystals results in plasmonic properties that resemble pure Ag nanocrystals.\textsuperscript{203,204} Therefore, the Au core simply functions as a template substrate and does not affect the plasmonic properties of the core-shell nanostructures. The advantage of Au@Rh bimetallic nanostructures comes from the use of a more abundant and less expensive core in conjunction with the unique UV LSPR effects from Rh shells. The TEM image of the Au@Rh bimetallic nanostructures shows the columnar growth of Rh around the Au substrates (Fig. A.5).

\textbf{Figure A.5. TEM image of Au@Rh nanostructures.}
Dendritic Rh surface is formed over an Au core.
Typically, the atomic arrangement of core@shell structures is related to the relative surface energies and reduction potentials.\textsuperscript{182,205} A large difference in reduction potential favors a core@shell structure whereas small differences favors the formation of an alloy.\textsuperscript{181} The surface and cohesive energy of Au and Rh generally favors the reverse configuration of an Au shell and Rh core.\textsuperscript{206} While Au is more noble and easier to reduce than Rh, the observed atomic arrangement of Au@Rh demonstrates that it is the kinetic product.

A.3.2 Plasmon-enhanced and thermal catalytic reactions

The as-synthesized bimetallic Au@Rh NPs of 33.7 ± 3.4 nm were supported on Al\textsubscript{2}O\textsubscript{3} with a ~1 wt% loading and tested CO\textsubscript{2} hydrogenation using our house-built gaseous system as described in Chapter 2 (Fig. A.6a). Under UV illumination, there is a selective enhancement of CH\textsubscript{4} production over CO as shown in Figure A.6b.

Figure A.6. CO\textsubscript{2} hydrogenation reaction on Au@Rh. (a) Schematic setup for catalytic reactions. (b) Selective enhancement of CH\textsubscript{4} over CO under UV illumination at 3.0 W cm\textsuperscript{-2}.
Figure A.7. CO₂ hydrogenation under illuminated conditions.
(a) Photocatalytic CH₄ production rate vs. UV light intensity. (b) CH₄ production rate under 3.0 W cm⁻² UV light, 2.4 W cm⁻² & 4.9 W cm⁻² blue light and no light vs. temperature. Circle points show steady-state reaction rate without additional heating. Arrhenius plots of (c) thermal and (d) photo reactions of CO² hydrogenation.

Several controlled conditions were studied for photocatalytic CO₂ hydrogenation on Au@Rh/Al₂O₃ catalyst including the effects of varied light wavelength/intensity, and light vs. dark (Fig. A.7). As the intensity of light increases, the measured CH₄ production rate transitions from linear to super-linear dependence (Fig. A.7a). An Arrhenius plot using the production rates and chamber temperature T_c can be used to determine the
apparent activation energy for various reaction conditions (Fig. A.7b). Under dark thermal conditions, the apparent activation energy for CH$_4$ and CO are calculated to be $97.6 \pm 2.3$ and $50.8 \pm 7.0$ kJ mol$^{-1}$ (Fig. A.7c). Under illuminated conditions, the apparent activation energy for CH$_4$ is reduced to $80.7 \pm 0.6$ kJ mol$^{-1}$ and is consistent for varied light intensities (Fig. A.7d).

The photocatalytic properties of Au@Rh are compared to that of Rh NC. In terms of product selectivity, Rh NCs are more selectively for both dark and illuminated conditions (Fig. A.8a). However, comparisons of CH$_4$ production rates show that Au@Rh are more active under dark thermal conditions due to increased surface area (A.8b). Under illuminated conditions, the Rh NCs are more active due to its sharp corners. Overall, bimetallic Au@Rh is a viable cost-friendly alternative to pure Rh NCs.

![Figure A.8](image)

**Figure A.8. Comparison of Bimetallic Au@Rh and Rh NC for CO$_2$ Hydrogenation.** Au@Rh NPs and Rh NCs are of similar size of $\sim 37$ nm diameter. CH$_4$ (a) selectivity and (b) production rate are shown as a function of $T_c$ temperature.
However, over the course of four days, the measured CH₄ production rates on the Au@Rh/Al₂O₃ is monitored for both dark thermal and illuminated conditions (Fig. A.9). For a $T_c$ of 350 ℃, the dark thermal rate decreased 6.5%. In contrast, for illumination with 3.0 W cm⁻² and a $T_c$ of 350 ℃, the measured CH₄ reaction rate decreased 16.8%. Drastic decreases in CH₄ production rates on Au@Rh/Al₂O₃ suggest that photocatalytic activity is particularly sensitive to reaction conditions and could be related to light induced morphological changes.

