Design and Synthesis of Metal Nanostructures for Plasmon-Enhanced Catalysis

by

Xiao Zhang

Department of Chemistry
Duke University

Date: 07/18/2017
Approved:

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Jie Liu, Supervisor

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Stephen L. Craig

___________________________
Henry O. Everitt

___________________________
Jeffrey T. Glass

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Michael J. Therien

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

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ABSTRACT

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Abstract

The chemical industry depends on heterogeneous thermocatalytic processes to satisfy the ever-increasing demand for fuels and fertilizers. High temperatures and high pressures are generally required to accelerate chemical transformations and operate at practical rates. These harsh conditions, however, lead to huge energy consumption and other side effects, such as the lifetime of catalysts and parasitic formation of by-products. Light is used as an alternative energy input to drive chemical reactions on semiconducting photocatalysts, but the slow reaction rates and insufficient control of product selectivity hinder wide adaptation of photocatalysis. Plasmonic metal nanoparticles have been recently proposed as a new type of catalysts with photoactivities. As already been widely used in thermocatalytic reactions, the strong light absorption capability from excitation of localized surface plasmon resonance (LSPR) of plasmonic catalysts could combine light and thermal energy to work cooperatively in enhancing rates of chemical reactions. This dissertation summarizes our efforts aiming to design plasmonic catalysts with high efficiency and high product selectivity. The catalytic properties of synthesized rhodium (Rh) and ruthenium (Ru) catalysts are investigated in two model reactions, carbon dioxide (CO$_2$) hydrogenation and ammonia (NH$_3$) synthesis.

Chapter 2 describes the development of slow-injection polyol methods to synthesize monodispersed Rh nanocubes with tunable size and resonant energy. The wide size tunability of slow-injection methods allows for the red-shift of resonant wavelength of small Rh nanostructures, which are in the deep ultraviolet (UV) region, to more
accessible and practical near-UV and visible regions by increasing the size of Rh nanocubes.

Chapter 3 focuses on the product selectivity of plasmonic Rh nanocubes in CO$_2$ hydrogenation. Rh nanocubes supported on aluminum oxide (Al$_2$O$_3$) nanoparticles equally produce methane (CH$_4$) and carbon monoxide (CO) in pure thermal conditions. Under illumination of UV and blue light, the rate of CH$_4$ production is significantly enhanced, and almost exclusive CH$_4$ production is observed. This photo-selectivity can be attributed to selective activation of specific reaction intermediate by photo-generated hot electrons among competing reaction pathways.

Chapter 4 describes the effects of catalyst support and morphology of plasmonic Rh nanostructures on the catalytic activities in plasmon-enhanced CO$_2$ hydrogenation. Significant improvements of reaction rates are observed by switching to reducible titanium oxide (TiO$_2$) support and shrinking the size of Rh nanostructures. The enhancement of reaction rates by light can be partially attributed to local heating of catalyst bed.

Chapter 5 focuses on the catalytic activities of Ru-based catalysts for NH$_3$ synthesis under light illumination. Photo-enhanced NH$_3$ production, which highly depends on the size, support, and promoter of catalysts, is observed.

Chapter 6 discusses conclusion and future directions of this project. Molecular level insights of plasmon-enhanced catalysis are highly desired for both fundamental research and practical applications.
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Figure A.5. Carbon yield evolution of CNT samples grown at 700°C, 850°C and 950°C with Fe-based catalyst. Figure reproduced with permission from ref. 137, © 2015, Tsinghua University Press and Springer-Verlag Berlin Heidelberg.

Figure A.6. The TEM images of metal nanoparticles in CNT samples grown at 850 °C for 10 min (a) and 60 min (b) and at 950 °C for 3 min (c) and 60 min (d). Scale bar: 100 nm. Figures reproduced with permission from ref. 137, © 2015, Tsinghua University Press and Springer-Verlag Berlin Heidelberg.

Figure A.7. Size distribution of active metal nanoparticles in CNT samples grown with different growth duration at 850 (c) and 950 °C (d). Figures reproduced with permission from ref. 137, © 2015, Tsinghua University Press and Springer-Verlag Berlin Heidelberg.

Figure A.8. Representative TEM images of CNTs grown for 40 min with Fe-W-based catalyst at 850 (a) and 950 °C (b). Scale bar: 100 nm, (inset: 20 nm). (c) Carbon yield evolution of CNT samples grown at 850 and 950 °C with Fe-based and Fe-W-based
catalysts. Figures reproduced with permission from ref. 137, © 2015, Tsinghua University Press and Springer-Verlag Berlin Heidelberg

Figure B.1. Schematic representation of synthesis of Rh NSs.

Figure B.2. TEM images of amine-functionalized SiO$_2$ spheres (a), Rh seed decorated SiO$_2$ spheres (b) and Rh NSs (c). Scale bar: 100 nm. (d) UV-vis spectra of Rh NSs in an ethanol dispersion.

Figure B.3. TEM images of Rh NSs with one-fourth of Rh precursor as in the standard method (a) and without the addition of HCl (b). Scale bar: 100 nm.

Figure B.4. TEM image (a) and corresponding UV-vis spectrum (b) of Rh tripods.

Figure B.5. TEM images of Al$_2$O$_3$ supported Rh NSs calcined in air at 350 °C (a) and Al$_2$O$_3$ supported Rh tripods reduced in H$_2$ at 350 °C (b). Scale bar: 50 nm.
Acknowledgements

First and foremost I would like to thank my advisor, Prof. Jie Liu, for bringing me into the fantastic world of nanoscience, and for his help and guidance throughout my PhD study at Duke University. His passion in science and education continuously pushed the quality of my research and writing skills to excellence. He also encouraged me to present my research at meetings and improve my presentation skills. I deeply appreciate all his efforts in training me to be an independent researcher. He is an incredible mentor and friend. It is my great pleasure to work with Prof. Liu in the last five years.

I would like to thank Prof. Stephen Craig, Prof. Henry Everitt, Prof. Jeffrey Glass, and Prof. Michael Therien for their interests in my research and being my committee member, and for spending time reading and commenting on my preliminary examination documents, annual research summaries, and dissertation.

I would also like to thank current and former Liu group members for their help over the years, including Dr. Yingwen Cheng, Mr. Hongbo Zhang, Dr. Pan Li, Dr. Jinhyun Cho, Dr. Songtao Lu, Ms. Yue Cai, Dr. Jinghua Li, Dr. Gyeonghee Lee, Dr. Danielle E. Gorka, Ms. Jennifer Sedloff, Mr. Keigo Otsuka, Dr. Yanwen Ma, Dr. Shujuan Jiang, Dr. Hao Tong, Dr. Dandan Zhao, Ms. Pingping Sun, Mr. Qiwei Han, Ms. Christine Kim, Ms. Xueqian Li, Mr. Dong Ji, Mr. Peter Novello, Mr. Yiwen Zhang, and Mr. Shi He.

I would like to acknowledge our fabulous collaborators. I thank Prof. Henry Everitt for a lot of helpful discussions throughout the plasmon-enhanced catalysis project,
Prof. Gleb Finkelstein and his group for helping me with surface-enhanced Raman spectroscopy, Prof. Fernando Moreno and his group for simulations of optical properties of metal nanostructures, and Prof. Weitao Yang and his group for calculations of the energetics of reaction intermediates.

I thank Duke University Shared Materials Instrumentation Facility (SMiF) and staff, especially Dr. Mark Walters and Michelle Plue, for helping me with material characterization.

I would like acknowledge financial support from the GPNano Fellowship, Paul M. Gross Fellowship, Peter Walter Jeffs Summer Research Fellowship, Katherine Goodman Stern Fellowship, and the generous donors.

Finally, I would like to express my deepest gratitude and respect to my parents. Their unconditional love is my strongest support all these years. This dissertation is dedicated to them.
Chapter 1: Introduction

1.1 Importance of heterogeneous catalysis

Catalysis plays a crucial role in almost every aspect of our life and even in the existence of living organisms. The core of catalysis is catalyst, which accelerates chemical reactions by reducing the activation barrier without being consumed during the reaction. Most physiological activities, from the extraction of chemical energy to the duplication of living cells, are accelerated by biological catalysts, enzymes. Chemical industries also heavily rely on catalytic processes to increase the reaction rates. Based on the phases of catalysts and reactants, catalytic processes can be categorized into heterogeneous catalysis (catalysts and reactants in different phases) and homogeneous catalysis (catalysts and reactants in the same phase).¹

Heterogeneous catalysis generally employs solids as catalysts and liquids or gases as reactants. The separation of catalysts and reactants in different phases in heterogeneous catalysis allows for continuous operation of chemical reactions and easy recycling of catalysts. These advantages of heterogeneous catalysis are highly desired in large-scale operation of chemical reactions, so most of current industrial processes utilize heterogeneous catalysis. One of the most successful employments of heterogeneous catalysis in chemical industry is ammonia (NH₃) synthesis through Haber–Bosch process.² In Haber–Bosch process, nitrogen (N₂) and hydrogen (H₂) pass through iron (Fe) catalysts at high temperature (~500 °C) and high pressure (~200 bar) to produce NH₃. Due to the low conversion of reactants at high temperature, NH₃ is separated from the stream and unreacted N₂ and H₂ are recirculated back to the reactor to increase the
overall conversion of reactants. NH$_3$ is further converted into fertilizers to support the continuous growth of world population.$^3$

Three-way catalytic converters in automobile exhaust system is another important example of heterogeneous catalysis. Combustion products from internal combustion engines contain unburned hydrocarbons and toxic nitrogen oxides (NO$_x$) and carbon monoxide (CO). These harmful compounds would be a significant environmental concern if directly released into the atmosphere. Before exiting the exhaust line, these toxic compounds react on the surface of platinum/rhodium (Pt/Rh) or palladium/rhodium (Pd/Rh) catalysts and are converted into non-toxic carbon dioxide (CO$_2$), water, and N$_2$.$^4$

The deployment of three-way catalytic converters in automobile exhaust system is the key to the reduced emission of harmful gases and the improvement of air quality in modern society.

Products from heterogeneous catalysis, such as fuels and fertilizers, make significant contributions to the sustainability and quality of the contemporary world. The research efforts of heterogeneous catalysis have been devoted to the design of high-performance catalysts to increase the reaction rates with reduced amount of catalysts, mitigate the generation of byproducts, possess high stability for long-term operation, and allow for operation of reactions under mild conditions.$^5$-$^7$ To achieve these goals, it is critical to understand the fundamental principles of heterogeneous catalysis.

**1.2 Fundamental principles of heterogeneous catalysis**

Heterogeneous catalysis accelerates chemical reactions through the interactions between catalysts and reactants/intermediates at the gas-solid or liquid-solid interfaces.
As shown in Figure 1.1, surface-catalyzed reactions involve three major steps: (i) adsorption of reactant molecules on exposed surface vacant sites of catalysts; (ii) surface reaction of adsorbates, which includes the dissociation, migration, and recombination of surface intermediates on the active sites; (iii) desorption of product molecules for product release and regeneration of surface vacant sites.\(^8\) In these steps, there is usually one particular step that is much slower than all the other steps and determines the rate of the overall reaction, called the rate-determining step (RDS). The identifications of the RDS and real active sites have proven to be difficult but extremely beneficial for the design of heterogeneous catalysts.

**Figure 1.1.** (a) Potential energy diagrams of a gas-phase uncatalyzed reaction (blue) and a surface-catalyzed reaction (red) through adsorption of reactants (i), surface reaction (ii), and desorption of products (iii). (b) Illustration of elementary steps involved in surface-catalyzed chemical reactions. Figure b adapted with permission from ref. 8, © 2014 John Wiley & Sons, Inc.
The stabilization of reaction intermediates through the bonding interactions between intermediates and catalyst surfaces significantly reduces the activation energy compared to gas-phase uncatalyzed reactions. Gas-phase uncatalyzed reactions generally proceed through radical mechanisms, which require huge energy input to activate reactants and generate free radicals. For example, uncatalyzed NH$_3$ synthesis requires the breaking of nitrogen-nitrogen triple bond with a bond strength of 945 kJ/mol to generate active atomic N. With the help of optimal catalysts to facilitate the dissociation of N$_2$, such as Fe and ruthenium (Ru), the activation energy can be reduced to ~100 kJ/mol.$^{9-10}$ The activation energy of gas-phase uncatalyzed reverse water-gas shift (CO$_2$+H$_2$→CO+H$_2$O), initiated by the generation of H radicals, was measured to be 320 kJ/mol.$^{11}$ On the surface of cooper (Cu) and gold (Au) catalysts, the reaction proceeds via alternative reaction pathways with reduced activation energies as small as 40 kJ/mol.$^{12-13}$ The interactions between exposed catalyst surfaces and reaction intermediates open new reaction pathways that do not exist in gas-phase uncatalyzed reactions, thus modifying the potential energy diagram and activation energies. The reduced activation energies allow reactions, which are only observable at extremely high temperatures in gas phase, to be operated at significantly reduced temperature with accelerated reaction rates.

Most of research efforts of heterogeneous catalysis in the 20$^{th}$ century was devoted to the discovery of catalysts with high activities, while a high selectivity was considered less important in most cases. However, understanding the origin of product selectivity has attracted more and more interests in the 21$^{st}$ century due to the expensive waste disposal, the well-documented negative environmental impacts, and the limited
supply of feedstocks, such as fossil fuels. The use of heterogeneous catalysis could also form products that cannot be formed in gas-phase reactions. As discussed earlier, the reaction between CO$_2$ and H$_2$ in gas phase produces CO and water through reverse water-gas shift process. By contrast, on properly designed Ru, Cu and metal oxide catalysts, CO$_2$ hydrogenation can form methane (CH$_4$), methanol (CH$_3$OH), and even gasoline.$^{14-15}$ Heterogeneous catalysts with high activities and high selectivity towards targeted products are the ultimate goals of this research field.

### 1.3 Structure of heterogeneous catalysts

Heterogeneous catalysts are generally composed of catalytically active particles, supports, and promoters. Active particles provide suitable surface sites to interact with reactants and intermediates. Catalyst supports offer high surface area and mechanical and thermal stability for active particles. Promoters are inactive for reactions by themselves but can interact with active particles to modify their properties. The general spatial arrangement of active particle, support, and promoter is shown in Figure 1.2. These three components function cooperatively to determine the activities, product selectivity, and stability of heterogeneous catalysts.
1.3.1 Active particle

Catalytically active particles are usually metals or metal oxides. Since reactions only occur on the surface of active particles, their sizes are normally in the range of a few nanometers to maximize the exposed surface area. Compared to the atoms in bulk, atoms on surface have lower coordination number with tendency to form chemical bonds with gas-phase molecules. These interactions stabilize surface intermediates and facilitate chemical reactions. The strength of these interactions depends on the intermediates, the nature of catalyst materials, and the expose crystal facets of catalytically active particles. Figure 1.3 shows the structure of a face-centered cubic (fcc) Pt nanoparticle with 561 atoms. Due to the higher coordination number and less dangling bonds of Pt atoms on (111) facets than that on (100) facets, intermediates bind weaker to the Pt(111) facet compared to the Pt(100) facet. This also results in that atoms located at the corners, steps, and edges bond to intermediates stronger than atoms located on facets.
According to the Brønsted–Evans–Polanyi (BEP) principle, the difference in the activation energy between two reactions of the same family is proportional to the difference of the enthalpy of reaction.\textsuperscript{16} This principle implies that fast adsorption/activation of reactants requires strong bonding of the intermediate/product on the catalyst surface. On the contrary, strong bonding of products on the catalyst surface covers most of the surface sites and hinders the adsorption of reactants for following cycles of reactions. Therefore, the optimal bonding strength of reactants on catalyst surface is a compromise of rates of adsorption of reactants and desorption of products.

\textbf{Figure 1.3.} Schematic illustration of a Pt nanoparticle consisting of 561 atoms. The particle is enclosed by (100) and (111) facets connected by edges, which are equivalent to the steps on (211) facets. Figure adapted with permission from ref. 8, \textcopyright 2014 John Wiley & Sons, Inc.
Figure 1.4. Transition state scaling relationship of the adsorption energy ($\Delta E$), the activation energy ($E_a$), and the reaction rate ($Log r$). The reaction rate shows a “volcano” dependence on the adsorption energy, which is determined by the adsorption rate of reactant (blue) in the weak-bonding region (right side) and by the desorption rate of product (black) in the strong-bonding region (left side).

The compromise of adsorption rate and desorption rate results in the well-known “volcano” curve of catalytic activities, as shown in Figure 1.4. On the left side of the plot where reactants/intermediates bond strongly to the surface, the activation of reactants is fast but the desorption of products is slow. The catalyst surface is covered by products, thus starving for vacant sites for following reaction. Therefore, the overall reaction rate is determined by the rate of desorption of products. By contrast, on the right side of the plot where reactants/intermediates bond weakly to the surface, the desorption of products is
fast but the activation of reactants is slow. Consequently, the catalyst surface is almost empty and the rate of adsorption of reactants dictates the overall reaction rate. Hence, the optimal catalyst for certain reactions should bond to reactants/intermediates neither too strong nor too weak to balance the rate of adsorption and desorption. This could be done by tuning the compositions, crystal facets, and special types of active sites (corners and edges) of catalysts.\textsuperscript{8}

Conventional industrial catalysts are mainly prepared by the impregnation method. Metal salts as catalyst precursor are dissolved in water or alcohols, which supports are dipped in. After evaporation of solvents, the solid is further treated by calcination and reduction at high temperatures to transform the metal salts into desired form and composition, such as metallic nanoparticles. The catalytic nanoparticles generated by the impregnation method usually have broad size distribution and lack control of the shape and exposed crystal facets.\textsuperscript{17} With deeper understandings of the mechanism of nanoparticle growth and rapid development of synthetic methods, the control of the shape, size, and composition of metallic nanoparticles comes to an unprecedented level. Metal nanoparticles with well-controlled composition (single-metallic and multi-metallic), size (from sub-nanometer to tens of nanometers), shape (sphere, cube, wire, and plate), and exposed crystal facets have been synthesized with high quality, uniformity, and reliability.\textsuperscript{18-19} Some common morphologies of single-crystalline nanoparticles with $fcc$ structure are shown in Figure 1.5.
Figure 1.5. Common morphologies of single-crystalline metal nanoparticles with polyhedral shapes (top) and nonpolyhedral shapes (bottom). Figure adapted with permission from ref. 18, © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The successful syntheses of metal nanoparticles with well-defined morphology allow for investigations of structure-property relationships in heterogeneous catalysis and could also contribute to the preparation of industrial catalysts. For example, M. A. El-Sayed and colleagues investigated effects of the shape of Pt nanoparticles on their catalytic activities in electron-transfer reaction.\textsuperscript{20} Tetrahedral, cubic, and spherical Pt nanoparticles with similar sizes (~6 nm) were obtained by modifying the reaction conditions and capping agents in syntheses. The tetrahedral nanoparticles are enclosed by
four (111) facets, while the cubic nanoparticles are enclosed by six (100) facets. The spherical nanoparticles have a mixture (100) and (111) facets. The authors measured the activation energy of the electron-transfer reaction between hexacyanoferrate (III) and thiosulfate ions on these Pt nanoparticles with different shapes and correlated the activities with exposed crystal facets. It was found that Pt tetrahedrons and cubes have the smallest and biggest activation energy, respectively, and Pt spheres give intermediate activation energy. The different activation energies indicate that Pt(111) facets are more active than Pt(100) facets for this reaction.

G. A. Somorjai and co-workers studied the effects of Pt nanoparticle size on their catalytic activities in ethylene (C\textsubscript{2}H\textsubscript{4}) hydrogenation and ethane (C\textsubscript{2}H\textsubscript{6}) hydrogenolysis.\textsuperscript{21} Pt nanoparticles in the size range of 1.7 to 7.1 nm were synthesized by reducing a Pt salt in different solvents and at different temperatures, which are further supported on mesoporous silica. The catalytic activities are presented as turnover frequency (TOF), which is defined as the number of revolutions of the catalytic cycle on a single active site per unit time with the unit of s\textsuperscript{-1}. The number of active sites was measured by stoichiometric chemisorption. They found that the activities of C\textsubscript{2}H\textsubscript{4} hydrogenation was insensitive to the size of Pt nanoparticles, while the activities of C\textsubscript{2}H\textsubscript{6} hydrogenolysis to form CH\textsubscript{4} was sensitive to the size of Pt nanoparticles. Smaller nanoparticles showed much higher TOF compared to bigger nanoparticles due to the different degree of carbon deposition during the reaction.

S. Linic and colleagues investigated the effects of silver (Ag) nanoparticle shape on product selectivity in C\textsubscript{2}H\textsubscript{4} epoxidation.\textsuperscript{22} They found that Ag nanowires synthesized
by a polyol reduction method showed higher selectivity towards the desired product, ethylene oxide, compared to spherical Ag nanoparticles prepared by an impregnation method. The high selectivity towards ethylene oxide on Ag nanowires was attributed to the higher proportion of exposed Ag(100) facets, supported by density functional theory (DFT) calculations.

These examples manifest the great successes and contributions of controllable synthesis of metal nanoparticles to the identification of catalytically active and selective sites and the preparation of heterogeneous catalysts with desired properties.

1.3.2 Catalyst support

Catalyst supports are generally high surface-area oxides, such as porous silicon dioxide (SiO₂), aluminum oxide (Al₂O₃), titanium dioxide (TiO₂) and zeolite. High surface-area activated carbon is also used as catalyst support. The catalyst support provides high surface area to accommodate active nanoparticles and improve their thermal stability by preventing the aggregation of active nanoparticles. The catalyst support is also required to be chemically inert to resist the operation conditions of reactions. Although supports were considered to play a passive role in catalytic processes, evidences have shown that supports can strongly influence the activity and selectivity of heterogeneous catalysts. The dependence of catalytic properties on the support materials could be due to the charge transfer between metal nanoparticles and supports and the generation of special active sites at the metal-support interface. The interactions between metals and supports could also lead to very different catalytic behaviors of supported metal nanoparticles compared to bulk metal surfaces.
Bulk Au has been considered to be catalytically inactive for long time. However, gold nanoparticles or clusters supported on different metal oxides were reported to be highly active and selective catalysts for low-temperature CO oxidation, alkene epoxidation, and CO₂ hydrogenation. Although explicit mechanism of these reactions on supported Au catalysts is still elusive, the interface between Au and oxide supports is believed to play an important in catalytic reactions. The charge transfer between Au clusters and TiO₂ could induce net positive or negative charges on the Au cluster, which helps activate reactants such as molecular oxygen (O₂). Au single atoms supported on cerium oxide (CeO₂) was reported to be an active and selective catalyst preferential oxidation of CO (PROX) in H₂-rich stream. The high selectivity towards CO oxidation was attributed to the unique property of single-atom catalysts that is unable to dissociatively adsorb H₂ and thus has a low reactivity toward H₂ oxidation.

The properties of support materials also exert strong influence on the activities of Ru catalysts for NH₃ synthesis. The RDS of NH₃ synthesis on Ru catalysts was identified to be the dissociative adsorption of molecular N₂, which requires the breaking of nitrogen-nitrogen triple bond. Basic supports, such as magnesium oxide (MgO), can donate electrons to Ru nanoparticles, thus raising their Fermi level. The raised Fermi level leads to higher tendency to transfer electrons from Ru to the anti-bonding orbitals of molecular N₂ and facilitate the bond breaking. Therefore, MgO supported Ru nanoparticles have higher activities for NH₃ synthesis than Al₂O₃ supported Rh nanoparticles. More recently, a chemically and thermally stable electride (an ionic compound in which free electrons act as anions) with high electron-donating efficiency
was employed as the support for Ru nanoparticles. Its activity in NH$_3$ synthesis was ~50 times higher than MgO supported Ru nanoparticles.$^{10}$

Zeolite can be used as catalyst support due to its mesoporous structure and as catalyst for some reactions due to the presence of Lewis/Brønsted acid sites. Zeolite is a kind of aluminosilicates with ordered porous structures, which can be modified with various metal cations to achieve properties of interest. Zeolite catalysts are heavily used industrial catalytic cracking of hydrocarbons to light olefins, which are catalyzed by their acid sites. Transition metals, such as Fe and Cr, were used to modify zeolite to improve their catalytic activities and the selectivity towards ethylene and propylene in catalytic cracking.$^{27}$

The catalyst support is a critical parameter determining the properties of catalysts. Through careful tuning of the properties of supports and designing the metal-support interfaces, the performance of catalysts can be significantly affected.

1.3.3 Promoter

Promoters are generally inactive for catalytic reactions but can interact with catalytically active nanoparticles and alter their surface charge, structural stability, and electronic structure to affect their catalytic properties. Promoters can be alkali metals, alkaline earth metals, and halogens.

Trace amount of chlorine (Cl$_2$) was found to be an effective promoter for Ag catalysts in C$_2$H$_4$ epoxidation. The strong electronegativity of Cl created partially positive-charged Ag atoms upon adsorption, which were found to be real active sites for C$_2$H$_4$ epoxidation.$^{28}$ Potassium (K) and Cu promoted Fe catalysts exhibited high activities
and stability in Fischer–Tropsch Synthesis. The addition of K and Cu prevented sintering of Fe nanoparticles during the reduction of iron oxide precursor, which generated small Fe nanoparticles with a high number of active sites. The promoters also stabilized the Fe nanoparticles and improve the stability of the catalysts in long-term operation.\(^\text{29}\)

### 1.4 Categories of heterogeneous catalysis

Most catalytic reactions require energy input to overcome the activation barrier and proceed at observable rates. Based on the source of energy, heterogeneous catalysis can be classified into three main categories: thermocatalysis, electrocatalysis, and photocatalysis.

#### 1.4.1 Thermocatalysis

Thermocatalysis uses thermal energy as the main energy input to drive catalytic reactions, which is the mostly widely used form of heterogeneous catalysis in chemical industries. Figure 1.6 shows a simplified block diagram of industrial NH\(_3\) synthesis process. N\(_2\) is separated from air and H\(_2\) is generated from natural gas via steam reforming (CH\(_4\)+H\(_2\)O→CO+3H\(_2\)). After purification of these feedstock, they are introduced into the catalytic reactor operated at high temperature and high pressure. The heterogeneous catalysts are heated to a high temperature to accelerate the reaction rate, and a high pressure is required to push the equilibrium towards the production of more NH\(_3\). After exiting the catalytic reactor, the reaction mixture is cooled to separate the product as liquid NH\(_3\), while unreacted N\(_2\) and H\(_2\) are recycled to mix with new feedstocks and increase the efficiency of the process.\(^\text{2}\) Several other industrial processes
are operated in a similar manner, including crude oil refinery and the production of sulfuric acid.

Heterogeneous thermocatalysis has achieved great successes in large-scale industrial processes. However, these reactions are usually operated at high temperatures and high pressures, which demand a large energy input and suffer from long-term stability issues. Using other types of energy sources, such as electricity and light, is under active research.

Figure 1.6. Block diagram of NH₃ synthesis with N₂ and H₂ as feedstocks and operated at high pressure and elevated temperature.
1.4.2 Electro catalysis

In electrocatalysis, electricity is used as the energy input to accelerate reaction rates and can also drive energetically unfavorable reactions. NH$_3$ was synthesized from N$_2$ and H$_2$ at atmospheric pressure in a solid-state proton–con ducting electrocatalytic cell.$^{30}$ H$_2$ was oxidized into protons, which transport to through solid electrolyte to the cathode and react with N$_2$ to form NH$_3$. This device did not require a high pressure to push the equilibrium, although a high temperature (570 °C) was required to increase the conductivity of the solid electrolyte. Water electrolysis for O$_2$ and H$_2$ production is another application of electrocatalysis. Noble metals (e.g., Pt and Ru) and transition metal hydroxides, sulfides, and phosphates (e.g., cobalt oxides and molybdenum disulfide) have been found to be active catalysts for these two half-reactions.$^{31-33}$

Fuel cells also rely on electrocatalysis to extract energy from chemicals with high efficiency (low overpotential) and high rate (large electric current), although no external electricity is required. Figure 1.7 shows the typical structure of a hydrogen-oxygen fuel cell. Carbon supported Pt catalysts are used for both cathode (oxygen reduction reaction, ORR) and anode (hydrogen oxidation reaction, HOR) parts. However, the scarcity and stability issue of Pt prevent the wide adaptation of fuel cells. ORR requires the transfer of four electrons to reduce molecular O$_2$ into H$_2$O, which is a kinetically sluggish reaction. New types of electrocatalysts other than Pt have been designed for ORR, including graphene supported transition metal oxides, nitrogen-doped graphene and carbon nanotubes, and metal alloys.$^{34-35}$ Deep understandings of the reaction mechanism could benefit the design of high-performance ORR electrocatalysts.
1.4.3 Photocatalysis

Heterogeneous photocatalysis relies on semiconductor photocatalysts to absorb light and excite electron-hole pairs. Electrons and holes then separate and transport in the conduction band and valence band to the surface of photocatalysts and drive the reduction and oxidation reaction, respectively. Due to the similarity of photocatalysis and electrocatalysis, these two types of catalytic processes can be combined in some cases as photoelectrochemical catalysis.

Figure 1.7. Schematic illustration of a hydrogen-oxygen fuel cell. H₂ lose electrons on anode catalyst, and O₂ gain electrons on cathode catalyst. The flow of electrons in the external circuit powers external load.
As shown in Figure 1.8, photocatalytic water splitting through one-step and two-step processes has attracted great research interest.\textsuperscript{36} Photo-degradation of organic pollutants exploiting the oxidizing power of photo-excited holes is another active research field.\textsuperscript{37} TiO\textsubscript{2}-based materials are the most commonly used photocatalysts, due to their high abundance, high photo-stability, and non-toxicity.\textsuperscript{38} However, TiO\textsubscript{2} only responds to ultraviolet (UV) light due to its wide band gap (3.2 eV for anatase phase),
thus limiting its performance under sunlight. Other semiconductors with smaller band gaps, such as iron oxide (Fe$_2$O$_3$) and silicon (Si), are under investigation to replace TiO$_2$, but generally suffer from stability issue.\cite{33} Therefore, exploring new kinds of high-performance photo-active catalysts is critical to drive chemical reactions with light.

### 1.5 Plasmon-enhanced catalysis

Plasmonic metal nanoparticles have been proposed as a new type of photo-active catalysts. They are characterized by strong light-matter interactions through excitations of collective oscillations of conduction electrons, called localized surface plasmon resonances (LSPRs).\cite{39} Due to the different light-absorption and reaction mechanism from semiconductor photocatalysts, plasmonic metal nanoparticles are promising catalysts that can work under sunlight.

![Schematic illustration of exciting LSPR in a plasmonic nanoparticle by light. Conduction electrons oscillate around the nanoparticle under the force from electromagnetic field and nuclei. Figure adapted from ref. 40.](image)

**Figure 1.9**.
1.5.1 Fundamentals of plasmonics

Upon light irradiation on plasmonic metal nanoparticles, the electric field displaces conduction electrons relative to the nuclei. A restoring force arises simultaneously because of the Coulomb attraction between electrons and nuclei, which results in resonant oscillation of the conduction electrons if the frequency of light matches the intrinsic plasmonic frequencies of the nanoparticles (Figure 1.9).\textsuperscript{40} The creation of intense electromagnetic field near the surface of plasmonic nanoparticles and their strong light absorption capabilities induced by LSPRs could contribute to many applications, including optical devices, photovoltaics, surface-enhanced spectroscopy, and photocatalysis.\textsuperscript{41-43}

The plasmonic properties of metal nanoparticles can be described by the Maxwell equations and be solved numerically by finite-difference time-domain or finite-element methods. Experimentally, plasmonic properties can be probed by various far-field optical measurements, including UV-vis extinction spectroscopy, dark-field scattering spectroscopy and surface-enhanced spectroscopy. The spatial distribution of the intense electromagnetic field caused by excitations of LSPRs is highly anisotropic and decays rapidly moving away from the plasmonic nanoparticle. This anisotropic field distribution can be measured by electron-microscopy-based methods, such as electron energy loss spectroscopy and cathodoluminescence spectroscopy, where the high-energy electron beam is used as exciting sources.\textsuperscript{44} The spatial distribution of LSPR-induced field can also be captured by numerical simulations.
Figure 1.10. (a) Normalized extinction spectra of spherical Ag (38 nm, blue), Au (25 nm, red), and Cu (133 nm, green) particles, overlaid with the intensity of solar radiation (black). (b) Normalized extinction spectra for Ag wires (90 nm diameter and >30 aspect ratio, green), cubes (79 nm edge length, red), and spheres (38 nm diameter, blue). (c) Normalized extinction spectra for Ag nanocubes of edge length 56 (orange), 79 (red), and 129 nm (blue). The inset shows a photograph of the three Ag nanocube samples suspended in ethanol. (d) Spatial distribution of the LSPR-induced enhancement of electric field intensity at the resonant wavelength (420 nm), from simulations of a 75 nm Ag nanocube. (e) Spatial distribution of the LSPR-induced enhancement of electric field intensity, from simulations of two 75 nm Ag nanocubes in an edge-to-facet configuration separated by 1 nm. Figures adapted from ref. 44, Macmillan Publishers Ltd: Nature Materials, copyright 2011.
Plasmonic nanoparticles have distinctly different light absorption behavior compared to semiconducting materials. The light wavelength at which a semiconductor starts absorbing is determined by its composition and associated band gap, but insensitive to its size until the size is smaller than its Bohr exciton radius (these small semiconductor particles are called quantum dots).\textsuperscript{45} By contrast, as shown in Figure 1.10, the absorption of a plasmonic nanoparticle strongly depends on its composition, shape, size, orientation (to the polarization direction of light), spatial arrangement (of nanoparticle ensemble), and surrounding media.\textsuperscript{44} Ag, Au, and Cu are the most widely investigated plasmonic materials, due to their high electron density and high conductivity. Their plasmonic properties can be tuned via changing their morphology to absorption visible and near-infrared light, which is particularly beneficial for sunlight-driven photocatalysis. Sharp tips and nanogaps of plasmonic nanoparticles can efficiently concentrate electromagnetic field, where the intensity can be up to a million times stronger than the incident field, to enhance the optical response of materials near these plasmonic hot spots.

**1.5.2 Fundamentals of plasmon-enhanced catalysis**

The unique optical properties of plasmonic nanoparticles promise potentials in photo-induced chemical reactions. Plasmon-enhanced catalysis utilizes photo-excited LSPRs to accelerate chemical reactions occurring on the surface of plasmonic nanoparticles. It has been successfully demonstrated for the oxidation of organic dyes, hydrogen dissociation, and reduction of small molecules.\textsuperscript{46-50} In some other reports, the intense electromagnetic field from excitation of LSRPs has also been used to enhance photocatalytic activities of nearby semiconductors, which is called plasmon-enhanced
In plasmon-enhanced photocatalysis, plasmonic nanoparticles act as antenna to enhance light absorption of semiconductors, and chemical reactions occur on the surface of semiconductors, different from the scheme of plasmon-enhanced catalysis. Unlike photocatalytic water splitting on semiconductors that drives energetically unfavorable reactions, plasmon-enhanced catalysis discussed in this dissertation focuses on increasing reaction rates without change of chemical equilibrium.

**Figure 1.11.** Schematic representation of excitation and relaxation of LSPRs in metal nanoparticles. (a) The excitation of LSPR deflects the light path (Poynting vector) towards the nanoparticle, collecting light from an area larger its physical cross-section. (b) After Landau damping, plasmons decay into hot electrons (red) and hot holes (blue) in a non-thermal distribution. (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 nanoparticles and environment. Figures adapted by permission from ref. 53, Macmillan Publishers Ltd: Nature Nanotechnology, copyright 2015.
Figure 1.11 shows the photo-physical process of excitation and relaxation of LSPR. Upon the excitation of LSPRs by incident photons, intense electromagnetic field is created near the plasmonic nanoparticle, which can interact strongly with light from an area larger than its physical cross-section. The in-phase electron oscillations then relax radiatively by re-emission of photons (scattering) or non-radiatively by Landau damping to generate hot electrons and holes (absorption). The lifetime of this flat, non-thermal distribution of hot carriers is 1-100 fs for extended metal surfaces and may be up to 2 ps for metal nanoparticles due to the reduced electron-electron collisions. In a longer timescale, the hot carriers form a Fermi-Dirac distribution with a high effective temperature up to 1000 K, followed by an even slower dissipation of the energy of hot carriers to the nanoparticle lattice and surrounding environment via electron-phonon interactions.

The excitation and relaxation of LSPRs can contribute to and interfere with chemical reactions by several mechanisms. First, the intense electric field near plasmonic nanoparticles upon excitation of LSPRs can polarize chemical bonds in surface intermediates when the orientation of chemical bonds aligns properly with the oscillating electric field, thus facilitating bond breaking and accelerating chemical reactions. This mechanism is most possible when intense pulsed lasers are used as exciting sources. Second, the energy of photo-excited hot electrons eventually dissipates as thermal energy to the crystal lattice, which locally heats up plasmonic nanoparticles and adsorbed reaction intermediates to enhance the reaction rates. Since the reaction proceeds on the ground-state potential energy surface (PES) in this mechanism, the product selectivity of
plasmon-enhanced reactions would resemble phonon-driven thermocatalytic reactions. Compared to conventional thermocatalysis that heats up all the reaction mixture, the local heating effect of LSPRs can efficiently direct energy to catalytic nanoparticles, where chemical reactions take place, without heating unreactive media. This photothermal process could reduce the energy input and ease the thermal management of catalytic reactors. Third, during the decay of LSPRs, photo-generated hot electrons can transfer from the plasmonic nanoparticle to unoccupied anti-bonding orbitals of surface adsorbates. The addition of electrons in the anti-bonding orbitals can excite the adsorbate to a charged state and weaken chemical bonds involved in the RDS of reactions, thus accelerating reactions (Figure 1.12). The adsorbate will decay back to ground state and dissipate its vibrational energy, if it does not have enough energy to overcome the activation barrier in the charged-state PES. In high photon flux (high light intensity), the ground-state adsorbate may be excited to the charge state again before it has completely dissipated its vibrational energy. The adsorbate in this case will have higher probability to overcome the activation barrier in the charged-state PES, thus leading to a compelling super-linear dependence of reaction rates on light intensity.

A unique feature of the hot electron transfer mechanism of plasmon-enhanced catalysis is its capability to selectively activate certain reaction pathways and control the product selectivity. During the electron transfer process, the probability of certain anti-bonding orbital to accept the hot electron depends on its density of states (DOS) and the energy matching between the anti-bonding orbital and the hot electron. Therefore, by tuning the wavelength of incident light and the energy of generated hot electrons, it is
Figure 1.12. Mechanisms of phonon- and hot-electron-driven chemical reactions on metals. (a) Thermal activation for the dissociation of a diatomic molecule on the ground-state PES. (b) Hot-electron-driven dissociation of a diatomic molecule. Addition of a hot electron excites the molecule to a charged-state PES and weakens chemical bonds. (c) At high photon flux, subsequent electron transfer can occur before the energy from last excitation has fully dissipated, thus leading to a superlinear dependence of the rate of reaction on light intensity. (d) Hot electron-driven reactions (top) on plasmonic metal nanoparticles may activate specific reaction pathways that are inaccessible in phonon-driven reactions (bottom). Figures adapted by permission from ref. 47, Macmillan Publishers Ltd: Nature Materials, copyright 2015.
possible to transfer photo-excited hot electrons to specific anti-bonding orbitals of reaction intermediates and activate specific reaction pathways. This mechanism offers a promising strategy to selectively form desired products in competing reaction pathways.\textsuperscript{56-57} New reaction pathways may be opened by this hot-electron-mediated mechanism that is completely inaccessible in phonon-mediated thermocatalytic reactions (Figure 1.1.d).

1.5.3 Rhodium nanoparticles for plasmon-enhanced catalysis

The excitation of LSPRs requires the metal nanoparticle to have a negative real part and a small imaginary part of complex dielectric function. Metals meet this requirement in the UV, visible, and near-infrared regions and are also the mostly investigated materials. Ag and Au are the most commonly used plasmonic materials, due to their small imaginary parts of complex dielectric functions and the consequent advantage of low optical loss.\textsuperscript{48} However, Ag and Au have filled d bands, thus interacting weakly with adsorbates. Consequently, they possess limited catalytic activities in thermocatalysis, which is an obstacle for their applications in plasmon-enhanced catalysis. Previous demonstrations of plasmon-enhanced catalysis on Ag and Au nanoparticles usually involved intense pulsed lasers as light sources or created plasmonic hot spots from aggregated nanoparticles.\textsuperscript{49-50, 54, 58} These requirements for Ag- and Au-based catalysts may prevent their wide adaptation in plasmon-enhanced catalysis.
Figure 1.13. Simulated absorption efficiency ($Q_{abs}$, black circles), surface-averaged electric field enhancement ($<|E|^2>$, blue triangles), and maximum electric field enhancement ($|E|_{\text{max}}^2$, red squares) as functions of photon energy for hemispheres of 20 nm radius on a sapphire substrate for Ag (a), Au (b), Rh (c), Pt (d), Ru (e), and Pd (f). Figure adapted with permission from ref. 59. Copyright 2013 American Chemical Society.

Group VIII metals, such as Rh, Pt, and Pd, have versatile catalytic activities and are widely utilized in current industrial catalytic transformations. Although their
plasmonic properties are inferior to Ag and Au, their excellent catalytic activities could be important to plasmon-enhanced catalysis. Figure 1.13 shows simulated plasmonic properties of hemispherical nanoparticles made of different metals sit on a sapphire substrate. The hemispherical nanoparticles are all with 20 nm radius to eliminate the impact of nanoparticle morphology. The materials investigated are Ag, Au, Rh, Pt, Ru, and Pd.