<table>
<thead>
<tr>
<th>Day</th>
<th>Thermal (μmol g⁻¹ s⁻¹)</th>
<th>UV (μmol g⁻¹ s⁻¹)</th>
<th>ΔRate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.2 ± 0.01</td>
<td>30.3 ± 0.09</td>
<td>6.5</td>
</tr>
<tr>
<td>4</td>
<td>5.8 ± 0.11</td>
<td>25.2 ± 0.10</td>
<td>16.8</td>
</tr>
</tbody>
</table>

**Figure A.9. Catalyst stability under thermal and illuminated conditions.**
The CH₄ production rate dramatically decreases under illuminated conditions over four days of continuous testing.

The morphology of the Au@Rh/Al₂O₃ catalyst is investigated using TEM in Figure A.10. The as synthesized Au@Rh nanoparticles have a diameter of 39.5 ± 2.1 nm and features well defined dendritic nanostructured shell (Fig. A.10a). After calcination in air at 450 ℃, the diameter is decreased to 33.7 ± 3.4 nm and the dendritic Rh shell appears smaller (Fig. A.10b). After exposure to reactant gases, elevated temperatures, and illumination by blue and UV light, the morphology of the Au@Rh nanoparticles is dramatically changed.
Figure A.10. Morphological changes under reaction conditions.
(a) As-prepared Au@Rh/Al2O3 catalyst, dendritic Rh structures are well-defined. (b) After calcination in air at 450 °C for two hours, the dendritic shell shrinks. (c) After exposure to experimental conditions, the nanostructures lose the distinct dendritic shell and resembles compact core-shell structures.

The dendritic structure is destroyed under reaction conditions and the diameter is further decreased to 28.8 ± 3.0 nm (Fig. A.10c). Since the Au NP core had an original diameter of ~18 nm and Au itself cannot promote CH4 production, it suggests that Rh is still present on the shell. Under reaction conditions, the dendritic bimetallic Au@Rh nanoparticles are transformed into core-shell structures with a compact Rh shell.

A.4 Conclusion and Outlook

Plasmon-driven CO2 hydrogenation on bimetallic Au@Rh nanostructures give rise to enhanced reaction rates and CH4 product selectivity. Future studies with precise temperature measurements are required to verify the thermal and nonthermal contributions. Additionally, synthetic efforts in decreasing thickness of the shell of Rh and adding a protection layer may offer interesting synergistic properties from both core and shell elements while maintaining catalyst stability.
Appendix B: Improved Thermometry Methods in Plasmonic Photocatalysis

B.1 Introduction

Thermal gradients are inevitable for light driven catalytic reactions in which the penetration depth of light is typically limited to a sub-micron scale. A challenge remains in obtaining a meaningful definition of temperature for the system. The basis of this dissertation focused on thermal profiles monitored using traditional thermocouples. Incorporation of improved nanoscale thermometry techniques requires modifications to the reaction chamber. The following explores a new setup combining non-contact infrared technology with contact thermocouples for in situ measurements of the thermal profile of catalysts under reaction conditions.

B.2 Cold-mirror setup

Our established multi-thermocouple setup has enabled the ability to monitor the thermal profiles of catalysts under reaction conditions. These imbedded thermocouples also allow for the ability to set the temperature of the specified location. However, the temperature indicated may be an underestimation of the surface temperature since the thermocouple tip must be slightly covered to prevent direct illumination from the light source. We have shown in Chapter 3 that thick thermocouples act as a cold finger and decreasing the diameter of the thermocouple significantly improves measured temperatures. Nevertheless, decreasing the thermocouple diameter \(< 0.25\) mm results in a flimsy probe that is extremely difficult to insert and position in our current reactor. Temperature measurements from a non-contact IR pyrometer may be
incorporated into the system to circumvent physical challenges with the use of thermocouples. Since IR temperature measurements are restricted to the surface, a thermocouple may be needed to monitor the bottom surface of the catalyst.

Typically, an IR pyrometer should be positioned perpendicular to the surface of interest for the most precise measurement. This requirement conflicts with the position of the light source when the surface of interest must also be illuminated. Both the light source and the IR pyrometer can be placed at an angle at the expense of uniform illumination or accurate temperature measurements. Instead, a cold mirror can be used to resolve this situation.