The quality of plasmonic properties can be justified by the absorption efficiency ($Q_{abs}$) and surface-averaged electric field enhancement ($<|E|^2>$). Absorption efficiency, defined as the ratio between absorption cross-section and physical cross-section, shows how efficient light is absorbed by the plasmonic nanoparticle. Surface-averaged electric field enhancement shows how efficiently light is concentrated near the surface of plasmonic nanoparticles. The absorption efficiency and surface-averaged electric field enhancement are plotted versus photon energy in Figure 1.13, which can be converted to wavelength by: $E(\text{eV})=1240/\lambda(\text{nm})$. For instance, 2 and 4 eV correspond to 620 and 310 nm, respectively. Ag and Au have excellent plasmonic properties, as seen by their large absorption efficiency and high electric field enhancement. It is worth noting that Rh has the best plasmonic properties among the investigated group VIII metals, despite not on a par with Ag and Au. Rh-based catalysts are also widely used in hydrogenation of aromatics and carbon oxides, hydroformylation of alkenes, and CO oxidation. Rh nanoparticles with excellent catalytic activities and plasmonic properties could be promising candidates for plasmon-enhanced catalysis. This majority of this dissertation is built on our work on plasmonic Rh nanoparticles.
Chapter 2: Size-Tunable Rhodium Nanostructures for Wavelength-Tunable Ultraviolet Plasmonics

The content of this chapter is adapted from our publication (Nanoscale Horizons, 2016, 1(1): 75-80). We acknowledge our coauthors, Ms. Ángela Barreda, Ms. Yael Gutiérrez, Dr. Francisco González, and Dr. Fernando Moreno at University of Cantabria, for the simulations of optical properties of Rh nanostructures. We also acknowledge our coauthor, Dr. Henry Everitt at Army Aviation & Missile RD&E Center, for helpful discussions about experimental design.

2.1 Introduction

As discussed in Chapter 1, Rh nanostructures are promising candidates for plasmon-enhanced catalysis, thanks to their excellent catalytic activities and plasmonic properties. In addition, they could exhibit plasmonic behaviors in the UV region, which could be used as substrates for surface-enhanced Raman spectroscopy under UV excitation (UV-SERS). UV-SERS have unique advantages over SERS under visible and near-infrared laser excitations. Most of bio-molecules absorb UV light, which could enable label-free detections of bio-molecules with UV-SERS. Furthermore, Raman signal and fluorescent signal are better spectrally separated in the UV region. This better spectral separation in the UV region allows larger Raman shift window and suppresses noise from fluorescence.

Au, Ag, and Cu are the mostly investigated plasmonic materials, but they cannot show plasmonic behaviors in the UV region, due to the onset of their inter-band transitions in the visible region. Al\textsuperscript{67-71} and Ga\textsuperscript{72-74} have been studied for UV plasmonics.
and are attractive because of their wide availability and compatibility with complementary metal–oxide–semiconductor (CMOS) processing. However, Al and Ga nanostructures suffer from fast oxidation in aerobic and aqueous environments, which changes the size and shape of the metal nanostructures as well as deteriorates their plasmonic properties, especially for applications where direct surface contact is necessary. A stable, noble metal with UV plasmonic effects is needed to serve as the UV counterpart to Au and promote research into UV plasmonics.

In 2003, Z. Tian and co-workers employed rough Rh and Ru electrodes as SERS substrates under UV excitation, which is the first observation of UV-SERS from transition metal electrodes. A 325 nm He-Cd laser was used as exciting source. SERS signals were observed from pyridine, a commonly used model analyte with large Raman scattering cross-section, under UV excitation on rough Rh and Ru electrodes, while were not observed on Ag and Au electrodes. Following experiments using thiocyanate as analyte to present analytes with regular Raman scattering cross-section further validated the feasibility of UV-SERS on Rh electrode.

In 2006, Y. Xia and colleagues reported the synthesis of Rh multipods with sharp tips. They found that these Rh multipods showed plasmonic resonances in the UV region (~360 nm), as revealed by UV-vis extinction spectra. The Rh multipods were further used to fabricate SERS substrates with 4-mercaptopyridine as a Raman reporter. Although SERS signals were observed, a 785 nm near-infrared laser was used as the excitation source, which did not exploit the UV plasmonic properties of Rh multipods.
We recently employed similar Rh multipods as SERS substrate in a quantitative spectroscopic study and observed enhanced photo-degradation of \(p\)-aminothiophenol (PATP) upon irradiation of UV laser, all in good agreement with numerical simulations.\textsuperscript{77-78} Although these Rh multipods exhibit UV plasmonic effects, most synthetic methods produce polydisperse mixtures of tripods and tetrapods whose sizes are difficult to adjust controllably, preventing plasmonic properties from being tailored for specific applications.\textsuperscript{76-77, 79} Hence, new synthetic methods are needed that controllably produce monodispersed Rh nanostructures with LSPRs in experimentally accessible UVA and UVB regions (280 - 400 nm, 4.4 - 3.1 eV).

In this project, we develop unseeded (no pre-synthesized Rh seeds added) and seeded (pre-synthesized Rh seeds added) slow-injection polyol methods to synthesize size-tunable, monodispersed Rh nanocubes (NCs) with wavelength-tunable LSPRs in the UV region. The size of Rh NCs is tuned by the amount of Rh precursor added during synthesis. The plasmonic properties of the Rh nanocubes are studied by UV-vis extinction spectroscopy and correlated with numerical modeling using finite element-based methods. These size-tunable Rh NCs are used to fabricate SERS substrates and accelerated photochemical decomposition of PATP are observed. The sample whose LSPRs are most resonant with the UV laser wavelength exhibits the fastest decomposition rate.
2.2 Experimental methods

2.2.1 Slow-injection synthesis of Rh nanocubes

The slow-injection polyol methods use a two-channel syringe pump to control the addition rate of Rh precursor. The experiment setup is shown in Figure 2.1. The hotplate is equipped with an external thermocouple directly immersed in an oil bath. The thermocouple head should be placed close to the reactor (glass vial) to ensure accurate temperature control during synthesis.

For the unseeded slow-injection method, 0.45 mmol potassium bromide (KBr, Acros, 54 mg) and 2 ml ethylene glycol (EG, J. T. Baker) were added to a 20 ml glass vial (cleaned with detergent and deionized water and dried in a vacuum oven at 80 °C) equipped with a Teflon-coated magnetic stir bar. The colorless solution was heated in an oil bath held at 160 °C for 40 min with loosely placed cap. Meanwhile, 0.045 mmol rhodium(III) chloride hydrate (RhCl₃·xH₂O, 38% Rh, Acros, 12 mg) and 0.225 mmol polyvinylpyrrolidone (PVP, in terms of repeating unit, M.W. ≈ 55,000, Aldrich, 25 mg) were separately dissolved in 2 ml EG at room temperature. These two solutions were injected simultaneously into the heated KBr solution by a two-channel syringe pump at a rate of 1 ml/h. After injection, the reaction mixture was held at 160 °C for another 10 min and then cooled to room temperature. 27 nm Rh NCs were obtained with this amount of Rh precursor and smaller NCs could be synthesized by reducing the amount of Rh precursor while keeping all other conditions identical.
Figure 2.1. A photograph of the experimental setup for slow-injection synthesis of Rh nanocubes.

For the seeded slow-injection method, a typical synthesis directly used 0.4 ml of the reaction mixture of 27 nm Rh NCs as the seed solution. The seed solution was diluted with 1.6 ml EG in a cleaned 20 ml glass vial with stirring and heated in an oil bath held at 160 °C for 40 min with loosely placed cap. 0.045 mmol RhCl₃·xH₂O (12 mg) was dissolved in 2 ml EG. 0.225 mmol PVP (25 mg) and 0.45 mmol KBr (54 mg) were co-dissolved in another 2 ml EG. These two solutions were injected into the seed solution simultaneously by the syringe pump at a rate of 1 ml/h. The reaction mixture was held at the reaction temperature for another 10 min and then cooled to room temperature. 59 nm Rh NCs were synthesized in this case. Rh NCs with edge length between 27 and 59 nm can be obtained by adjusting the ratio of Rh precursor and seeds. Seeded syntheses can be
reproduced with high success rates when the atomic ratio of Rh between added Rh precursor and Rh seeds is below 3.5. This atomic ratio corresponds to a size enlargement of ~1.6 for each round of seeded synthesis (20 nm Rh NC seeds grow into 32 nm Rh NCs). Rh NCs with edge length up to 120 nm and narrow size distribution can be synthesized by applying multiple rounds of seeded syntheses.

After synthesis, the Rh NC reaction mixtures were diluted with acetone to ~45 ml and centrifuged at 12k rpm for 10 min. The colorless supernatant was discarded and the black precipitate was dispersed in ~5 ml deionized (DI) water (with sonication if needed). The Rh NC dispersion was diluted with acetone again to ~45 ml and centrifuged at 12k rpm for 10 min. The supernatant is discarded and the precipitate was usually treated with this DI-water/acetone washing step for another two times to remove excess PVP, KBr, Cl\(^-\), and EG. The black precipitate was finally dispersed in ~5 ml ethanol (200 proof, anhydrous, KOPTEC) for further characterizations.

2.2.2 Material Characterization

Scanning electron microscopy (SEM) images were obtained by using an FEI XL30 FEGSEM. Samples for SEM were prepared by drop-coating 50-time dilutions of Rh NCs in ethanol solutions on the shiny side of aluminum foils (cut into ~4×4 mm squares) and drying in ambient condition.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected by a FEI Tecnai G\(^2\) Twin operating at 200 kV. Samples for TEM were prepared by drop-coating 50-time dilutions of Rh NCs in ethanol solutions on
carbon/formvar-coated Cu grids (carbon type-b, 01813-F, Ted Pella) and drying in ambient condition.

UV-vis extinction spectra were obtained on a Varian Cary 50 spectrometer with a Xeon flash lamp and a Shimadzu UV-3600 spectrometer with a Tungsten lamp (visible) and a Deuterium lamp (UV). UV-vis spectra were measured with quartz cuvettes and ethanol dilutions of the Rh NC solutions to ensure an absorbance smaller than one. The spectra of quartz cuvettes filled with ethanol were taken as background and subtracted from the spectra of Rh NCs.

Raman spectroscopy was carried out on a Horiba Jobin Yvon LabRam ARAMIS. Atomic force microscopy (AFM) images were collected by a Digital Instruments Dimension 3100 operating in tapping mode.

2.2.3 Sample preparation for SERS measurements

Si wafers (SQI, 100 nm oxide layer, single-side polished) were cut into ~4×4 mm substrates. The Si substrates were cleaned by sonicating in acetone (ACS, BDH) and isopropanol (ACS, BDH) for 30 min, respectively. After sonication, the substrates were rinsed with DI-water and dried in a vacuum oven at 80 °C. 10 μL of 21, 39, and 59 nm Rh NCs dispersed in ethanol were drop-coated on the polished side of Si substrates and dried in ambient condition, respectively. These substrates were rinsed with ethanol and dried by air to leave a sub-monolayer of Rh NCs on the surface as UV-SERS substrates. Each substrate was subsequently immersed in 1.5 ml of 5 mM PATP in ethanol solution in a 2.0 ml Eppendorf tube (covered with aluminum foil to avoid light exposure). After
reacted for 24 h, these samples were rinsed with ethanol to remove excess PATP not attached to the surface of Rh NCs. The surface coverage of Rh NCs on Si substrates was measured SEM after SERS measurements.

For control experiments, a cleaned Si substrate treated with the same procedure of PATP coating and ethanol washing but without Rh NC deposition was prepared to confirm the absence of specific bonding between PATP and Si substrate. A neat PATP sample was prepared by dip-coating a cleaned Si substrate in 5 mM PATP solution and drying in ambient condition to obtain the intrinsic Raman signal from PATP. The average thickness of this PATP layer was measured by AFM.

2.3 Results and discussion

2.3.1 Plasmonic properties of small Rh nanoparticles

As discussed in Chapter 1, Rh nanoparticles possess excellent catalytic activities, and numerous efforts have been devoted to controllable synthesis of Rh nanoparticles for applications in catalysis. Syntheses of small Rh NCs, tetrahedra, icosahedra, and hollow frames with sizes smaller than 15 nm have been reported, due to the preferences for smaller nanoparticles in catalysis.\textsuperscript{80-84} We reproduce the polyol synthesis of Rh NCs with edge length of 3.5 nm.\textsuperscript{82} As shown in Figure 2.2a, these Rh NCs have slight truncated corners and are mixed with some spherical nanoparticles. UV-vis spectrum of this Rh NC sample measured in an ethanol solution shows increasing absorption with decreasing light wavelength, but no peak is observed until the shorter wavelength end of the spectrometer, 250 nm (Figure 2.2b).
Figure 2.2. (a) Representative TEM image of Rh NCs with edge length of 3.5 nm. (b) UV-vis extinction spectrum of corresponding Rh NCs in an ethanol solution. Figures adapted from Ref. 65 with permission from The Royal Society of Chemistry.

Numerical simulations of the optical properties of Rh NCs with edge lengths smaller than 10 nm show that their resonant wavelengths locate in the deep UV region (shorter than 250 nm or higher than 5 eV, Figure 2.3), consistent with our experimental observations. The deep UV resonance makes it hard for currently available lasers to excite LSPRs of small Rh nanoparticles, which could be the reason for limited reports regarding the plasmonic properties of Rh nanostructures. Since the resonant wavelength of plasmonic nanoparticles red-shifts with increasing particle size\(^{44}\), Rh nanostructures larger than 15 nm could show plasmonic properties in more experimentally accessible near UV region. Therefore, new synthetic methods are needed that controllably produce larger, monodispersed Rh nanostructures with LSPRs in UVA and UVB regions (280 - 400 nm, 4.4 - 3.1 eV).
Figure 2.3. Simulated UV-vis spectra of Rh NCs with edge length of 3 (black), 5 (red), and 10 nm (blue) in ethanol solutions. The LSPR energies of dipolar modes of Rh NCs smaller 10 nm are higher than 4.8 eV. Figures adapted from Ref. 65 with permission from The Royal Society of Chemistry.

2.3.2 Morphology and optical properties of Rh nanocubes from unseeded slow-injection methods

We choose cubic Rh nanoparticles as our target shape due to the following considerations. First, the sharp corners of cubic nanoparticles can concentrate light and generate intense electromagnetic field more efficiently than the smooth surface of spherical nanoparticles. Second, the LSPR wavelength of cubic plasmonic nanoparticles red-shifts compared to spherical nanoparticles. This will ease the tuning of resonant
wavelength of Rh nanostructures into the near UV region. Third, the mechanism of shape control for cubic Rh nanostructures is relatively well understood. The preferential adsorption of bromide ion (Br\(^-\)) on Rh(100) facets facilitates the growth of cubic nanoparticles.\(^{82, 85}\) Therefore, we can focus on the tunability of sizes of Rh NCs and associated LSPR energies.

To tune the size of Rh NCs, it is important to understand the mechanism of solution-based metal nanoparticle synthesis. It has been proposed that metal precursors, usually in the form of metal salts, are first reduced to metal atoms. When the concentration of metal atoms reaches saturation concentration, metal atoms have the tendency to form precipitate but cannot nucleate due to surface tension. With further increase of concentration to nucleation concentration, nuclei are generated in the reaction mixture, which consumes metal atoms and lowers its concentration. Subsequent growth into larger nanoparticles will occur with following supply of metal atoms. Although metal cations may directly deposit on the surface of existing nanoparticles before being reduced, the size of nanoparticles is still primarily determined by the ratio of generated seeds to supplied metal precursor.\(^{19}\) To prepare large Rh NCs, the concentration of generated Rh atoms must be maintained at low supersaturation to minimize the formation of seeds while injecting enough Rh precursor into the reaction mixture to grow those few seeds to larger sizes.

To solve the paradox of low supersaturation and high supply of Rh, an unseeded polyol method is developed to synthesize Rh NCs. The Rh precursor, RhCl\(_3\), and polymer stabilizer, polyvinylpyrrolidone (PVP), solutions were injected simultaneously into a hot
EG solution at a slow rate by a two-channel syringe pump. The Rh precursor was reduced immediately by EG upon addition into the hot reaction mixture, as observed from the color change (colorless to brown). The slow injection rate ensured that the RhCl₃ in each droplet of the precursor solution was consumed before the next precursor droplet was added, thereby maintaining a low concentration of Rh atoms throughout the synthesis. Under these conditions, small Rh seeds form during the addition of the first few drops of the Rh precursor, and subsequently added precursor deposits Rh atoms on the surface of existing seeds rather than forming new seeds. By controlling the injection time t, and thus the total volume of precursor solution added to the reaction mixture, Rh NCs with edge lengths between 10 and 27 nm were successfully synthesized. TEM images of monodispersed Rh NCs with edge lengths of 15 nm (t = 20 min), 21 nm (t = 50 min) and 27 nm (t = 120 min) are shown in Figure 2.4b-d. Figure 2.5 shows the size distribution and standard deviation (SD) of the Rh NCs from unseeded slow-injection methods, counted over 50 nanoparticles for each sample. The small SD of the NC size (smaller than 1.2 nm) confirms its high size uniformity. These Rh NCs have slightly concave surfaces as observed by TEM, consistent with the growth mechanism in which Rh atoms first deposit on the corners of the seeds and then migrate to the edges and faces.⁸⁵

The optical properties of these Rh NCs are studied by UV-vis extinction spectroscopy and compared with numerical simulations (Figure 2.4a, e). The UV-vis extinction spectra were measured, and the LSPR peaks for 15, 21, and 27 nm Rh NCs dispersed in ethanol were found at 4.51 eV (275 nm), 4.23 eV (293 nm) and 3.96 eV (313 nm), respectively. The resonant energy increasingly red-shifted with increasing size,
Figure 2.4. UV-vis extinction spectra (a: experimental; e: theoretical) of monodispersed Rh NCs in ethanol, with corresponding TEM images from unseeded slow-injection methods of average edge lengths of 15 (b), 21 (c), and 27 nm (d), respectively. The scale is 50 nm. Figures reproduced from Ref. 65 with permission from The Royal Society of Chemistry.

in good agreement with predictions from a finite element electromagnetics simulation in which a linearly polarized plane wave illuminated a perfect structured Rh NC immersed in ethanol. The spectral extinction cross-section was calculated as the sum of the absorption and scattering spectral cross-sections.
2.3.3 Morphology and optical properties of Rh nanocubes from seeded slow-injection methods

To red-shift the LSPR of Rh NCs to lower UV energies, even larger Rh NCs must be synthesized. One approach to synthesize larger NCs would be to continue increasing the amount of Rh precursor in the unseeded method, but this would be unnecessarily time-consuming since the amount of precursor required, and thus the time required, grows cubically with edge length. Moreover, the prolonged time could affect the shape control of nanoparticles due to parasitic side reactions or the dilution of other reagents. Instead, a more time-efficient, seeded method was developed to obtain larger Rh NCs. The reaction mixture containing 27 nm Rh NCs was directly used as a seed solution without any post-synthesis purification or washing treatment. Larger NCs grew as the RhCl$_3$ solution was injected into EG containing a predetermined volume of this seed solution held at 160 °C. To help maintain the cubical shape of the Rh NCs, KBr was co-dissolved with PVP and injected to the reaction mixture along with the RhCl$_3$ solution.
By tuning the amount of precursor added, Rh NCs with edge lengths between 27 and 59 nm were synthesized within 2 h using this seeded method.

Representative TEM images of these larger Rh NCs are shown in Figure 2.6b-d. These NCs are uniform in size and have slightly concave faces as well. A problem of seeded synthesis of nanoparticles is secondary nucleation, which forms new seeds with the addition of metal precursor. Following reduced metal atoms will deposit on pre-added seeds as well as the newly formed seeds, thus leading to a bimodal distribution of the nanoparticle size. The slow injection rate of Rh precursor in the seeded method keeps a low concentration of atomic Rh and prevents the generation of new seeds. Only a few small Rh NCs were observed from TEM, indicating successful prevention of secondary nucleation of our seeded slow-injection method.

The optical properties of these Rh NCs were also investigated by extinction spectroscopy and compared with the numerical simulation (Figure 2.6a, e). The experimentally measured LSPR peaks of 39, 47, and 59 nm Rh NCs were found to be 3.65 eV (340 nm), 3.44 eV (360 nm) and 3.25 eV (381 nm), respectively, increasingly red-shifted toward the lower edge of UV region with increasing size.

The size distribution of Rh NCs from seeded slow-injection method with different ratio of Rh seeds and added Rh precursor are shown in Figure 2.7. The small SD (smaller than 1.5 nm) indicates the excellent size control of this method.

The narrow distribution of particle size (< ± 1.5 nm) could be attributed to the separation of seed formation and time-controlled nanocrystal growth in both unseeded and seeded methods. Seeds formed in the early stage of synthesis, whether formed in situ
Figure 2.6. UV-vis extinction spectra (a: experimental; e: theoretical) of monodispersed Rh NCs in ethanol, with corresponding TEM images from seeded slow-injection methods of average edge lengths of 39 (b), 47 (c), and 59 nm (d), respectively. The scale bar is 250 nm (inset: 20 nm). Figures reproduced from Ref. 65 with permission from The Royal Society of Chemistry.

(unseeded) or intentionally added (seeded), experience the same opportunity to receive new Rh atoms from subsequent addition of Rh precursor, thereby growing into NCs with uniform sizes. By tuning the amount of precursor added to the reaction mixture, the sizes of the produced nanocubes and the associated LSPR energies can be precisely controlled
Figure 2.7. Edge length distribution and standard deviation (SD) of Rh NCs with edge length of 37 (a), 47 (b), 59 nm (c), respectively. Figures adapted from Ref. 65 with permission from The Royal Society of Chemistry.

with an excellent match to numerical predictions.

The seeded slow-injection method can be applied for multiple rounds to synthesize Rh NCs larger than 60 nm. The product of one round of seeded synthesis can be directly used as the seed solution without any purification for the next round of seeded synthesis. Figure 2.8 shows SEM images of Rh NCs synthesized with 27 nm NCs as seed and applying up to four rounds of seeded synthesis.

The edge length of Rh NCs from the first, second, third and fourth rounds of seeded synthesis is 35, 53, 80, and 120 nm, respectively. The increase of size red-shifts the resonant wavelength of these large Rh NCs to the visible, which can be directly seen from the color of the solution (Figure 2.9a). The color of Rh NCs from the first and second rounds of seeded synthesis is brown, similar with Rh NCs with smaller sizes. The color of Rh NCs becomes purple and dark gray with further increase of size.
Figure 2.8. SEM images of Rh NCs from the first (a), second (b), third (c), and fourth (d) rounds of seeded slow-injection synthesis with average edge length of 35, 53, 80, and 120 nm, respectively.

The red-shift of resonant wavelength with increasing size of Rh NCs is also shown in extinction spectra (Figure 2.9b). The plasmonic resonances of 80 and 120 nm Rh NCs get into the visible region, although the absorption peaks are broader than those of smaller NCs. This peak broadening could be attributed to the decrease of size uniformity with more rounds of seeded synthesis and the excitation of higher-order plasmonic modes in large nanoparticles.
2.3.4 UV-SERS with Rh nanocube substrates

The intensity of concentrated electromagnetic field near plasmonic Rh NCs is simulated with finite-element method. The simulated near field intensity distribution $|E|^2$ for resonant illumination at the surface of a 27 nm Rh NC is depicted in Figure 2.10. Large enhancements of incident radiation intensity are observed at the NC edges, reaching factors as high as 700 at the NC corners. Comparing the enhancements of the edges parallel and perpendicular to the polarization of the incident light reveals a minimum $|E|^2$ of ~10 occurs at the edge center for parallel polarization. The intense electromagnetic field of plasmonic Rh NCs could enhance the optical response from nearby analyte, making them promising substrates for SERS under UV excitation. This concentrated high-energy fields and hot electrons from the excitation of UV LSPR in Rh
NCs could also be important sources for photochemical reactions, in much the same way that Au, Ag, and Cu have been used for visible light applications.\textsuperscript{47, 87}

To probe the efficacy of photochemical reactions accelerated by Rh NCs, UV photo-degradation of organic molecules was comparatively studied neat and attached to the surfaces of 21, 39, and 59 nm Rh NCs using Raman spectroscopy with a 325 nm wavelength He-Cd laser. PATP was used as the model reporter molecule in the experiments. Although PATP may be converted into 4,4′-dimercaptoazobenzene

![Simulation](image)  

**Figure 2.10.** Simulated near-field intensity distribution $|E|^2$ at the surface of a 27 nm Rh NC at the resonant energy 3.96 eV (313 nm), along with the coordinates used for the finite-element modeling. The light is polarized along the X-axis and propagating in Z-axis in the simulation. Figures reproduced from Ref. 65 with permission from The Royal Society of Chemistry.
(DMAB) under laser radiation, the intensity of the C-C stretch mode of PATP near 1590 cm⁻¹ is a well representative of the amount of organics and used to quantify the reaction kinetics.

As shown in Figure 2.11a and b, the neat PATP sample exhibits a slow decay of the Raman signal with increasing exposure to UV light, while the signal from PATP attached to the surfaces of 39 nm Rh NCs exhibits a much faster decay under identical experimental conditions. Assuming that the photocatalytic reaction is first order on PATP, an exponential decay model is used to fit the Raman data, and the results are shown in Figure 2.11c. The model fit the data well, and the rate constants for these four samples are extracted. The neat PATP sample shows the slowest decay with a rate constant of 0.020 s⁻¹. The 21, 39, and 59 nm Rh NC samples have much higher rate constants of 0.066, 0.084, and 0.051 s⁻¹, respectively. The measured LSPR energy of 21, 39, and 59 nm Rh NCs in ethanol is 4.23, 3.65, and 3.25 eV, respectively. Since the LSPR energy of Rh nanoparticles on Si substrates blue-shifts ~0.2 eV compared to the case in ethanol, the 39 nm Rh NCs on a Si substrate are most resonant with the 325 nm (3.81 eV) laser, and attached PATP decomposed fastest. Conversely, the 21 and 59 nm Rh NCs are non-resonant with the excitation, and the attached PATP decomposed more slowly but still faster than the neat PATP under otherwise identical conditions. The observation that PATP attached to 39 nm Rh NCs shows the fastest decay (4 times faster than neat PATP) validates the expected enhancement of photochemical reactions by the excitation of a UV LSPR in Rh nanoparticles.
Figure 2.11. Raman spectra of neat PATP (a) and PATP with 39 nm Rh NCs (b) at representative times (each spectrum integrated over five seconds). (c) Summary of 1590 cm\(^{-1}\) Raman signal decay for PATP neat (black squares) and attached to 21 (red circles), 39 (green up triangles), and 59 nm (blue down triangles) Rh NCs. The lines are fitting curves with an exponential decay model. Figures reproduced from Ref. 65 with permission from The Royal Society of Chemistry.

2.4 Conclusion and outlook

In conclusion, uniform Rh NCs with edge lengths ranging from 10 to 120 nm have been successfully and controllably synthesized with unseeded and seeded slow-injection methods. UV-vis extinction spectra of these Rh NCs reveal the existence of
LSPRs in the UV region that red-shift with increasing size in a manner consistent with numerical simulations. The sizes and associated resonant energies of Rh NCs can be precisely controlled by the ratio between Rh seeds and Rh precursor added to the reaction. These UV plasmonic Rh NCs are employed in the photochemical decomposition of PATP under UV illumination and exhibited accelerated reaction rates that were fastest when the LSPR coincided with the laser wavelength. The precise control of particle morphology and LSPR wavelength of noble metal Rh NCs, and the associated field-enhanced spectroscopic and photochemical processes, could prove transformative to the nascent field of UV plasmonics.

Future work could involve UV-SERS measurements with reporter molecules that do not undergo photochemical transformations, such as crystal violet and 4-mercapto pyridine, to obtain stable Raman signal under UV exposure. This would allow quantitative assessments of the enhancement factor of the Raman signal from plasmonic response of substrates. The ability to decompose organic molecules on plasmonic Rh nanostructures with light could be used to fabricate pollutant degradation devices that work under sunlight. The effects of size and associated LSPR energy of the Rh NCs on the performance of photo-degradation devices is worthwhile for investigation.
Chapter 3: Product Selectivity in Plasmon-Enhanced Catalysis for Carbon Dioxide Hydrogenation

The content of this chapter is adapted from our publication (Nature Communications, 2016, 8: 14542).\(^9\) We acknowledge our coauthors, Dr. Du Zhang, Dr. Neil Qiang Su, and Dr. Weitao Yang at Duke University, for DFT calculations. We also acknowledge our coauthor, Dr. Henry Everitt at Army Aviation & Missile RD&E Center, for helpful discussions about experimental design.

3.1 Introduction

The societal need for industrial scale catalysis continues to grow in response to increasing demands for fertilizer, fuels, and materials. In order for heterogeneous catalytic reactions with large activation energies to achieve practical rates, heated catalysts are used, but these demand high energy inputs, shorten catalyst lifetimes through sintering deterioration,\(^{90-91}\) and require product selectivity to mitigate unfavorable side reactions. Rising atmospheric CO\(_2\) concentrations may be reduced, for example, by reacting ambient CO\(_2\) with renewably generated H\(_2\),\(^{33, 92}\) but product selectivity is essential to ensure production of hydrocarbons such as CH\(_4\) instead of the kinetically preferred product carbon monoxide CO.\(^{14, 93}\) Selective CO\(_2\) hydrogenation is also an essential purification step for the feedstock used in ammonia synthesis to fix nitrogen for fertilizers\(^2\). Ideal catalysts simultaneously lower operating temperatures, accelerate reaction rates, and preferentially select products without being consumed or altered. In spite of extensive research on the subject, no photocatalyst has yet achieved this lofty objective. Semiconductor-based photocatalysts offer a promising route to room
temperature reactions, but they exhibit limited selectivity and reaction rates that typically scale only as the square root of the light intensity \( R_{\text{photo}} \propto I^{0.5} \), making it impractical to increase the reaction rate by increasing light intensity.

As discussed in Chapter 1, it has been discovered that plasmonic metal nanoparticles are photocatalytically active, driving chemical reactions with photo-generated hot carriers and exhibiting a compelling super-linear dependence on light intensity \( R_{\text{photo}} \propto I^n, n > 1 \). The strong light absorption of plasmonic nanoparticles due to excitation of LSPRs may be spectrally tuned throughout the visible or UV by choice of metal, size, shape, and host medium. Of particular interest is the decay of LSPRs into hot carriers and their subsequent transfer to adsorbates where they may affect reaction pathways and rates. The distribution of photo-excited carriers depends on the local density of states in the metal and the associated band structure, the LSPR of the nanostructure, and the energy of the photon. By tuning photon and LSPR energies so that hot carriers are injected into specific anti-bonding orbitals of specific reaction intermediates, product selectivity may be achieved.

These early demonstrations of plasmonic photocatalysis either featured intense laser pulses (\( \sim \text{kW cm}^2 \)) on nanoparticle clusters to generate high concentrations of hot carriers, or they used alloyed or hybrid nanostructures composed of plasmonic (Au, Ag, Al) and catalytic (Pt, Co, Pd) metals. The ideal photocatalytic metal should simultaneously exhibit good plasmonic and catalytic behaviors to increase the rates and selectivity of the reaction. As discussed in Chapter 2, the size- and shape-dependent plasmonic properties of Rh nanoparticles have been demonstrated at energies
tunable throughout the UV and visible regions.\textsuperscript{59, 65, 75-78} Like Au and Pt, Rh is a transition metal without a native oxide coating, and direct bonding between adsorbates and the metal surface greatly facilitates the transfer of hot carriers for plasmonic photocatalysis. Supported Rh nanoparticles and molecular complexes are widely used as catalysts in automotive catalytic converters to reduce nitrogen oxides, as well as in industrial hydrogenation, hydroformylation, and ammonia oxidation reactions.\textsuperscript{60, 114-115}

Here we discuss the discovery that plasmonic Rh nanoparticles are photocatalytic, simultaneously lowering activation energies and exhibiting strong product photo-selectivity, as illustrated through the CO$_2$ hydrogenation reaction. CO$_2$ hydrogenation on transition metals at atmospheric pressure proceeds through two competing pathways: CO$_2$ methanation (CO$_2$ + 4H$_2$ $\rightarrow$ CH$_4$ + 2H$_2$O), and reverse water gas shift (RWGS, CO$_2$ + H$_2$ $\rightarrow$ CO + H$_2$O).\textsuperscript{116} We observe that mild illumination of the Rh nanoparticles not only reduced activation energies for CO$_2$ hydrogenation \textasciitilde 35\% below thermal activation energies, it also produces a strong selectivity towards CH$_4$ over CO. Specifically, under illumination from low-intensity (~W cm$^{-2}$), continuous wave blue or UV light-emitting diodes (LEDs), the photocatalytic reactions on unheated Rh nanoparticles produce CH$_4$ with selectivity of >86\% or >98\%, respectively, with a reaction rate twice that of the thermocatalytic reaction rate at 623 K (350°C). This high selectivity towards CH$_4$ disappears when the Rh nanoparticles are not illuminated, in stark contrast to plasmonic Au nanoparticles that only catalyze CO production whether illuminated or not. DFT calculations indicate 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. Our discovery that plasmonic Rh nanoparticles exhibit a photocatalytic activity with strong product photo-selectivity opens an exciting new pathway in the long history of heterogeneous catalysis by offering a compelling advantage of light over heat.

3.2 Experimental methods

3.2.1 Preparation of plasmonic catalysts

3.2.1.1 Plasmonic Rh catalyst

Rh nanocubes with edge length of 37 nm were synthesized by a modified unseeded slow-injection polyol method.⁶⁵ 54 mg KBr (ACS, Acros) was dissolved in 2 ml EG (J. T. Baker) in a 20 ml glass vial (cleaned with detergent and deionized water and dried in a vacuum oven at 80 °C) equipped with a Teflon-coated magnetic stir bar. The KBr solution was stirred in an oil bath at 160 °C for 1 h. 12 mg RhCl₃·xH₂O (38% Rh, Acros) and 25 mg 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⁻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.

After synthesis, the Rh NC reaction mixtures were diluted with acetone to ~45 ml and centrifuged at 12k rpm for 10 min. The colorless supernatant was discarded and the black precipitate was dispersed in ~5 ml deionized (DI) water (with sonication if needed). The Rh NC dispersion was diluted with acetone again to ~45 ml and centrifuged at 12k rpm for 10 min. The supernatant is discarded and the precipitate was usually treated with
this DI-water/acetone washing step for another three times to remove excess PVP, KBr, Cl\textsuperscript{−}, and EG. It is important to remove all Cl\textsuperscript{−} and Br\textsuperscript{−}, since they will strongly affect the catalytic activities of metal nanoparticles. The complete removal of Cl\textsuperscript{−} and Br\textsuperscript{−} was proved by the AgNO\textsubscript{3} test of the supernatant. The black precipitate was finally dispersed in 20 ml ethanol (200 proof, anhydrous, KOPTEC).

Optically and chemically inert Al\textsubscript{2}O\textsubscript{3} nanoparticles (Degussa, Alu Oxide C, specific surface area 85~115 m\textsuperscript{2} g\textsuperscript{−1}) was used as catalyst support. It was activated in air at 400 °C for 5 h and kept in an oven at 80 °C before use. 90 mg Al\textsubscript{2}O\textsubscript{3} nanoparticles was added to a beaker and appropriate amount of Rh NC suspension was added dropwise to the beaker. The total volume of the suspension was adjusted to ~20 ml with ethanol and sonicated for 30 min. After that, the suspension was stirred at room temperature overnight and centrifuged at 15k rpm for 20 min. The supernatant was discarded and the solid is dried in an oven at 80 °C for 5 h. 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\textsubscript{2}O\textsubscript{3} support and behaved as isolated nanoparticles.

3.2.1.2 Plasmonic Au catalyst

A deposition-precipitation method was used to prepare highly dispersed small Au nanoparticles on an Al\textsubscript{2}O\textsubscript{3} support.\textsuperscript{58} 100 mg Al\textsubscript{2}O\textsubscript{3} nanoparticles was dispersed in 10 ml DI-water in a cleaned 20 ml glass vial equipped with a Teflon-coated magnetic stir bar by sonication. 16 mg gold(III) chloride trihydrate (HAuCl\textsubscript{4}\cdot xH\textsubscript{2}O, 99.9+%, Aldrich) was added into the suspension and stirred in an oil bath at 80 °C. The pH was adjusted to ~8 by adding 1 M sodium hydroxide (NaOH) solution dropwise. After 4 h, the suspension
was cooled to room temperature. The suspension was washed with copious deionized water/acetone by centrifuge until no Cl\textsuperscript− was detected in the supernatant. The solid was dried in an oven at 80 °C overnight and ground into powder. The light purple/pink powder was calcined at 300 °C for 2 h and becomes dark purple.

### 3.2.2 Photocatalytic reactor design

To carry out heterogeneously photocatalytic reactions with gas-phase reactants and solid-phase catalysts, we designed and built a customized reactor system. Digital components are preferred in setting up this system to allow for interface with computer and programmable control.

#### 3.2.2.1 Photocatalytic reactor setup

The photocatalytic reactor system is composed of four major sub-systems: a gas delivery system, a photocatalytic vertically fixed-bed reactor, LED light sources, and a mass spectrometer for online product quantification. Photographs of the photocatalysis system and the reactor are shown in Figure 3.1.

Hydrogen (H\textsubscript{2}, Research grade), carbon dioxide (CO\textsubscript{2}, Research grade) and argon (Ar, UHP) were obtained from Airgas. The flow rates of gases were controlled individually by mass flow controllers (GFC, 200 ml min\textsuperscript{−1} maximum flow rate, Aalborg). The mass flow controllers were calibrated in-house by a water-displacement method with both N\textsubscript{2} and Ar as the reference gases. The flow rates of working gases were converted from the flow rates of reference gases with corresponding volumetric thermal capacity.
The photocatalytic reactor (Harrick, HVC-MRA-5) contained a stainless-steel body, a catalyst cup inside the body, and a detachable dome. The reactor had two water ports to circulate cooling water and cool the body of the reactor. Cooling water supplied from a chiller was turned on for all the measurements. The catalyst cup had a diameter of
6 mm and a height of 4 mm. The detachable dome was equipped with a quartz window with a diameter of 8 mm for top UV and visible light illumination of the catalyst bed. The temperature was measured by a thermocouple under the catalyst bed. The temperature of the photocatalyst bed was controlled by a PID temperature controller kit (Harrick, ATK-024-3), managing the resistive heating power of the reaction chamber, and cooling water to mitigate heating caused by LED illumination.

Three LEDs with emission of 365 nm wavelength, 460 nm wavelength, and 5700 K white light (Prizmatix, UHP-F) were used as light sources. Light from LEDs were coupled into a liquid light guide with a diameter of 5 mm to deliver to the reactor. The output power of LEDs was controlled by 0~5 V analog signal and measured with a thermopile power meter (Thorlabs, PM310D). The emission spectra of the light sources were measured with a CCD-based spectrometer (Thorlabs, CCS200).

The effluent from the reactor was analyzed by a quadrupole mass spectrometer (Hiden, HPR-20) equipped with a Faraday cup detector. The detection limit of the mass spectrometer is ~0.001% conversion of CO₂. The responsivity for each reactant and product gas was calibrated with standards or mixtures with known composition.

3.2.2.2 Programmable control of photocatalytic reactor system

The temperature of the reactor and the light intensity of LEDs are important parameters in plasmon-enhanced catalysis and can be controlled with programmable function. The temperature was controlled with a software provided by the vendor. The output power of LEDs was controlled by 0~5 V analog signal with a customized setting.
The light intensity of LEDs was controlled with a home-built virtual instrument (VI) coded with LabVIEW and a data acquisition (DAQ) device (USB-6002, National Instruments) for the generation of 0–5 V analog signal. The input-voltage vs output power relationship of each LED was measured with the DAQ device and the light power meter and re-calibrated quarterly to ensure consistency between measurements. Figure 3.2 shows a screenshot of the front panel of the LED control software. It has a step

Figure 3.2. A screenshot of the front panel of the LabVIEW VI for programmable control of the light intensity of LEDs.
structure and users can specify the voltage (light intensity) and the duration of each step. The elapsed time window shows the time that has elapsed in this time. When the elapsed time equals the duration of the current step, the current step will finish, and the program will jump to the next step. If the duration of a step is 0 min, that step will be skipped. The current version of the LED control software has 20 steps, so users can set up to 20 voltages (light intensities) for automated measurements. This function is extremely helpful when studying light-intensity dependent reaction rates. This software also allows cycling function: the setting of step 1 to step 20 can be repeated several times as users specified.

Figure 3.3 shows a screenshot of the block diagram of the LED control software. It has a hierarchical structure to implement different functions. The first level is a for loop structure, and users can specify the number of cycles the loop runs. This corresponds to the cycling function of the software. The second level is a flat sequence structure composed of 20 frames. Each frame corresponds to a step of the status of LEDs. Inside each frame, a DAQ Assistant generates the voltage signal on the specified analog output channel that connected to the analog input of LEDs to control their light intensities. A while loop with elapsed time function inside a frame allows the timing function. The elapsed time function reads the user-input duration and compares it with the time spent in this frame. When these two times equal, the Time has Elapsed output will stop the while loop and the program will move to the next frame. This software realizes programmable control of the light intensity of LEDs and improves the productivity of this system.
3.2.2.3 Operation of photocatalytic reactions

For plasmon-enhanced CO$_2$ hydrogenation, ~15 mg of Al$_2$O$_3$-supported catalysts was loaded on a stainless-steel mesh inside the catalyst cup to form a 4-mm thick catalyst bed. The plasmonic catalysts were first reduced under 60.1 ml min$^{-1}$ H$_2$ and 27.6 ml min$^{-1}$ Ar at 350 °C for 2 h and then another 10.9 mL min$^{-1}$ CO$_2$ was introduced to achieve an H$_2$-rich CO$_2$:H$_2$ ratio of 1:5.5 and activate the photocatalysts for ~12 h to reach stable
catalytic activities. The experiments with a H$_2$-deficient CO$_2$:H$_2$ ratio of 1:3.1 were conducted under 19.5 ml min$^{-1}$ CO$_2$, 60.1 ml min$^{-1}$ H$_2$, and 16.5 ml min$^{-1}$ Ar. The reactions were all operated in the low-conversion and light-controlled regime. For each temperature and light intensity condition, at least 15 min elapsed before reaching steady state and seven sequential measurements using the mass spectrometer were made to determine the steady-state concentration of each gas and the associated reaction rates and uncertainties. The 15 atomic mass unit (amu) signal was used to quantify CH$_4$ production rate. The 28 amu signal was used to quantify CO production rate, from which the background from CO$_2$ feedstock was subtracted. Deuterium (D$_2$, Sigma Aldrich, 99.8% atom D) was used in place of H$_2$ for the isotopic labeling experiments.