A cold mirror is a dichroic filter that reflects ~90% of the UV and visible light while efficiently transmitting ~80% of the NIR and IR wavelengths. Cold mirrors can be designed for an incidence angle ranging between zero and 45 degrees. While they are typically used to remove heat from a system, cold mirrors can allow UV and visible light to be reflected and IR to be transmitted to the same location by placing the light source and IR pyrometer on opposite sides as shown in Figure B.1. For IR transmission through the reactor to the catalyst surface, the quartz window must be replaced also be replaced with an IR compatible material. KBr is a common choice as it is transparent from the near UV to long-wave IR wavelengths (0.25 – 25 um) However, its high solubility and hygroscopic nature makes it incompatible for reactions that produces water such as in CO2 reduction. Instead, a sapphire (Al2O3) window with a wide transmission band from UV to near-infrared (0.15-5.5 um) is desired sufficient for this setup. Sapphire is highly resistant to scratching and abrasion and can withstand extremely high temperatures.
Figure B.1. Schematic of cold-mirror setup.
Allows for the incorporation of light sources and non-contact IR pyrometer without compromising the incident illumination angle or angle of detection.

This setup is evaluated in two parts. First, the power of a blue LED is tested for direct illumination and reflected illumination (Fig. B.2). The overall distance between the liquid light guide and the power meter is maintained at 5.4 cm for each setup. Due to bulkiness of the cold mirror setup, it is difficult to shorten the distance between the light source and the illuminated surface. This in turn requires a more powerful light source to provide illuminated conditions at higher intensities of light.
The output power of our LEDs can be controlled by analog signals from 0 to 5 V. The measured power in through direct illumination and reflected through the cold mirror is compared in Figure B.3.

Figure B.2. Illumination through a cold mirror.
Photographs of illumination setup (a) through a cold mirror versus (b) direct illumination.

Figure B.3. Comparison of measured power from illumination.
(a) Schematic of direct illumination and cold mirror setup. (b) Measured illumination power as a function of input voltage. ~94% of the LED light is reflected using the cold mirror setup when compared to identical distance of direct illumination.
Nearly 94% of the LED light is reflected as expected based on the properties of
the cold mirror. As a result, this validates part of our proposed cold mirror setup. Next,
we must test the IR transmission through the cold mirror and the accuracy of measured
temperatures. To do so, the IR pyrometer (Micro-Epsilon, CTLM-3H1CF2-C3) is
secured above a hot plate as shown in Figure B.4. This high-performance pyrometer has a
temperature range of 150-1000 °C with a focus of 0.5 mm at 150 mm away. It is also
equipped with double laser spot marking to indicate the measured spot size (Fig. B.4a).
When a cold mirror is positioned at 45°, a small portion of the laser spot is transmitted
while the majority is reflected onto the back wall of the hood (Fig. B.4b). A second laser
light is pointed parallel to the surface to simulate the position of a visible light source
(Fig. B.4c). The cold mirror successfully reflects the laser pointer and the setup is ready
to test temperature measurements.

Figure B.4. Proof of concept setup for IR pyrometer and cold mirror setup.
(a) IR pyrometer is positions on top of a hot plate. (b) After incorporating the cold mirror, the
laser guide light is reflected onto the wall whereas a small portion is transmitted. (c) A red laser
pointer is placed at the light source position to test reflection onto the hot plate surface.
The IR pyrometer can be connected to a computer via USB and the data can be logged in real time. While fluctuations in temperatures can be detected instantaneously by the IR pyrometer, the measured temperature has an error of ~2% when compared to that of a contact thermocouple (Fig. B.5). However, this error can be compensated by adjusting settings in the detection mode to calibrate for transmission through a cold mirror and optical window in the final reactor setup.

![Image of temperature vs. time graph](image)

**Figure B.5. Sensitivity of IR pyrometer.**
The cold mirror will transmit ~80% of NIR and IR wavelengths. The IR pyrometer can be calibrated to account for transmission through a cold mirror.

Although IR temperature measurements can be easily obtained, the real challenge is in understanding the difference between apparent and actual IR temperatures. Emissivity is the ratio of how well a material radiates infrared energy compared to a perfect radiator called a “black body.” Emissivity varies by surface condition, viewing
angle, temperature and spectral wavelength. Therefore, measurements of materials with unknown emissivity can result in huge errors. The emissivity of catalyst samples may be determined experimentally through material heating. The catalyst of interest should be heated to a known uniform steady-state temperature in a furnace or hot plate. The temperature measured by the IR pyrometer can be calibrated to a contact temperature probe. The emissivity setting of the IR pyrometer should be adjusted until the correct value is reacted. This value is the correct emissivity for the measured material.

**B.3 Reaction chamber modifications**

**B.3.1 Enlarged window mount**

An enlarged chamber window can allow for additional *in situ* monitoring of the catalyst under reaction conditions (Fig. B.6). Here, the window viewing area is increased from a diameter of 8 mm to 20 mm.