**3.2.3 Material Characterization**

TEM images were collected by a FEI Tecnai G$^2$ Twin operating at 200 kV. The TEM samples of solid plasmonic catalysts were prepared by dispersing the catalysts in ethanol with sonication for 30 min and depositing on a copper grid coated with a carbon/formvar film (Ted Pella, 01813). Diffuse reflectance UV-vis absorption spectra were obtained on an Agilent Cary 5000 equipped with an external diffuse reflectance accessory (DRA-2500). Transmission UV-vis extinction spectra were obtained on a Varian Cary 50 spectrometer with a Xeon flash lamp. The composition of the plasmonic catalysts was measured by a Kratos Analytical Axis Ultra X-Ray Photoelectron Spectrometer (XPS).
3.3 Results and discussion

3.3.1 Plasmon-enhanced and thermocatalytic reactions

The Rh catalyst was prepared by dispersing 37 nm Rh nanocubes on Al₂O₃ nanoparticles with a mass loading of 1.02% (Rh/Al₂O₃, Figure 3.4a). The unseeded slow-injection method used produces cubic nanoparticles whose size and LSPR wavelength can be precisely tuned, and whose sharp corners concentrate light and liberate hot carriers. The narrow size distribution of Rh NCs synthesized by the slow-injection method has been discussed in Chapter 2. The Rh NCs were well separated on the Al₂O₃ support and would show plasmonic properties of individual nanoparticles. Plasmonic “hot spots” from the nanogaps of aggregated nanoparticles are not expected in this Rh catalyst. For these experiments, the 334 nm (3.71 eV) LSPR of the Rh NCs in ethanol is broadened and blue-shifted on a porous Al₂O₃ support (Figure 3.4b).

The Al₂O₃ supported Au catalyst was prepared by a deposition-precipitation method with a mass loading of 1.70% (Au/Al₂O₃). The Au nanoparticles have a spherical shape with an average diameter of 2.6 nm (Figure 3.4c, d) and wider size distribution compared to the Rh NCs. This wider size distribution can be attributed to the poor control of size uniformity of the synthetic method.

The absorption spectra of Rh/Al₂O₃ and Au/Al₂O₃ catalysts overlaid with the emission spectra of the UV (365 nm, 3.40 eV), blue (460 nm, 2.70 eV), and white LEDs are shown in Figure 3.5. The strong plasmonic behavior of the Rh/Al₂O₃ catalyst overlapped the UV light source. The blue LED was used to study the influence of excitation wavelength on the catalytic properties. The band structure of Rh indicates...
Figure 3.4. (a) TEM images of the Rh/Al$_2$O$_3$ catalyst. Scale bar: 100 nm (inset: 25 nm). (b) UV-vis spectra of Rh nanocubes in ethanol solution (black) and on a porous Al$_2$O$_3$ support (blue). The resonant peak of plasmonic Rh nanocubes is blue-shifted and broadened when supported on an Al$_2$O$_3$ support due to the change of dielectric environment. (c) TEM image of spherical Au nanoparticles supported on Al$_2$O$_3$ nanoparticles. Scale bar: 50 nm. (d) Size distribution of Au nanoparticles in the Au/Al$_2$O$_3$ catalyst. More than 80 nanoparticles were measured to obtain the size distribution. Figures adapted from ref. 89.
that the UV and blue excitations avoid lower energy parasitic inter-band absorption of Rh in the near-infrared region and generate nearly free hot electrons with energies 2.5 and 2.1 eV above the Fermi level,\textsuperscript{59, 111} respectively. An LSPR near 517 nm (2.40 eV) is observed for the Au/Al\textsubscript{2}O\textsubscript{3} catalyst. A white LED (400-800 nm) was used for the Au catalyst to excite its LSPR, unless otherwise stated.
A fixed-bed reaction chamber equipped with a quartz window was used to carry out the photocatalytic reactions with controlled light illumination. The photocatalysts were packed with a thickness of ~4 mm (~15 mg) to ensure complete absorption of light. For the heated experiments, the temperature of the powder catalysts was precisely measured with a thermocouple and controlled by resistive heating and cooling water. However, the unheated “ambient” experiments were initiated at room temperature and used no cooling water, so the temperature was allowed to rise and equilibrate. A mass spectrometer was connected to the chamber outlet for real-time, quantitative analysis of gaseous products. The conversion of CO$_2$ was maintained <5% to eliminate reactant-transport limitations and ensure that the concentrations of products in the effluent represent the reaction rates. In dark conditions, the reaction rates represent the thermocatalytic activities of the catalysts, while under illumination, the overall reaction rates are considered as the sum of thermocatalytic and plasmon-enhanced contributions. Thus, the plasmon-enhanced reaction rates are obtained by subtracting the thermal reaction rates (light off) from the overall reaction rates (light on) at the same temperature. All reactions were performed at atmospheric pressure with either an H$_2$-rich 1:5.5 or H$_2$-deficient 1:3.1 mixture of CO$_2$:H$_2$ (as compared to the 1:4 stoichiometry of CO$_2$ methanation) and argon (Ar) as internal standard.

### 3.3.2 Product selectivity of CO$_2$ hydrogenation

On the Rh catalyst (Figure 3.6a, solid lines), CH$_4$ and CO were produced at comparable rates at 623 K under dark, H$_2$-rich conditions (e.g., 0-8 min). Upon illumination of UV light (e.g., 8-22 min), a seven-fold increase in the CH$_4$ production rate
Figure 3.6. (a) Rates of CH$_4$ (green) and CO (black) production at 623 K in a H$_2$-rich CO$_2$:H$_2$ ratio of 1:5.5 condition on Rh/Al$_2$O$_3$ (solid lines) and Al$_2$O$_3$ (dotted lines) under dark and UV illumination at 3.0 W cm$^{-2}$. CH$_4$ production is strongly and selectively enhanced by UV light on the Rh catalyst. Neither CH$_4$ nor CO production was detected on Al$_2$O$_3$. (b) Rates of CO (black) and CH$_4$ (green) production at 623 K in a H$_2$-rich CO$_2$:H$_2$ ratio of 1:5.5 condition on Au/Al$_2$O$_3$ under dark and white light at 3.0 W cm$^{-2}$. A light-enhanced reaction rate is observed, but CO remains the exclusive product under both conditions. Figures adapted from ref. 89.

was observed, while only a slight increase in CO production was detected. No other carbon-containing product was observed above the detection limit of the mass spectrometer in our experiments, and the reaction rates responded to light instantly and reversibly. Control experiments using pure Al$_2$O$_3$ nanoparticles (Figure 3.6a, dotted lines) showed that the reaction did not occur on the support. Isotopic labeling experiments was carried out using D$_2$ to replace H$_2$ (Figure 3.7). 13, 14, and 15 amu channels,
Figure 3.7. (a) CO$_2$ hydrogenation reaction with H$_2$ on plasmonic Rh/Al$_2$O$_3$ catalyst. Signals from 13 (blue), 14 (red) and 15 (black) amu channels are monitored by the mass spectrometer at 623 K in dark (0~25 min) and under UV illumination at 3.0 W cm$^{-2}$ (25~55 min). (b) Isotopic labeling experiments with D$_2$ on Rh/Al$_2$O$_3$ catalyst. The reaction condition is at 623 K in dark (0~25 min) and under UV illumination at 3.0 W cm$^{-2}$ (25~55 min). Figures adapted from ref. 89.

corresponding to different fragments of CH$_4$, were monitored by the mass spectrometer with H$_2$ or D$_2$ as reductants. When H$_2$ was used, increased signals from all these three channels are detected, corresponding to CH$^+$, CH$_2$$^+$ and CH$_3$$^+$ fragments from CH$_4$, upon illumination of UV light (~25 min). When D$_2$ was used, increased signal was only detected in the 14 amu channel, corresponding to CD$^+$ fragments from CD$_4$, upon UV illumination (~25 min). These results confirmed that CH$_4$ and CO were produced from the plasmon-enhanced reactions on Rh NCs, rather than from the decomposition of organic residues left from the synthesis of catalyst or from the Al$_2$O$_3$ support.
Figure 3.8. Plasmon-enhanced CO$_2$ hydrogenation on the Au/Al$_2$O$_3$ catalyst under UV and white light with the same intensity (1.18 W cm$^{-2}$) at 623 K in a H$_2$-rich CO$_2$:H$_2$ ratio of 1:5.5 condition. The production rate of CO (black) increases under both UV and white light illumination, but no production of CH$_4$ (green) is observed. Figure adapted from ref. 89.

Comparable photo-enhanced CO$_2$ hydrogenation was also observed on the Au catalyst under white light illumination of similar intensity (Figure 3.6b). At 623 K, CO was produced in dark (e.g., 0-8 min), whose production rate was increased under illumination of white light (e.g., 8-24 min). However, the product selectivity is distinctly different from the reaction on the Rh catalyst: CO was the exclusive carbon-containing product on the Au catalyst under both dark and light conditions. Even under the same UV illumination as the Rh catalyst, CO was exclusively produced on the Au catalyst (Figure 3.8), indicating that wavelength alone cannot account for the different selectivity.
These results demonstrate that the different selectivity of thermocatalytic and plasmon-enhanced reactions on the Rh and Au nanoparticles is primarily determined by the properties of metals, specifically the differing metal-adsorbate interactions. On Rh catalysts, previous experimental and theoretical investigations\textsuperscript{64, 116, 119-125} showed that CO\textsubscript{2} first dissociatively adsorbs on the Rh surface to generate adsorbed CO and oxygen (O). The adsorbed CO can either desorb from the surface or be hydrogenated to form CHO. The dissociation of CH-O generates CH, followed by further hydrogenation to form CH\textsubscript{4} (Figure 3.9). The desorption of CO from the metal surface was identified as the rate-determining step (RDS) of CO production, and the dissociation of CH-O was the RDS for CH\textsubscript{4} production.\textsuperscript{116} Thus, competition between CO desorption and C-O bond cleavage in CHO dictates the product selectivity. The O adsorption energy, $E_{\text{ads,O}}$, on late transition-metal surfaces is known to be an effective descriptor of the selectivity of CO\textsubscript{2} hydrogenation.\textsuperscript{116} A high $E_{\text{ads,O}}$ partially compensates the energy cost for C-O bond cleavage in the CHO intermediates and increases the selectivity towards CH\textsubscript{4}. Although the reaction on the Au catalysts has been reported to involve additional reaction intermediates,\textsuperscript{102, 126-127} the selectivity observed here is consistent with the corresponding $E_{\text{ads,O}}$ of Rh (5.22 eV) and Au (3.25 eV):\textsuperscript{128} the Rh catalyst had a slight preference towards CH\textsubscript{4} production under dark conditions, whereas the Au catalyst exclusively produced CO.
Figure 3.9. Elementary steps of CO₂ hydrogenation on the Rh/Al₂O₃ catalyst. The * denotes vacant sites or adsorbed intermediates on the Rh surface. The desorption of CO from the Rh surface is reported to be the rate-determining step (RDS) for CO production. The dissociation of CH-O into CH and O is reported to be the RDS for CH₄ production. The competition between these two steps dictates the product selectivity. Figure adapted from ref. 89.

The selectivity of these reactions is changed when hot carriers are photo-excited in plasmonic Rh nanoparticles. The different selectivity of thermocatalytic and plasmon-enhanced reactions on Rh nanoparticles is depicted in Figure 3.10. The dark thermocatalytic reaction exhibited mild selectivity, with a CH₄:CO ratio of ~60:40 in the tested range of temperatures and reaction rates. In contrast, under UV illumination the CH₄ production rate was significantly and selectively enhanced. The plasmon-enhanced reactions exhibit >95% selectivity towards CH₄, and the resulting selectivity towards CH₄ from the overall reaction is >90% under 3.0 W cm⁻² UV illumination and H₂-rich
conditions (CO$_2$:H$_2$=1:5.5) over the tested temperature range. Experiments under H$_2$-deficient conditions (CO$_2$:H$_2$=1:3.1) maintained this high selectivity under illumination but exhibited even lower selectivity under dark conditions, confirming that illumination, not heat or excess H$_2$ feedstock, is responsible for the highly selective production of CH$_4$ (Figure 3.10b). CH$_4$ selectivity of pure thermal reaction at reaction temperatures higher than our test range was calculated with CH$_4$ and CO production rates extrapolated using the Arrhenius equation. The results suggested that a reaction temperature higher than 1123 K (850 °C) was required to achieve a CH$_4$ selectivity higher than 85%. This requirement of high temperature for pure thermal reaction and the observed high photo-selectivity towards CH$_4$ over CO at the same reaction rate as the thermal reaction indicate that the photo-enhanced reaction rates do not mainly originate from thermal or plasmonic photothermal heating on the Rh nanoparticle surface. Instead, it is the plasmon-generated hot electrons that selectively activate CHO intermediates and accelerate CH$_4$ production while minimally affecting the CO-metal bond for CO production (desorption). This analysis is based on the assumption that thermocatalytic and plasmon-enhanced reactions have the same elementary steps and surface intermediates, a claim supported by a recent kinetic study of RWGS on Au photocatalysts. Although the selectivity is derived almost entirely from light, heat significantly increases the reaction rate.
Figure 3.10. (a) Selectivity towards CH$_4$ as a function of overall reaction rates in dark (black circles) and under UV light at 3.0 W cm$^{-2}$ (red squares) in a H$_2$-rich CO$_2$:H$_2$ ratio of 1:5.5 condition. (b) Selectivity towards CH$_4$ of the thermocatalytic (black circles) and plasmon-enhanced reactions under UV (365 nm, red squares) and blue (460 nm, blue triangles) illumination as a function of temperature under H$_2$-rich (CO$_2$:H$_2$=1:5.5, solid symbols) and H$_2$-deficient (CO$_2$:H$_2$=1:3.1, open symbols) conditions. The plasmon-enhanced rates are calculated by subtracting the thermocatalytic reaction rates from overall reaction rates at the same temperature. Figures adapted from ref. 89.

For the ambient experiments (no heating from the reactor and no cooling water), efficient plasmon-enhanced CH$_4$ production with high selectivity was demonstrated on the Rh catalyst under UV illumination at 3.0 W cm$^{-2}$ and H$_2$-rich conditions with a reaction rate (circled red square in Figure 3.11) comparable to the thermocatalytic reaction rate at 548 K (275 °C). The slightly elevated steady-state temperature, measured to be 328 K ($\Delta T = 29$ K), was caused by photothermal heating of the catalyst bed (separately measured to be 25 K by a non-reactive control experiment with flowing Ar and H$_2$) and the exothermic nature of the CO$_2$ methanation reaction ($4$ K, $\Delta H^o = -165.01$
kJ mol\(^{-1}\) at 298 K). Likewise, the ambient reaction rate for the highest intensity of our blue LED (4.9 W cm\(^{-2}\), \(\Delta T = 48\)K, circled blue diamonds in Figure 3.11) was two times higher than that of the thermocatalytic reaction rate at 623 K (350 °C) with an apparent quantum efficiency (AQE), defined as the molar ratio of methane generated to photons delivered, of 0.82%. It is important to recognize that these high reaction rates with high selectivity were achieved using an efficient, low-intensity LED.

![Graph](image)

**Figure 3.11.** Overall CH\(_4\) production rates in dark (black circles) and under UV (red squares, 3.0 W cm\(^{-2}\)) and blue (blue triangles, 2.4 W cm\(^{-2}\)) LEDs with the same photon flux, and with twice the blue photon flux (blue diamonds, 4.9 W cm\(^{-2}\)) in a H\(_2\)-rich CO\(_2\):H\(_2\) ratio of 1:5.5 condition. UV light is more efficient at enhancing the reaction rates than blue light with the same photon flux. Circled points show the unheated steady-state temperatures and reaction rates. Error bars represent the s.d. of measurements by the mass spectrometer. Figure adapted from ref. 89.
Under illumination from the blue LED with the same photon flux (2.4 W cm\(^{-2}\)) as the UV LED at 3.0 W cm\(^{-2}\), the reaction rate and AQE were smaller (blue triangles in Figure 3.11). Nevertheless, the reaction rate under low-energy blue photons becomes higher than that under high-energy UV photons with increased light intensity. At the highest intensity of the blue LED (4.9 W cm\(^{-2}\)), the enhancement factor for CH\(_4\) production \((EF = R_{\text{overall}}/R_{\text{thermal}})\) and AQE at 623 K reached 27.8 ± 1.4 and 7.50\%, respectively (blue diamonds in Figure 3.11).

### 3.3.3 Light-intensity dependent reaction rate

The effects of LED intensity on the reaction rates using the Rh catalyst were carefully studied by varying the output power of the light source. Under UV illumination near ~1 W cm\(^{-2}\), the photoreaction rate under H\(_2\)-rich conditions changed from linear to super-linear dependence on light intensity \((R_{\text{photo}} \propto I^n, n = 2.1 \text{ at } 623 \text{ K and } 2.4 \text{ at } 573 \text{ K, Figure 3.12})\). This super-linear relationship confirms that the photoreactions are mediated by hot electrons\(^{54}\) and can be attributed to multiple excitations of the vibrational mode(s) of the adsorbed RDS intermediate by hot electrons.\(^{55}\) In the low-intensity linear region, the slope is significantly higher at 623 K than at 573 K (Figure 3.12, inset) as heat accelerates the photocatalytic rate. Conversely, the plasmon-enhanced reaction rates were greatly enhanced at the highest intensity of the UV LED (3.0 W cm\(^{-2}\), red squares in Figure 3.11), compared to the thermocatalytic reaction rates at the same temperature. The \(EF\) was 7.41 ± 0.37 at 623 K and increased to 24.4 ± 1.2 at 523 K. The AQE for CH\(_4\) production was measured to be 3.70\% at 623 K.
Figure 3.12. Plasmon-enhanced rates of CH$_4$ production as a function of UV light intensity at 623 (black squares) and 573 K (red circles) in a H$_2$-rich CO$_2$:H$_2$ ratio of 1:5.5 condition. The plasmon-enhanced rate is calculated by subtracting the thermal reaction rate from the overall reaction rate under light at the same temperature. The intensity-dependent reaction rates show a linear to super-linear transition with increasing light intensity. The inset shows the intensity-dependent reaction rates in the linear region. Error bars represent the s.d. of measurements by the mass spectrometer. Figure adapted from ref. 89.

Unlike the sub-linear rate increase with increased light intensity characteristic of conventional semiconductor photocatalysis,$^{37, 97}$ this super-linear dependence indicates that very high reaction rates will not require very high light intensities.
3.3.4 Reaction kinetics of plasmon-enhanced and thermocatalytic reactions

To understand the mechanism, the reaction kinetics of CO$_2$ hydrogenation on Rh and Au catalysts in light and dark H$_2$-rich conditions were studied experimentally in the temperature range of 523 and 623 K. The light intensity was chosen to be within the linear intensity dependence region to eliminate the effect of multiple excitation events. By fitting the measured temperature-dependent reaction rates with an Arrhenius equation, the apparent activation energy ($E_a$) of the thermocatalytic and plasmon-enhanced reactions was obtained (Figure 3.13). In virtually every case, the equation fits the data well, and the $E_a$ was ascertained with less than 5% uncertainty. For the thermocatalytic reactions on Rh, the $E_a$ for CH$_4$ and CO production was measured to be 78.6 ± 2.0 and 64.7 ± 6.0 kJ mol$^{-1}$ (0.81 and 0.67 eV), respectively, consistent with previous reports on supported Rh catalysts.$^{119, 129}$ Under UV illumination, the plasmon-enhanced CH$_4$ production showed a reduced $E_a = 50.4 \pm 1.8$ kJ mol$^{-1}$ (0.52 eV) for all light intensities. This reduction of $E_a$ was also observed for CO production on the Au catalyst with visible light, decreasing from 55.8 ± 0.5 kJ mol$^{-1}$ (0.58 eV) for the thermocatalytic reaction to 39.5 ± 2.0 kJ mol$^{-1}$ (0.41 eV) for photoreactions. The photoreaction rates of CO production on the Rh catalyst were too small for the activation energy to be deduced reliably.
Figure 3.13. Apparent activation energy on the Rh and Au catalysts in a H₂-rich CO₂:H₂ ratio of 1:5.5 condition. (a) Thermocatalytic reaction rates of CH₄ (black squares) and CO (red circles) production on Rh/Al₂O₃ as a function of temperature. The apparent activation energies are obtained by fitting the results with an Arrhenius equation. (b) Photoreaction rates for CH₄ production on Rh/Al₂O₃ under 1.18 (black squares), 0.59 (red circles) and 0.24 W cm⁻² (blue triangles) UV illumination as a function of temperature. Photoreaction rate is calculated by subtracting the thermal reaction rate from the overall reaction rate under light at the same temperature. (c) Thermocatalytic reaction rates of CO production on Au/Al₂O₃ as a function of temperature. (d) Photoreaction rates of CO production on Au/Al₂O₃ under 1.27 (black squares) and 0.89 W cm⁻² (red circles) white light as a function of temperature. Error bars represent the s.d. of measurements by the mass spectrometer. Figures reproduced from ref. 89.
3.3.5 Reaction mechanism of plasmon-enhanced catalysis

The observed kinetics and selectivity of CO$_2$ hydrogenation on the Rh and Au catalysts shed light on the reaction mechanism of plasmon-enhanced catalysis. In thermocatalytic reactions, interactions between surface intermediates and catalysts dictate the propensity of competing pathways. For example, the higher selectivity towards CH$_4$ in the thermocatalytic reactions on Rh has already been ascribed to its higher $E_{ads,O}$,$^{128}$ while the exclusive selectivity for CO on the Au catalyst was caused by the low $E_{ads,O}$ and the deficiency of surface H atoms under our experimental conditions.$^{23}$ By contrast, in photoreactions, the transfer of hot electrons from plasmonic metal nanoparticles to specific intermediates critically depends on the energies of the hot electrons and the antibonding orbitals, thereby selectively activating certain reaction pathways and offering an additional means to tune the selectivity.$^{103-104, 113}$

To explain the photo-selectivity we observed from the plasmonic Rh nanoparticles, DFT calculations were carried out by our collaborators to understand how hot electrons may affect the intermediates in the rate-determining steps of CH$_4$ and CO production. The projected local density-of-states (LDOS) for the adsorbed CHO and CO, key intermediates established in previous reports for CH$_4$ and CO production,$^{64, 116, 119-125}$ respectively, on the dominant Rh nanocube facet, Rh(100), are presented in Figure 3.14a and b, respectively. Figure 3.14c and d show the side view and top view of optimized configurations used in calculations. For clarity, only the orbitals involved in C-O bond cleavage for the Rh-CHO system and Rh-C bond cleavage for the Rh-CO system are plotted. The bonding interactions in both the CHO and CO systems lie ~6 eV below the
Fermi level, suggesting a minimal role of hot holes in this process. For CHO, the C-O $\pi^*$ anti-bonding bands, which can accept hot electrons to weaken the C-O bond and facilitate CH$_4$ production, can be easily identified on the C($p_z$) and O($p_z$) orbitals at $\sim$2.0 eV (Figure 3.14a). On the other hand, the very weak and broad anti-bonding Rh-C interactions observed on the C($p_x$) orbital at $\sim$1.0 eV for CO (Figure 3.14b) suggests a much smaller possibility of accepting UV photoexcited hot electrons by the CO intermediate compared to the CHO intermediate. Thus, the photo-generated hot electrons preferentially activated the CHO intermediate and enhanced CH$_4$ production, while only a small enhancement was observed for CO production. This mechanism is further verified by the lower selectivity towards CH$_4$ observed under non-resonant, lower energy blue light ($\sim$85%); the lower energy hot electrons had a lower probability of transferring to the higher energy anti-bonding orbital of the CHO intermediate ($\sim$2.0 eV) and a higher probability of transferring to the lower energy orbital of the CO intermediate ($\sim$1.0 eV). We note that due to the rapid decay via electron-electron and electron-phonon scatterings, the actual energies of the hot electrons are distributed below the associated photon energies of UV and blue light. Nevertheless, our computed relative magnitude of the LDOS peaks and the energy ordering for the relevant antibonding bands still offer a valid qualitative interpretation both for overall preference for CH$_4$ (under either UV or blue light) and for the slightly reduced CH$_4$ selectivity under blue light. Generally speaking, 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.
Figure 3.14. Calculated local density-of-states (LDOS) for adsorbed CHO (a) and CO (b) and structures used in calculations of CHO (c) and CO (d) adsorbed on Rh(100) surface. Figures adapted from ref. 89.
The deduced process of thermocatalytic and plasmon-enhanced CO₂ hydrogenation on plasmonic Rh photocatalysts is summarized in Figure 3.15. In the thermocatalytic reactions, phonons activate both CHO and CO intermediates and produce CH₄ and CO at comparable rates on the ground-state reaction coordinate (black curve in the bottom part of Figure 3.15). In the plasmon-enhanced reactions, hot electrons...
selectively transfer to the anti-bonding orbitals of CHO intermediates to weaken the chemical bonds and drive the reaction on a charged-state reaction coordinate characterized by a reduced activation energy (red curve in the top part of Figure 3.15). This scenario is consistent with similar schemes proposed for other reactions on plasmonic metal photocatalysts.49, 58, 98, 105-106

3.4 Conclusion and outlook

In conclusion, we show how the recently demonstrated plasmonic behavior of Rh nanoparticles profoundly improves their already excellent catalytic properties by simultaneously reducing the activation energy and selectively producing a desired but kinetically unfavorable product for the important CO₂ hydrogenation reaction. CH₄ is almost exclusively produced when Rh nanoparticles are mildly illuminated as hot electrons are injected into the antibonding orbital of a critical intermediate, CO and CH₄ are equally produced without illumination. The product selectivity is distinctly different from plasmonic Au catalyst, where CO is the only product regardless of illumination. The reduced activation energy and super-linear dependence on light intensity cause the unheated plasmon-enhanced CH₄ production rate to exceed the thermocatalytic rate at 350 °C.

In the future, red-shifting the plasmonic resonance of Rh nanoparticles farther into visible region, assembling Rh nanoparticles into closely packed clusters to create “hot spots”, and optimizing the reactant composition could achieve even more selective and efficient photocatalytic CH₄ production from CO₂ hydrogenation, even under direct or mildly concentrated sunlight. Our findings demonstrate that efficient plasmonic
photocatalysis requires metals with both excellent catalytic and plasmonic properties. Although the mechanism analyzed is based on CO$_2$ hydrogenation, the concept of selective activation of specific reaction intermediates to control the product selectivity can be applied to other plasmonic catalytic systems in ways that could prove to be transformative.
Chapter 4: Observation of High Apparent Quantum Efficiency and Possible Explanations for Plasmon-Enhanced Carbon Dioxide Hydrogenation

4.1 Introduction

As discussed in Chapter 3, plasmon-enhanced catalysts have been exploited in several chemical reactions, such as hydrogen dissociation, cross-coupling reactions, dehydrogenation, and redox reactions of small molecules. Upon excitation of LSPRs, hot electrons with appropriate energy can transfer to unpopulated anti-bonding orbitals of reaction intermediates in the rate-determining step (RDS), thus weakening the chemical bonds and lowering the activation barrier to enhance chemical transformations. The hot electrons then transfer back to the metal nanoparticles and dissipate excess energy as heat. Due to the fast recombination of photo-generated hot carriers and the loss of energy, plasmonic catalysts generally suffer from low efficiency. Since hot electrons activate the surface intermediates involved in the RDS of chemical reactions, we use apparent quantum efficiency (AQE), defined as the ratio between the rate of photo-induced RDS and the photon flux, to evaluate the efficiency of plasmon-enhanced catalysis. Examining previous demonstrations of plasmon-enhanced catalysis, AQEs are mainly found below 10% with a few reports reaching up to 30%. Therefore, it is important to establish design principles of plasmonic photocatalysts to efficiently drive chemical reactions with photons.

It is well acknowledged that support materials offer much more than passive mechanical and thermal stabilizations of the metal nanoparticles in catalytic processes.
Supports can play a critical role in determining the catalytic activities and selectivity by modifying the Fermi level of metal nanoparticles, interacting with surface intermediates, and forming special types of active sites at the metal-support interface.\textsuperscript{130} In plasmon-enhanced hydrogen dissociation, the activities of insulating SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} supported Au nanoparticles were found to be two orders of magnitude higher than the semiconducting and reducible TiO\textsubscript{2} supported catalyst.\textsuperscript{58} The differences were attributed to the semiconductor-metal junction between the TiO\textsubscript{2} support and Au nanoparticles that trapped the photo-induced hot electrons in TiO\textsubscript{2}, an absent feature in insulating SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}. On the contrary, the rate of reverse water-gas shift on TiO\textsubscript{2} and cerium oxide (CeO\textsubscript{2}) supported Au nanoparticles under illumination were more than one order of magnitude higher than the Al\textsubscript{2}O\textsubscript{3} supported catalyst, probably due to highly active sites at the interface of gold and reducible oxides.\textsuperscript{102} Hence, in addition to the specified reaction and choice of plasmonic metals that need to be considered in the design of plasmonic catalysts, the effects of chemical and charge transport properties of supports worth carefully examinations.

In Chapter 3, we demonstrated plasmon-enhanced CO\textsubscript{2} hydrogenation on Al\textsubscript{2}O\textsubscript{3} supported plasmonic Rh nanostructures, and the product selectivity can be controlled by light. Illumination of UV or blue light not only enhanced the conversion of CO\textsubscript{2}, but also altered the product selectivity from equation production of CH\textsubscript{4} and CO in dark conditions to highly selective CH\textsubscript{4} production.\textsuperscript{89} In this project, the AQE of plasmon-enhanced CO\textsubscript{2} hydrogenation at 350 °C reaches \(\sim350\%\) and \(\sim300\%\) under 0.95 W cm\textsuperscript{-2} UV light and blue illumination, respectively, by replacing Al\textsubscript{2}O\textsubscript{3} with TiO\textsubscript{2} support and
changing the morphology of Rh nanostructures. By directly measuring the temperature of catalyst bed under illumination, this high AQE can be partially attributed to the photothermal effects that induce a temperature gradient vertically along the catalyst bed.

4.2 Experimental methods

4.2.1 Preparation of plasmonic Rh catalysts

Rh nanospheres and nanocubes are synthesized by polyol methods. For Rh nanospheres, 25 mg PVP (M.W. ≈ 55,000, Aldrich) was dissolved in 5.6 ml EG (J. T. Baker) in a 20 ml glass vial and stirred in an oil bath at 160 °C for 30 min. 12 mg 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 discussed in Chapter 2. 54 mg 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 for four times until no Cl⁻ and Br⁻ was 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), TiO₂ (Degussa, P25, specific surface area 35~65 m² g⁻¹), SiO₂ (Sigma, S5130, specific surface area 370~420 m² g⁻¹), and CeO₂ (Nanostructured & Amorphous Materials, Inc., 99.9%, specific surface area 30~50 m² g⁻¹). The supports were activated in air at 500 °C for 5 h before impregnation. Upon evaporation of the solvent at 70 °C with stirring, the obtained solid was dried in a vacuum oven at 80 °C for 5 h, ground into powder, and calcined in air at 400 °C for 2 h to remove organic residues.

### 4.2.2 Catalytic reaction measurements

The catalytic reaction was carried out on a custom-built gaseous reaction system as discussed in Chapter 3. The system consists of a gas delivery system, a fixed-bed stainless-steel reactor equipped with a quartz window and a programmable temperature controller, LED light sources, and an online mass spectrometer. 10~30 mg of Rh catalysts were loaded in the catalyst cup held by a stainless-steel mesh to fill a 4-mm height and 6-mm diameter catalyst cup and ensure complete absorption of light for the catalytic measurements. H₂ (UHP), CO₂ (Research grade) and Ar (UHP) were obtained from Airgas. The Rh catalysts were first reduced under 60 ml min⁻¹ H₂ and 20 ml min⁻¹ 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 200 or 250 ml min⁻¹. The detection limit of the mass spectrometer is ~0.001% conversion of CO₂. For each temperature and light intensity condition, at least 15 min elapsed before reaching steady state and seven sequential measurements were made to determine the steady-state concentration of each gas and the associated reaction rates and uncertainties.
4.2.3 Direct measurements of catalyst temperature

To directly measure the temperature of the catalyst bed and assess the contribution from photothermal effect, the reaction setup was modified to accommodate external thermocouples (Figure 4.1). Two external thermocouples were inserted through the gas outlet line and stuck vertically into the catalyst cup. A piece of inert quartz wool instead of a metal mesh was placed at the bottom of the catalyst cup to hold the catalyst and allow the thermocouples to penetrate. The tip of one thermocouple was at the same level as the bottom surface of the catalyst bed and the other one was just covered by the top surface of catalyst. Therefore, temperatures measured by these two thermocouples represent the temperature of the top \( T_1 \) and bottom surface \( T_2 \) of the catalyst bed in dark and under light illumination, which could be used to estimate the temperature gradient along the catalyst bed. The internal thermocouple was embedded in the heating block of the reaction chamber, which served as the temperature input for the temperature controller.

A uniform vertical temperature gradient can be assumed along the catalyst bed and an equivalent temperature \( T_e \) can be calculated using the Arrhenius equation with the activation energy:

\[
\frac{-E_a}{e^{RT_e}} = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} e^{-\frac{E_a}{RT}} \,dT
\]

The obtained \( T_e \) can be used to calculate the reaction rate enhancement by light from the photothermal effect.
4.2.4 Material characterization

TEM images were collected by a FEI Tecnai G² Twin operating at 200 kV. The TEM samples were prepared by dispersing the catalysts 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).
4.3 Results and discussion

4.3.1 Effects of catalyst support and morphology of Rh nanoparticles

The influences of catalyst support on plasmon-enhanced catalysis are investigated using plasmonic Rh nanocubes (NCs) as the model catalyst. The oxide supports under investigation are semiconducting and reducible TiO$_2$ and CeO$_2$, and insulating and non-reducible Al$_2$O$_3$ and SiO$_2$. Monodispersed Rh NCs with edge length of 34.4 nm were synthesized by a modified slow-injection method as discussed in Chapter 2 (Figure 4.2a).$^{65}$ The supported Rh NC catalysts were prepared by an impregnation method with a Rh loading of ~5 wt% and denoted as Rh-c/oxides. Figure 4.2b shows the TEM image of Rh-c/TiO$_2$ catalyst. The high-surface-area TiO$_2$ support (P25) is an agglomerate of TiO$_2$ nanoparticles with diameters ~15 nm, on which the plasmonic Rh NCs supported.

![Figure 4.2. TEM images of as-synthesized 34 nm Rh NCs (a) and TiO$_2$ supported Rh NC catalyst (b, Rh-c/TiO$_2$).](image)

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UV-vis spectra show that these Rh NCs have a resonant absorption peak at 331 nm (3.75 eV) and its tail extends into the visible region in an ethanol suspension (Figure 4.3). The plasmonic resonances of Rh NCs blue-shifted upon impregnation on the oxide supports due to the change of surrounding media as revealed by diffuse-reflectance UV-vis spectra, but still overlapped with the emission spectra of our UV (365 nm) and blue (460 nm) LED light sources. Since the semiconducting TiO$_2$ and CeO$_2$ supports also absorb light at wavelength shorter than 400 nm, the peaks of the Rh NCs cannot be distinguished in the Rh-c/TiO$_2$ and Rh-c/CeO$_2$ catalysts.

The catalytic activities of oxide supported Rh NCs were measured in our fixed-bed photoreactor as described in Chapter 3. A mixture of CO$_2$, H$_2$, and Ar with a molar ratio of 1:3:1 was introduced into the reaction chamber, and the effluent was analyzed with an online mass spectrometer to quantify the reaction rates. The Rh weight loading and CH$_4$ production rates in dark, under 2.8 W cm$^{-2}$ UV light, and under 4.9 W cm$^{-2}$ blue light at 350 °C of different oxide supported Rh NCs are summarized in Table 4.1. A significant support effect is observed for both the thermocatalytic and plasmon-enhanced reactions. By replacing non-reducible Al$_2$O$_3$ with reducible TiO$_2$, the thermal reaction rate shows a seven-fold increase. The thermocatalytic activities of supported Rh catalysts follow the order of Rh-c/TiO$_2$ > Rh-c/CeO$_2$ > Rh-c/ Al$_2$O$_3$ > Rh-c/SiO$_2$, which is consistent with previous reports of oxide supported Rh catalysts. As discussed in Chapter 3, the dissociation of CH-O into CH and O was identified to be the RDS of CO$_2$ hydrogenation on Rh catalysts, followed by fast hydrogenation of CH to produce CH$_4$.

The rate enhancement by replacing Al$_2$O$_3$ with TiO$_2$ can be attributed to the
interactions between reduced Ti$^{3+}$ centers on TiO$_2$ support and O in the CH-O intermediate, which facilitates the bond breaking.$^{123}$

![Graphs showing UV-vis absorption spectra of Rh NCs in ethanol suspension (red), supported on Al$_2$O$_3$ (a), TiO$_2$ (b), CeO$_2$ (c), and SiO$_2$ (d, black) and the pure supports (blue). The spectra of Rh NC suspension, catalysts, and the pure TiO$_2$ and CeO$_2$ support are normalized to the maximum absorbance. The spectra of pure Al$_2$O$_3$ and SiO$_2$ supports are normalized to the same absorbance as pure TiO$_2$ support at 800 nm. The absorbance of supported Rh catalysts are measured in diffuse-reflectance mode with an integrating sphere.](image)

**Figure 4.3.** UV-vis absorption spectra of Rh NCs in ethanol suspension (red), supported on Al$_2$O$_3$ (a), TiO$_2$ (b), CeO$_2$ (c), and SiO$_2$ (d, black) and the pure supports (blue). The spectra of Rh NC suspension, catalysts, and the pure TiO$_2$ and CeO$_2$ support are normalized to the maximum absorbance. The spectra of pure Al$_2$O$_3$ and SiO$_2$ supports are normalized to the same absorbance as pure TiO$_2$ support at 800 nm. The absorbance of supported Rh catalysts are measured in diffuse-reflectance mode with an integrating sphere.
Table 4.1. The composition of oxide supported Rh catalysts and the reaction rate in dark and under illumination with a mixture 40 ml min⁻¹ CO₂, 120 ml min⁻¹ H₂, and 40 ml min⁻¹ Ar. The reaction temperature is 350 °C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rh loading (wt%)</th>
<th>CH₄ production rate (μmol g⁻¹ s⁻¹)</th>
<th>Maximum AQE (and condition)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Thermal</td>
<td>2.8 W cm⁻² UV</td>
</tr>
<tr>
<td>Rh-s/TiO₂</td>
<td>6.0</td>
<td>40.4</td>
<td>150.0ᵇ</td>
</tr>
<tr>
<td>Rh-c/TiO₂</td>
<td>4.6</td>
<td>4.0</td>
<td>20.5</td>
</tr>
<tr>
<td>Rh-c/CeO₂</td>
<td>5.6</td>
<td>1.6</td>
<td>11.3</td>
</tr>
<tr>
<td>Rh-c/Al₂O₃</td>
<td>4.0</td>
<td>0.6</td>
<td>3.8</td>
</tr>
<tr>
<td>Rh-c/SiO₂</td>
<td>4.5</td>
<td>0.5</td>
<td>2.1</td>
</tr>
</tbody>
</table>

*a Reactant is a mixture of 50 ml min⁻¹ CO₂, 150 ml min⁻¹ H₂, and 50 ml min⁻¹ Ar. b Reaction rates limited by reactant transport (conversion of CO₂ > 15%).

Under illumination of UV or blue light, significant enhancements on the CH₄ production rates were observed for all the examined Rh catalysts, and a rate increase up to a factor of 34 was seen on Rh-c/Al₂O₃. Control experiments on pure CeO₂, Al₂O₃, and SiO₂ supports did not yield any detectable products under both dark and light conditions, while TiO₂ showed a small response to UV light with CO as the only product (<0.01 μmol g⁻¹ s⁻¹). These results prove that the activities for CH₄ production are from the Rh nanostructures. The reaction mechanism implies that the rate of CH₄ production from CHO dissociation also represents the rate of RDS. Therefore, the AQE can be calculated as the ratio between the photo-induced CH₄ production rate and the photon flux. Despite the lower magnitude of rate enhancement by light on Rh-c/TiO₂ (16-fold under 4.9 W cm⁻² blue light) than that on Rh-c/Al₂O₃, the AQE on Rh-c/TiO₂ reaches 34%, compared to the 4.2% AQE on Rh-c/Al₂O₃. Furthermore, the selectivity towards CH₄ of Rh-c/TiO₂ is >90% in dark and >95% under illumination, with CO as the only by-
product. This improvement of AQE by switching from Al₂O₃ to TiO₂ confirms the importance of support materials in plasmon-enhanced catalysis. The enhanced activities of Rh NCs on reducible TiO₂ and CeO₂ than on insulating Al₂O₃ and SiO₂ suggest that the chemical properties of support materials are more important than the charge transport properties in this reaction.

Rh spheres with 6.0 nm diameter supported on TiO₂ (Rh-s/TiO₂, Figure 4.4a) were further prepared to investigate the effects of nanostructure morphology on the activities in plasmon-enhanced CO₂ hydrogenation. The plasmonic resonance of small Rh spheres blue-shifts into the deep UV region and the peak cannot be observed in the UV-vis spectra. However, its relatively broad absorption feature also extends into the near UV and visible regions (Figure 4.4b) and responds well to our UV and blue LEDs.

**Figure 4.4.** (a) TEM image of Rh-s/TiO₂ catalyst after calcination in air at 350 °C. Scale bar: 50 nm. (b) UV-vis absorption spectra of Rh-s/TiO₂ (blue) and TiO₂ (black) measured by an integrating sphere and Rh spheres measured in an ethanol suspension (red).
By shrinking the size of the Rh nanostructures, the higher portion of exposed surface Rh atoms and low-coordinated edge and corner sites in Rh-s/TiO$_2$ enabled a tenfold increase in thermal reaction rates. More importantly, the reaction rates for Rh sphere catalysts are enhanced much more efficiently with light compared to that of the Rh NC catalysts. The AQE of Rh-s/TiO$_2$ at 350 °C reaches 349% and 293% under illumination of 0.95 W cm$^{-2}$ UV and blue light, respectively (Table 4.1). In fact, the reactions under the highest intensity UV and blue light suffer from strong reactant-transport limitation (conversion of CO$_2$ > 15%), which will be discussed in the next section. The highly efficient plasmon-enhanced reaction can be partially attributed to the increased number of active sites on small Rh spheres. A high number of active sites can form more critical CHO intermediates on the surface, thus leading to more empty states to accept photogenerated hot electrons and increase the efficiency. By carefully tuning the support and the morphology of plasmonic catalysts to generate highly active sites and facilitate charge transfers, the AQE of plasmon-enhanced catalysis can be significantly increased.