![Enlarged window mount](image)

*Figure B.6. Enlarged window mount.*
Viewing port can be increased to a diameter of 20 mm for increased illumination and future changes in sample cup design.
B.3.2 Reduced cup depth

To isolate nonthermal light effects, the thickness of the catalyst should be reduced. The current catalyst sample cup can be fitted with a small copper rings of different heights to prop up the base of the mesh holder, therefore decreasing the overall thickness of the catalyst sample (Fig. B.7). This allows for comparisons of thick versus thin catalyst samples and ensures that the illuminated surface is at the same top location. It is important to note that the catalyst of interest must be extremely active as reducing the thickness denotes indicates significant decrease in the amount of catalyst used. For catalysts with lower activity, decreasing the amount of catalyst may not generate measurable reaction rates.

![Copper rings for testing catalysts with decreased thickness.](image)

(a) Schematic and (b, c) photographs of the copper ring setup. This props up the bottom of sample cup and reduces the depth of the sample cup.
As the thickness of the catalyst is decreased, high thermal conductivity of the catalyst also decreases the thermal gradient within. For a thin layer, the temperatures measured by the top and bottom thermocouples are virtually the same (Fig. B.8a).

**Figure B.8. CO\textsubscript{2} methanation on thin layer Rh-s/TiO\textsubscript{2} catalyst.**
(a) Decreasing the thickness of the catalyst also reduces the thermal gradient within. (b) Photograph of cup mesh in thin catalyst setup. (c) CH\textsubscript{4} production rate as a function of light intensity and corresponding \( T_2 \) for \( T_1 \) set at 250 °C under direct and indirect illumination. The flow is CO\textsubscript{2} 20 sccm, H\textsubscript{2} 60 sccm, and Ar 120 sccm for a total 200 sccm.
A copper ring with 1.5 mm thickness reduces the sample cup depth to ~1.5 mm. For a thin catalyst setup, a cup-style mesh cup is more difficult to construct and position especially when ~1 mm of head space is required for the Ti2O3 overlayer (Fig. B.8b). For ~3 mg of Rh/TiO2, the sample has an estimated thickness of 0.28 mm. This miniscule amount of catalyst is insufficient to support the side panels of the cup-style mesh and new catalyst holder designs to accommodate small amounts of catalyst are necessary. The total CH4 production rate differs from the characteristic “U” shape as seen in thick catalysts from Chapter 2 and 4. Instead, the reaction rate only increases with light intensity. Because the sample is very thin, $T_1 \sim T_2$ for all conditions and the thermal profile does not change with light intensity when $T_1$ or $T_2$ is set at a constant temperature. The measured thermal contribution from indirect illumination with a Ti2O3 layer matches calculated rates with slight deviations at higher intensities.

**B.4 Conclusion and outlook**

*In situ* nanoscale thermometry techniques can provide additional insight to the underlying mechanism for plasmonic photocatalysis. The incorporation of a cold mirror setup allows for simultaneous illumination and IR temperature measurements while modifications to the reaction chamber can improve the overall quality of data. Incorporating these techniques to monitor the temperature of thin layer catalysts can further reveal insight to the fundamental knowledge of plasmonic photocatalysis.
References


74 Gutierrez, Y. *et al.* How an oxide shell affects the ultraviolet plasmonic behavior of Ga, Mg, and Al nanostructures. *Optics Express* **24**, 20621-20631 (2016).


187 Atae-Esfahani, H., Wang, L., Nemoto, Y. & Yamauchi, Y. Synthesis of Bimetallic Au@Pt Nanoparticles with Au Core and Nanostructured Pt Shell


Biography

Xueqian (Lucy) Li completed her undergraduate studies in May of 2014 at New York University in New York City, New York where she received a B.S. in Chemistry with highest honors. In August of 2014, Xueqian began her doctoral studies at Duke University in Durham, North Carolina in the Department of Chemistry under the supervision of Dr. Jie Liu. Xueqian has presented her research at several local and national conferences and published several first-author research articles.

Publications


Presentations


7. Li, X. et al., “Design of Au@Rh Plasmonic Photocatalysts for Carbon Dioxide Hydrogenation.” *American Chemical Society Spring Meeting*, San Francisco, CA, April 2017. (Poster)

8. Li, X. et al., “Bimetallic Au@Rh Nanostructures for Carbon Dioxide Hydrogenation.” *Fitzpatrick Institute for Photonics Symposium*, Durham, NC, March 2017. (Poster)


Fellowships


2. Graduate Program in Nanoscience Fellowship, Duke University, 2015