The change of support material and morphology of Rh nanostructures also affect the product selectivity of CO$_2$ hydrogenation. Under both light and dark conditions, the selectivity towards CH$_4$ is higher than 98% on the Rh-s/TiO$_2$ catalyst (Figure 4.5a) with CO as the main by-product. Trace amount of ethylene and methanol (selectivity smaller than 0.02%) is also observed. However, on the Rh-c/Al$_2$O$_3$ catalyst, selectivity towards CH$_4$ for the thermal reaction is only ~55%. This difference could be due to the higher portion of edge and corner sites on small Rh spheres, which may be more selective for CH$_4$ production.
Figure 4.5. Selectivity towards CH$_4$ in dark (black squares) and under 2.8 W cm$^{-2}$ UV (red circles) and blue (blue triangles) illumination as a function of reaction temperature on TiO$_2$ supported Rh spheres (a) and Al$_2$O$_3$ supported Rh cubes (b).

4.3.2 Intensity-dependent reaction rates

The dependence of reaction rates and AQE, plotted in logarithmic scale, on the intensity of UV and blue light at different temperatures is illustrated in Figure 4.6. With increasing intensities of both UV and blue light, a superlinear dependence of reaction rates ($R_{\text{photo}} \propto I^n, n > 1$) was observed at all temperatures, which is a signature of hot-electron-mediated chemical reactions.$^{54-55, 89, 107}$ Due to the high conversion of reactants and the associated transport limitation, the reaction rates level off with further increases of light intensity.
Figure 4.6. Intensity-dependent reaction rates under UV (a) and blue illumination (b) at 150 (black squares), 250 (cyan circles), 300 (blue up triangles) and 350 °C (red down triangles). Intensity-dependent apparent quantum efficiency under UV (c) and blue illumination (d) at different temperature. The reactant feedstock is 50 ml min$^{-1}$ CO$_2$, 150 ml min$^{-1}$ H$_2$, and 50 ml min$^{-1}$ Ar.

The light intensity at which the plateau begins decreases with increasing reaction temperature. For instance, under both UV and blue illumination, plateaus of rates start at
~2 W cm\(^{-2}\) at 300 °C and ~1 W cm\(^{-2}\) at 350 °C. At temperatures of 150 and 250 °C, plateaus of rates begin at ~4.5 and 3.5 W cm\(^{-2}\) under blue illumination, respectively, while absent under UV illumination up to 2.9 W cm\(^{-2}\). The reactions level off at slightly higher rates with increase of reaction temperature and independent of light wavelength, further supporting that it is limited by the reactant transport.

The AQEs of the plasmon-enhanced reaction initially increase with increasing light intensity, resulted from the compelling superlinear relationship between reaction rate and light intensity. Due to the plateaus of reaction rates, the AQE drops at high light intensity since more photons cannot further accelerate the reaction. The AQE also increases with increasing reaction temperature, indicating the collaborative relationship between light and heat in plasmon-enhanced catalysis. With the synergetic effects of light and heat, a maximum AQE of 349% was achieved at 350 °C under 0.95 W cm\(^{-2}\) UV illumination. The AQEs under blue light are slightly smaller than that under UV light at the same reaction temperature and light intensity.

Although the TiO\(_2\) support can also absorb UV light\(^{38, 94}\), the major contribution of the photo-induced reactions should not result from the bandgap excitation of TiO\(_2\). First, the super-linear relationship between the reaction rate and light intensity in this study is distinctly different from the typical sub-linear relationship of semiconductor photocatalysts\(^{54-55, 97}\). Second, the AQEs under blue light are only slightly smaller than that under UV light at the same intensity. If the catalytic activities of Rh-s/TiO\(_2\) under light results from the light absorption by TiO\(_2\), the activities under blue light (2.7 eV) should be much smaller than that under UV light due to the inadequate energy for the
bandgap excitation of TiO$_2$ (3.2 eV)$^{94}$. Third, the activities of plasmonic Rh NCs supported on optically inert Al$_2$O$_3$ and SiO$_2$ also suggest the active role of Rh nanostructures in the light absorption process. The photocatalytic activities of previously reported CO$_2$ hydrogenation on TiO$_2$ supported oxidized Rh under a mercury lamp were attributed to the bandgap excitation of TiO$_2$ but the main product was CO.$^{131-132}$ Therefore, the high AQE observed on the Rh-s/TiO$_2$ catalyst cannot be attributed to the photocatalytic activities of TiO$_2$ support.

4.3.3 Reaction order of thermo- and photo-reactions

To investigate the role of light in plasmon-enhanced catalysis, reaction orders on CO$_2$ and H$_2$ were measured under dark and light conditions. A thin layer of Rh-s/TiO$_2$ catalyst (~0.6 mm) was used in the measurements to minimize the temperature difference between top and bottom parts of the catalyst bed and the reaction conditions were tuned to have similar conversion of reactants in dark and under illumination. The results are plotted in double logarithmic scales (Figure 4.7a, b) and fitted with the following equation to extract the reaction order:

$$R = k p_{CO2}^x p_{H2}^y$$

where $p_{CO2}$ and $p_{H2}$ are the partial pressure of CO$_2$ and H$_2$, and $x$ and $y$ are the reaction order of CO$_2$ and H$_2$, respectively.
Figure 4.7. Reaction rate as a function of CO$_2$ (a) and H$_2$ partial pressure (b) in dark at 200 (black squares) and 350 °C (red up triangles) and under 3.2 W cm$^{-2}$ blue illumination at 200 °C (blue circles) on the Rh-s/TiO$_2$ catalyst. Reaction rate as a function of CO$_2$ (c) and H$_2$ partial pressure (d) in dark at 300 (black squares) and 350 °C (blue up triangles) and under 2.84 and 2.37 W cm$^{-2}$ blue illumination at 300 (red circles) and 350 °C (magenta down triangles) on the Rh-c/Al$_2$O$_3$ catalyst.

It shows that the reaction rates under both light on and off conditions are almost insensitive to the partial pressure of CO$_2$. By contrast, the reaction rates show a strong
dependence on the partial pressure of H$_2$. The reaction orders on H$_2$ are 0.48 for the dark reaction at 350 °C and -1.74 for the reaction under 3.2 W cm$^{-2}$ blue light at 200 °C. It is obvious that AQE highly depends on the composition of gas feedstock. This positive dependence of thermal reaction and negative dependence of photo-reaction on the partial pressure of H$_2$ were also observed on the Rh-c/Al$_2$O$_3$ catalyst (Figure 4.7c, d), suggesting that this trend is not support- and morphology-specific.

To reveal possible mechanism for the change of reaction order on H$_2$ by light, we derived the rate equation based on the elementary steps and RDS of CO$_2$ hydrogenation. Since CO and H were identified to be the dominant surface intermediates on Rh catalysts under reaction condition by *in-situ* IR measurements,$^{122, 124}$ only the surface coverage of CO and H intermediates were considered in the rate equation. Since AQE depends on the composition of reactant feedstock, we first assume that the enhancement to the rate constant of RDS by light does not depend on the reactant feedstock. The elementary steps through the CH-O dissociation mechanism is shown as following:

1. CO$_2$(g) + 2 * $\rightleftharpoons$ CO* + O*
2. H$_2$(g) + 2 * $\rightleftharpoons$ 2 H*
3. CO* + H* $\rightleftharpoons$ CHO* + *
4. CHO* + * $\rightleftharpoons$ CH* + O*
5. O* + H* $\rightleftharpoons$ OH* + *
6. OH* + H* $\rightarrow$ H$_2$O(g) + 2 *
7. CH* + H* $\rightleftharpoons$ CH$_2$* + *
8. CH$_2$* + H* $\rightleftharpoons$ CH$_3$* + *
9. CH$_3$* + H* $\rightarrow$ CH$_4$(g) + 2 *
Since CH-O dissociation (step 4) has been found to be the RDS, the rate equation can be written as:

\[
R = \frac{(K_1K_3K_5k_4k_6/2)^{1/2}K_2^{3/4}}{1 + K_2^{1/2}P_{H_2}^{1/2} + (K_1K_2^{1/2}K_5k_6/2K_3k_4)^{1/2}P_{CO_2}^{1/2}P_{H_2}^{3/4}} \]

where \( K_i \) and \( k_j \) represent the equilibrium constant and the rate constant of step \( i \) and \( j \), respectively. In this case, the most negative possible reaction order on \( H_2 \) is -0.25, which can be as negative as the observed -1.74 for the photoreaction. It is possible that light changes the RDS to different steps, thus affecting the reaction order. With the assumption of CHO formation (step) as the RDS, the rate equation can be written as:

\[
R = \frac{(K_1K_3k_6/2)^{1/2}K_2^{3/4}}{1 + K_2^{1/2}P_{H_2}^{1/2} + (K_1K_2^{1/2}K_3k_6/2k_3)^{1/2}P_{CO_2}^{1/2}P_{H_2}^{3/4}} \]

The most negative possible reaction order on \( H_2 \) in this case is still -0.25. Since the order of CO hydrogenation and C-O bond breaking is still under debate, we also derived rate equations with other possible reaction mechanisms. The elementary steps through a C-O dissociation mechanism is:

1. \( CO_{2(g)} + 2^* \rightarrow CO^* + O^* \)
2. \( H_{2(g)} + 2^* \rightarrow 2 H^* \)
3. \( CO^* + ^* \rightarrow C^* + O^* \)
4. \( C^* + H^* \rightarrow CH^* + ^* \)
5. \( O^* + H^* \rightarrow OH^* + ^* \)
6. \( OH^* + H^* \rightarrow H_2O_{(g)} + 2^* \)
7. \( CH^* + H^* \rightarrow CH_2^* + ^* \)
8. \( CH_2^* + H^* \rightarrow CH_3^* + ^* \)
9. \( CH_3^* + H^* \rightarrow CH_4(g)_{(g)} + 2^* \)
With C-O dissociation (step 3) as the RDS, the rate equation is:

\[
R = \frac{(K_1K_2K_5^2k_6/2)^{1/2}}{\left[1 + K_2^{1/2}P_{H_2}^{1/2} + (K_1K_2K_5^2/2k_3)^{1/2}P_{CO2}^{1/2}P_{H_2}^{1/2}\right]^{2}}P_{CO2}^{1/2}P_{H_2}^{1/2}
\]

The most negative possible reaction order on H$_2$ in this case is -0.5. With C hydrogenation (step 4) as the RDS, the rate equation is:

\[
R = \frac{(K_1K_2K_5^2k_6^2)^{1/3}K_2^{5/6}}{\left[1 + K_2^{1/2}P_{H_2}^{1/2} + (K_1^2K_5k_6/2K_3k_4)^{1/3}K_2^{1/6}P_{CO2}^{2/3}P_{H_2}^{1/6}\right]^{2}}P_{CO2}^{1/3}P_{H_2}^{5/6}
\]

The most negative possible reaction order on H$_2$ in this case is -0.17. The elementary steps through a CH$_2$O dissociation mechanism is:

1. CO$_2$(g) + 2 * $\rightleftharpoons$ CO* + O*
2. H$_2$(g) + 2 * $\rightleftharpoons$ 2 H*
3. CO* + H* $\rightleftharpoons$ CHO* + *
4. CHO* + H* $\rightleftharpoons$ CH$_2$O* + *
5. O* + H* $\rightleftharpoons$ OH* + *
6. OH* + H* $\rightarrow$ H$_2$O$_{(g)}$ + 2 *
7. CH$_2$O* + * $\rightleftharpoons$ CH$_2$* + O*
8. CH$_2$* + H* $\rightleftharpoons$ CH$_3$* + *
9. CH$_3$* + H* $\rightarrow$ CH$_4$(g) + 2 *

With CH$_2$O dissociation (step 7) as the RDS, the rate equation is:

\[
R = \frac{(K_1K_3K_4K_5k_6k_7)^{1/2}K_2}{\left[1 + K_2^{1/2}P_{H_2}^{1/2} + (K_1K_5k_6/2K_3K_4k_7)^{1/2}P_{CO2}^{1/2}\right]^{2}}P_{CO2}^{1/2}P_{H_2}
\]

The most negative possible reaction order on H$_2$ in this case is 0.
Based on the analysis above, the assumption that the enhancement to the rate constant of RDS by light does not depend on the reactant feedstock cannot result in reaction order on $H_2$ as negative as -1.74. Other effects should be involved in this process and lead to the observed reaction order on $H_2$.

4.3.4 Possible explanation of the observed high AQE and negative reaction order on $H_2$

Due to the fast recombination of hot electrons and holes in metal nanoparticles, the efficiency of hot-electron-driven processes, including charge transfer between plasmonic metal nanoparticles and adjunct semiconductor and plasmon-enhanced catalysis, is generally low. Although the efficiency of hot electrons from plasmonic Au nanoparticles transferring to nearby strongly coupled cadmium selenide (CdSe) nanorods could reach 24% through a direct interfacial process, it is still hard to explain the AQE of ~350% for plasmon-enhanced CO$_2$ hydrogenation observed here. It was also proposed that the excess energy of hot electrons after one round of reaction may re-emit as photons to be absorbed again and increase the AQE. This mechanism, however, may not explain the dependence of the efficiency on the composition of gas feedstock.

In plasmon-enhanced catalysis, reaction rate enhancement from the photo-induced hot electron transfer is sometimes difficult to discriminate from the photothermal effect. It was reported that light can locally heat the exposed top surface of an aqueous dispersion of plasmonic Au nanoparticles and create a temperature gradient towards the colder unilluminated part. The reaction temperature in our experiments was measured by a thermocouple embedded in the heating block of the reaction chamber, which may
not respond to local heating of the top surface of catalyst bed exposed to light. To probe the possible temperature gradient in the catalyst bed, we modified the reactor and used two external thermocouples to measure the temperatures of top and bottom surface of catalyst bed (Figure 4.1).

A thin layer of Rh-s/TiO₂ catalyst was loaded into the catalyst cup on a piece of quartz wool as the holder. The tip of one thermocouple was right below the top surface of catalyst bed and the other one was touching the bottom surface, measuring the temperature of top (T₁) and bottom surface (T₂) of the catalyst bed. The temperature measured by the internal thermocouple in the reaction chamber is denoted as Tᵢ. The equivalent reaction temperature (Tₑ) based on the T₁, T₂ and the activation energy of CO₂ hydrogenation (Eₐ) was calculated using

\[
\frac{-E_a}{e^{RT_e}} = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} e^{\frac{-E_a}{RT}} dT
\]

Preliminary measurements of top and bottom surface temperature of a Rh-s/TiO₂ catalyst bed with flowing 40 ml min⁻¹ Ar and 60 ml min⁻¹ H₂ and under different setting temperature and light intensity are shown in Figure 4.8. Because the heating block is at the bottom of the catalyst cup and the cool reactant gases go through the catalyst bed from top to bottom, the temperature of top surface is lower than that of the bottom surface, which are both lower than the internal temperature of heating block in dark conditions. With the increase of light intensity, both top and bottom surface temperatures of catalyst bed increase and the top surface temperature increases faster due to top-illumination configuration of the reactor. It is worth noting that the direction of
temperature gradient is reversed at high light intensity compared to that in dark conditions. With a setting temperature of 200 °C (equal to the temperature measured by the internal thermocouple), the top and bottom surface temperature in dark were 170 and 180 °C, respectively. Under 4.74 W cm\(^{-2}\) blue illumination, the top and bottom surface temperature were 297 and 223 °C, respectively. These results confirm that there is a difference between the top and bottom surface temperature of catalyst bed and the temperature measured by the internal thermocouple of the reaction chamber. Therefore, photothermal heating of catalyst bed, which was not compensated by the temperature controller of our system, indeed contributed to the rate enhancement by light.

**Figure 4.8.** (a) Temperature measured by external thermocouples as a function of temperature measured by the internal thermocouple in dark (black squares) and under 1.18 (red circles) and 4.74 W cm\(^{-2}\) (blue triangles) blue illumination. Solid and open symbols are top and bottom surface temperatures, respectively. The dotted line is where the temperature of internal thermocouple equals to that of external thermocouples. (b) Temperature measured by external thermocouples as a function of blue light intensity with temperature measured by the internal thermocouple set at 200 (black squares) and 350 °C (red circles).
The top and bottom surface temperatures of the catalyst bed were also measured with different H\textsubscript{2} partial pressure to investigate the effect of local heating on the reaction order measurements. As shown in Figure 4.9a, the surface temperature of catalyst bed under 3.20 W cm\textsuperscript{-2} blue light decreases with increasing H\textsubscript{2} partial pressure, which could be attributed to the high thermal conductivity of H\textsubscript{2} (230.4 mW m\textsuperscript{-1} K\textsuperscript{-1} at 400 K) compared to Ar (22.6 mW m\textsuperscript{-1} K\textsuperscript{-1} at 400 K). The gaseous mixture with higher H\textsubscript{2} partial pressure can cool the catalyst bed under light more efficiently and lead to a lower temperature.

Since the actual temperature of catalyst bed is different from the setting temperature of the temperature controller, the activation energy of 70 kJ mol\textsuperscript{-1}, calculated using the setting temperature, may not be accurate. However, the calculation of equivalent temperature is insensitive to the value of activation energy. For example, the top and bottom surface temperatures with setting temperature of 200 °C and 3.20 W cm\textsuperscript{-2} blue illumination are 263 and 210 °C, respectively. The equivalent temperature calculated with activation energy of 60, 70, and 80 kJ mol\textsuperscript{-1} is 239.3, 239.8, and 240.3 °C, respectively. The equivalent temperature can be calculated first with an activation energy of 70 kJ mol\textsuperscript{-1}. The equivalent temperature can then be used to calculate the real activation energy with the Arrhenius equation.

The calculated equivalent temperatures and measured photoreaction rates at different H\textsubscript{2} partial pressure are shown in Figure 4.9b. The fast decrease of reaction rate with increasing H\textsubscript{2} partial pressure (negative reaction order on H\textsubscript{2}) can be partially explained by the change of catalyst temperature. After correcting the reaction rate to the
same temperature, the reaction order on H$_2$ could be in the reasonable range derived from the rate equation.

The observed high AQE of CO$_2$ hydrogenation on the Rh-s/TiO$_2$ catalyst and the negative reaction order on H$_2$ could both be partially attributed to the local heating effect of light, which was not measured by the internal thermocouple of reaction chamber located in the heating block. Quantitative evaluation of the reaction rate enhancement from photothermal and hot-electron-driven contributions requires simultaneous measurements of the reaction rates and temperature profile of the catalyst bed, which is achievable on our modified reactor setup.

Figure 4.9. (a) Temperature measured by external thermocouples as a function of H$_2$ partial pressure with a H$_2$ and Ar mixture of a fixed 100 ml min$^{-1}$ total flow rate. The setting temperature is 200 °C and the blue light intensity is 3.20 W cm$^{-2}$. (b) Equivalent temperature (black squares) and reaction rate (red circles) as a function of H$_2$ partial pressure with a H$_2$ and Ar mixture of a fixed 100 ml min$^{-1}$ total flow rate. The equivalent temperature is calculated with an activation energy of 70 kJ mol$^{-1}$.
4.4 Conclusion and outlook

In conclusion, the morphology of plasmonic metal nanoparticles and catalyst support are important factors for the performance of plasmonic catalysts. A remarkably high AQE of up to 350% and negative reaction order on H₂ are observed in plasmon-enhanced CO₂ hydrogenation on a TiO₂ supported Rh sphere catalyst. The high reaction rate under light can be partially attributed to the local heating effect by light, as revealed by direct measurements of surface temperature of catalyst bed. However, the reaction rate increase due to heating can only account for roughly 50% of the observed value. The origin of the other 50% rate increase is still under investigation and possibly due to a hot-electron-mediated mechanism.

In the future, simultaneous measurements of reaction rates and temperature profile of catalyst bed is required to quantitatively evaluate the reaction rate enhancement from hot-electron-driven and photothermal contributions. It also emphasizes the importance of measuring the actual temperature of catalyst in experiments, which the community of plasmon-enhanced catalysis should be aware of. Although the local heating of catalyst bed complicates the research of plasmon-enhanced catalysis, it may be beneficial from the practical point of view. Locally heating the catalyst nanoparticles, where chemical reactions occur, but not the reactor by light could remedy the energy input and ease the thermal management of the reaction system.
Chapter 5: Photo-Enhanced Ammonia Synthesis on Promoted Ruthenium Catalysts

5.1 Introduction

Ammonia (NH\textsubscript{3}) is an important industrial chemical to produce fertilizers, nitric acid, and detergents and as a hydrogen carrier for fuel cells. Due to the strong nitrogen-nitrogen triple bond, nitrogen molecules (N\textsubscript{2}) is extremely hard to activate to form NH\textsubscript{3} through the Haber-Bosch process. A reaction temperature of higher than 500 °C is required to accelerate the reaction to practical rate. However, due to the exothermic nature of the reaction (N\textsubscript{2} + 3 H\textsubscript{2} → 2 NH\textsubscript{3}, ΔH° = −91.8 kJ mol\textsuperscript{-1}), a high reaction temperature is not favored from the thermodynamic point of view. Thus, a high pressure of ~200 atm is used to push the equilibrium towards the production of NH\textsubscript{3}.\textsuperscript{2} Despite being investigated for more than a century, developing high-performance catalysts for NH\textsubscript{3} synthesis that can be used at low temperature and low pressure still attracts a great interest of the research community.

Various strategies have been utilized to improve the activities of NH\textsubscript{3} synthesis catalysts, including alloying different metals, tuning catalyst supports and addition of promoters.\textsuperscript{2, 9-10, 30} Among them, alkali-metal-promoted Ru nanoparticles supported on basic oxides have been found to be highly active NH\textsubscript{3} synthesis catalysts. As discussed in Chapter 1, Ru nanoparticles could also absorb UV and visible light. It is interesting to investigate if light can be used to enhance the performance of Ru-based catalysts for NH\textsubscript{3} synthesis to allow for operation at low temperature and low pressure.
In this project, we prepare oxide-supported Ru catalysts by a one-step co-precipitation method (CP) and a two-step impregnation method (IM). The effects of mass loading of Ru, oxide supports, and promoters on the activities of photo-enhanced NH$_3$ synthesis are investigated. The activities of Rh-based catalysts, which have been shown to be photoactive catalysts for CO$_2$ hydrogenation in Chapter 3 and 4, for NH$_3$ synthesis are measured and compared to the Ru-based catalysts.

5.2 Experimental methods

5.2.1 Preparation of catalysts for NH$_3$ synthesis

The Ru/MgO (CP) catalyst with a nominal Ru loading of 2.5 wt% was prepared by a published co-precipitation method.$^{135}$ 19 mg ruthenium(III) chloride hydrate (RhCl$_3$·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 EG in a cleaned 20 ml glass vial and stirred in an oil bath at 110 °C for 2 h. The black reaction mixture was then cooled and a solution of KOH with stoichiometric molar ratio was added. The product was aged for 10 min and washed by DI-water for four times to remove K$^+$ and Cl$^-$ ions. The solid was dried at 120 °C for 5 h, calcined in air at 450 °C for 2 h, and reduced under H$_2$ at 450 °C for another 2 h. The Cs-promoted Ru catalyst, Ru-Cs/MgO (CP), was prepared by a wet impregnation method before the calcination of Ru/MgO (CP) using an ethanol solution of Cs$_2$CO$_3$ to achieve a molar ratio of Ru:Cs=1:2. The Ru/Al$_2$O$_3$ (CP) catalyst was prepared in similar manner, but commercial Al$_2$O$_3$ nanoparticles were added to the EG solution.
MgO supported Ru catalysts were also prepared by a two-step impregnation (IM) method, in which Ru nanoparticles were first synthesized by a polyol method and then impregnated on a commercial MgO support (US Research Nanomaterials, Inc, 99+%, 20 nm). 12.4 mg RuCl₃ hydrate and 7.2 ml EG were added to a cleaned 20 ml glass vial and stirred at RT to dissolve. After ~40 min, 54 mg PVP dissolved in 0.8 ml EG was added to the vial and the dark red to black solution was stirred in an oil bath at 180 °C for 1 h. The product was washed with DI-water/acetone for three times and impregnated on the MgO support. The catalyst, Ru/MgO (IM), was calcined in air at 450 °C for 2 h and reduced under H₂ at 450 °C for another 2 h. The Cs-promoted Ru catalyst, Ru-Cs/MgO (IM), was prepared by the same wet impregnation method to achieve a molar ratio of Ru:Cs=1:2. A Ru-Cs/TiO₂ (IM) catalyst was prepared by replacing MgO with TiO₂ (P25).

A Rh-Cs/MgO (IM) was prepared to compare with Ru-based catalysts. 25 mg PVP was dissolved in 5.6 ml EG in a 20 ml glass vial and stirred in an oil bath at 160 °C for 30 min. 12 mg 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 product was washed with DI-water/acetone for three times and impregnated on the MgO support, followed by calcining in air at 450 °C for 2 h and reducing under H₂ at 450 °C for another 2 h.

5.2.2 Catalytic measurements

The catalytic reaction was carried out on a custom-built gaseous reaction system as discussed in Chapter 3. 10–40 mg of catalysts were loaded in the catalyst cup held by a
stainless-steel mesh to fill a 4-mm height and 6-mm diameter catalyst cup and ensure complete absorption of light for the catalytic measurements. H₂ (UHP), N₂ (UHP) and Ar (UHP) were obtained from Airgas. The catalysts were conditioned under 15 ml min⁻¹ N₂, 45 ml min⁻¹ H₂, and 15 ml min⁻¹ Ar at 400 °C for 2 h before catalytic measurements. To avoid the interference of water to NH₃ during the measurements of mass spectrometer, the filament setting was changed to 18 V and 100 μA. The 17 amu channel was used to quantify the concentration of NH₃. A standard NH₃ sample (100 ppm in air, GASCO) was used to calibrate the relative responsivity of NH₃ and N₂. For each temperature and light intensity condition, at least 30 min elapsed before reaching steady state and seven sequential measurements were made to determine the steady-state concentration of each gas and the associated reaction rates and uncertainties.

5.2.3 Material characterization

TEM images were collected by a FEI Tecnai G² Twin operating at 200 kV. The TEM samples were prepared by dispersing the catalysts 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).

5.3 Results and discussion

5.3.1 Morphology and optical properties of Ru-based catalysts

The morphology of Ru-based catalysts prepared by different methods and different mass loadings were characterized with TEM. 1~2 nm Ru nanoparticles were
Figure 5.1. TEM images of Ru-Cs/MgO (CP) with Ru mass loadings of 2.5 (a) and 5.0 wt% (b) and 2.5 wt% Ru-Cs/MgO (IM) catalysts (c). (d) Diffuse-reflectance spectra of 2.5 wt% Ru-Cs/MgO (CP, black) and MgO (red). The absorbance is converted to Kubelka-Munk intensity.

observed in the 2.5 wt% Ru-Cs/MgO (CP) catalyst (Figure 5.1a), indicating the well dispersed small catalytic nanoparticles on the MgO support. With the increase of Ru
loading to 5.0 wt% in the co-precipitation method, the Ru nanoparticles grown into larger size of 2~7 nm (Figure 5.1b). However, the Ru nanoparticles had diameters of 3~10 nm synthesized by the impregnation method (Figure 5.1c). These results show that the co-precipitation method can produce fine Ru nanoparticles, which is favored as catalysts for NH₃ synthesis.

The optical properties of Ru-based on catalysts and pure MgO support were measured by diffuse-reflectance UV-vis spectroscopy (Figure 5.1d). Pure MgO support did not show any absorption in the measured 270~800 nm wavelength range, due to its large band gap. Ru-based catalysts prepared by different methods showed similar absorption spectra: the absorption decreased with increasing light wavelength. The absorption of light in the UV and visible regions can be attributed to the properties of Ru nanoparticles, which may exhibit photo-activities in NH₃ synthesis.

5.3.2 Catalytic activities of Ru- and Rh-based catalysts in photo-enhanced NH₃ synthesis

The catalytic activities of Ru- and Rh-based catalysts in dark and under UV and blue light illumination in NH₃ synthesis were characterized in our reactor system and summarized in Table 5.1. The 2.5 wt% Ru-Cs/MgO (CP) showed the highest catalytic activities in dark condition. Upon illumination of UV and blue light, an enhancement on the reaction rates was observed. The larger Ru nanoparticle size in the 5.0 wt% Ru-Cs/MgO (CP) catalyst leaded to lower activities, which was also observed in the case of promoted Ru catalyst prepared by an impregnation method. The addition of Cs promoter increased the reaction rate of MgO supported Ru catalyst with a factor of ~20 in both
dark and light conditions, proving the importance of promoter in catalytic reactions. It has been proposed that Cs promoter could generate highly active sites in the Ru/MgO system and accelerate NH₃ synthesis.\(^{136}\)

Cs-promoted Ru nanoparticles on a basic CaO support also showed catalytic activities of NH₃ synthesis, but inferior to the Ru-Cs/MgO catalyst. It is interesting to note that acidic TiO₂, which can be used as a photocatalyst, supported Ru nanoparticles are inactive for NH₃ synthesis from N₂. Rh nanoparticles, which have been used in plasmon-enhanced CO₂ hydrogenation, are inactive for NH₃ synthesis. Since the RDS of NH₃ synthesis on Ru catalysts has been identified to be the dissociatively adsorption of N₂,\(^{10}\) the basic supports and electron-rich Cs promoter should facilitate the breaking of nitrogen-nitrogen triple bond, which could be attributed to the electron transfer from the support and promoter to Ru nanoparticles. These experiments also show the importance of the choice of metals and the support materials in design of catalysts for NH₃ synthesis.

| Table 5.1. | The composition of Ru- and Rh-based catalysts, the reaction rate in dark and under illumination, and the activation energy of thermal reactions. The experiments are carried out with a mixture of 15 ml min⁻¹ N₂, 45 ml min⁻¹ H₂, and 15 ml min⁻¹ Ar, and the reaction temperature is 400 °C. |
|---|---|---|
| Metal loading (wt%) | NH₃ production rate (μmol g⁻¹ s⁻¹) | Activation energy (kJ mol⁻¹) |
| | Thermal | 2.84 W cm⁻² UV | 4.85 W cm⁻² blue | |
| Ru-Cs/MgO (CP) | 2.5 | 0.39 | 1.5 | 1.5 | 126±1 |
| Ru-Cs/MgO (CP) | 5.0 | 0.15 | - | 0.46 | 125±2 |
| Ru/MgO (CP) | 2.5 | 0.015 | 0.085 | 0.12 | 128±2 |
| Ru/Al₂O₃ (CP) | 5.0 | 0.0008 | - | 0.040 | - |
| Ru-Cs/MgO (IM) | 2.5 | 0.046 | 0.085 | 0.18 | 0.39 | 132±6 |
| Ru-Cs/CaO (IM) | 2.5 | 0.0031 | 0.0061 | 0.028 | - | 125±15 |
| Ru-Cs/TiO₂ (IM) | 2.5 | Inactive | - | - | - | |
| Rh-Cs/MgO (IM) | 2.5 | Inactive | - | - | - | |
5.3.3 Intensity-dependent reaction rates

Since the 2.5 wt% Ru-Cs/MgO (CP) catalyst exhibited the best catalytic activities for NH₃ synthesis, we further investigated the dependence of reaction rates on light intensity. A thin layer of catalyst was loaded in the reaction chamber to minimize the thermal gradient in the catalyst bed. As shown in Figure 5.2, the reaction rates monotonically increase with increasing light intensity at 300, 350 and 400 °C. However, a decrease of reaction rate is observed when the light intensity is higher than 3.4 W cm⁻² at 450 °C. This decrease of reaction rate contradicts the hot-electron-mediated mechanism, since more photo-generated hot electrons should help break nitrogen-nitrogen triple bond at higher rate.

![Figure 5.2](image_url)

**Figure 5.2.** NH₃ production rate as a function of blue light intensity at 450 (black squares), 400 (red circles), 350 (blue up triangles) and 300 °C (yellow down triangles) on a thin layer of 2.5 wt% Ru-Cs/MgO (CP) catalyst loaded at the bottom of the catalyst cup.
We propose two possible explanations for the decrease of reaction rate at high light intensity. The first explanation is the local heating of catalyst bed by light as observed in Chapter 4. Although the reaction chamber was set at 450 °C during the experiments, the top surface of catalyst bed could be heated to a higher temperature. Since a high reaction temperature decreases the equilibrium conversion towards NH₃, the observed decrease of reaction rate could be limited by the thermodynamics of the reaction. The other explanation is that light induces desorption of surface intermediates. It has been reported that Ru catalysts are poisoned by adsorbed H in NH₃ synthesis. The photo-induced desorption of H could create more empty active sites to increase the reaction rate at low light intensity. However, at high light intensity, the photo-induced desorption is too strong and the reaction is starved for H or other reaction intermediates, lowering the reaction rate. To discriminate these two effects, direct measurements of catalyst temperature need to be carried out.

5.4 Conclusion and outlook

The highly active Cs-promoted Ru supported on MgO catalyst in thermocatalytic NH₃ synthesis from N₂ and H₂ shows an enhancement on reaction rate under illumination of UV and blue light. The activities in both dark and light conditions depend on the choice of catalytic metal, catalyst support, and promoter. A decrease of reaction rate using the Ru-Cs/MgO (CP) is observed when the blue light intensity is higher than 3.4 W cm⁻² at 450 °C.

To reveal the mechanism of rate enhancement by light, the temperature profile of Ru catalysts under illumination needs to be measured to estimate the contribution from
photothermal effect. The surface coverages of reaction intermediates during reaction should be measured by operando IR spectroscopy to investigate the effect of light on the surface coverage. Isotopic exchange of $^{14}\text{N}_2$ and $^{15}\text{N}_2$ could help discriminate the effect of light on the RDS of NH$_3$ synthesis on Ru catalysts.
Chapter 6 : Conclusion and Outlook

In this dissertation, synthetic methods for monodispersed Rh nanostructures with tunable plasmonic properties in the UV and visible regions are developed, and their activities of plasmon-enhanced catalysis in CO$_2$ hydrogenation are investigated. Rh nanocubes with unprecedently large sizes are synthesized by unseeded and seeded slow-injection methods to solve the paradox between minimizing nucleation and increasing Rh supply. The Rh nanocubes with tunable plasmonic properties in the UV region are ideal platform to investigate UV plasmonics.

Plasmonic Rh catalysts are prepared by impregnating Rh nanocubes on an inert Al$_2$O$_3$ support. The catalytic activities and selectivity of Rh catalysts for plasmon-enhanced CO$_2$ hydrogenation are measured on a home-built photoreactor under UV and blue illumination. Light not only enhances the production rate of CH$_4$, but also alters the product selectivity from equal production of CH$_4$ and CO in dark to almost exclusive production of CH$_4$ under illumination. The selective enhancement of CH$_4$ production can be attributed to the selective activation of reaction intermediate between competing reaction pathways, which is supported by DFT calculation.

By replacing Al$_2$O$_3$ with TiO$_2$ support and tuning the morphology of Rh nanostructures, an apparent quantum efficiency of 350% is observed in CO$_2$ hydrogenation under UV light. This significant reaction rate enhancement by light can be partially attributed to local heating of catalyst, which is probed by directly measuring the catalyst temperature with external thermocouple but not probed by the thermocouple in
the reaction chamber. These results emphasize the importance of accurate temperature measurements in study of plasmon-enhanced catalysis.

Promoted Ru catalysts are prepared and investigated for photo-enhanced NH$_3$ synthesis from N$_2$ and H$_2$. Although the Ru nanoparticles are not resonant with light from the UV and blue LEDs, reaction rates exhibit enhancements upon light illumination. Strong dependences of catalytic activities on the size of Ru nanoparticles, the catalyst support, and the promoter are observed in NH$_3$ synthesis. Decrease of reaction rate with increasing light intensity at high temperature is observed, but the mechanism needs further exploration.

Future work of plasmon-enhanced catalysis should involve five major parts. First, simultaneous measurements of reaction rates and temperature profile of catalyst bed can help quantify the contribution of reaction rate enhancement from hot-electron-driven reaction and photothermal effect. A uniform temperature gradient is proposed in this dissertation, but more accurate description of the temperature profile of catalyst bed needs to be developed or simulated numerically. Second, the mechanism of plasmon-enhanced catalysis at molecular level should be developed. The elementary steps of plasmon-enhanced catalysis, especially the generation of hot electrons in plasmonic metal nanoparticles, transfer of hot electrons from metal nanoparticles to adsorbates, and hot-electron-induced surface reaction, can be studied by ultra-fast spectroscopy to obtain the time scale and efficiency of these steps. With understandings of these processes, the design principles of plasmonic catalysts can be established. Third, the plasmonic properties of multi-metallic nanoparticles should be investigated. Our work discussed in
this dissertation focuses on mono-metallic plasmonic catalysts. Synthesizing alloys or ordered nanostructures with multiple metallic components can be a promising strategy to design high-performance plasmonic catalysts. Fourth, the efficacy of plasmon-enhanced catalysis in other important chemical reactions should be investigated, such as direct CO\textsubscript{2} hydrogenation to olefins and liquid fuels, catalytic CH\textsubscript{4} conversion, and degradation of organic pollutants. Fifth, photoreactors suitable for large-scale operation should be designed for the implementation of plasmon-enhanced catalysis in industrial processes.

In plasmon-enhanced catalysis, light and thermal energy can work cooperatively to improve the activities and selectivity of chemical reaction. This unique advantage could remedy the energy input of conventional thermocatalytic reaction and mitigate side-reactions. With abundant sunlight resources and advances of efficient artificial light sources, plasmon-enhanced catalysis is a promising strategy to achieve the ultimate goals of operating chemical reactions under mild conditions and with exclusive formation of desired products.
Appendix A: Understanding the discrepancy between the quality and yield in the synthesis of carbon nanotubes

The content of this appendix is adapted from our publication (Nano Research, 2015, 8(1): 296-302).

A.1 Introduction

Carbon nanotubes (CNTs) have attracted great interests because of their excellent thermal, optical, electrical, and mechanical properties. These merits, which require high-quality CNTs in most cases, make them as promising materials in many applications, such as high strength composites, nanoelectronics, catalysis and energy-storage devices. As a consequence, high-yield synthesis of high-quality CNTs is important to the development of CNT-based products. Chemical vapor deposition (CVD) is considered the most suitable method for mass production of CNTs. Multi-walled carbon nanotubes (MWNTs) with more than 6 graphene layers can be synthesized by CVD method with carbon yield, defined as the weight of produced carbon over that of the catalyst, more than 1000%. But these CNTs usually have high defect density and lose the excellent properties expected from ideal nanotube structures. In contrast, single-walled carbon nanotubes (SWNTs) and few-walled carbon nanotubes (FWNTs, with 2-5 graphene layers) have low defect density and resulting excellent properties, but the carbon yield is unsatisfied for industrial practice. Understanding the discrepancy between quality and yield in CNT synthesis is an important step toward synthesis of CNTs with both high yield and high quality.
In this project, we aim to understand the differences in their yield for MWNTs and FWNTs. Usually they are synthesized by different catalyst and precursor combinations, which creates difficulties in identifying the reasons behind their differences in quality and yield.\textsuperscript{146-148} Herein, we design a system to synthesize MWNTs and FWNTs by the same catalyst and precursor combination, but only varying the CNT growth temperature. This system involves FeMgAl layered double hydroxides (LDHs) as catalyst and ethanol as carbon feedstock. We find that low-quality MWNTs are synthesized with high yield at low growth temperature, while high-quality FWNTs form with low yield at high growth temperature. We are able to understand the reasons for the low yield in the synthesis of FWNTs and modify the catalyst to improve the yield of high-quality FWNTs. We believe this new understanding will make the production of high-quality FWNTs more economical for large scale applications.

A.2 Experimental methods

A.2.1 Synthesis of LDH catalysts

Fe(NO$_3$)$_3$·9H$_2$O and Al(NO$_3$)$_3$·9H$_2$O were purchased from Fisher. Mg(NO$_3$)$_2$·6H$_2$O and Na$_2$WO$_4$·2H$_2$O were purchased from Acros. Urea was purchased from Alfa Aesar. All reagents were used as-received without any treatment.

The Fe-based LDH was prepared by a modified urea assisted co-precipitation method.\textsuperscript{149-150} Fe(NO$_3$)$_3$·9H$_2$O (2 mmol), Mg(NO$_3$)$_2$·6H$_2$O (10 mmol), Al(NO$_3$)$_3$·9H$_2$O (5 mmol) and urea (250 mmol) were dissolved in 80 mL DI-water. The solution was refluxed for 12 h under stirring and then kept at 90°C for another 12 h without stirring. The suspension was then filtered and washed with copious DI-water until neutral
condition. The collected solid product was freeze dried and milled into powder as catalyst. The Fe-W-based LDH was prepared by the same method but also dissolving Na$_2$WO$_4$·2H$_2$O (1 mmol) in the solution.

**A.2.2 Growth of CNT with CVD method**

CNT synthesis was carried out in a fused quartz tube inserted in a tube furnace. A photograph of the CVD system is shown in Figure A.1. Ethanol was introduced by passing an Ar flow through an ethanol bubbler held at room temperature (23 °C). Typically, 50 mg catalyst was loaded in a porcelain boat and sealed into the quartz tube. The system was heated to 600 °C under an Ar atmosphere at a flow rate of 250 ml/min and then reduced under a H$_2$ flow (80 ml/min) for 10 min. After being heated to the CNT growth temperature under an Ar flow, the system was kept under a H$_2$ (80 ml/min) and Ar/ethanol (250 ml/min) flow for the desired growth duration, followed by being cooled down under an Ar atmosphere.

**A.2.3 Material characterization**

The phase and crystallinity of catalysts was characterized by a Panalytical X’Pert PRO MRD HR X-ray diffraction (XRD) system at 45 kV and 40 mA with Cu Kα radiation. The Brunauer–Emmett–Teller (BET) specific surface area of catalysts was measured by N$_2$ adsorption at liquid N$_2$ temperature using a Micromeritics Tristar 3000 analyzer. The calcination process of catalysts was monitored through thermogravimetric analysis (TGA) with a TA instrument SDT2960 under a N$_2$ flow with a heating rate of 10 °C/min from room temperature to 800 °C. The morphology of as-grown CNTs was
Figure A.1. A photograph of CVD system for CNT growth.

characterized by a FEI Tecnai G² Twin TEM operating at 200 kV. Raman spectrum of CNT samples was done by Horiba Jobin Yvon LabRam ARAMIS using 633 nm He-Ne laser.

A.3 Results and discussion

A.3.1 Morphology and yield of CNTs

The XRD patterns and thermal behaviors of the LDH catalysts are shown in Figure A.2. The strong and symmetric features at around 11.6° and 23.5° are ascribed to the (003) and (006) diffraction peaks of the layered structure, suggesting a high degree of crystallization of the as-prepared LDH catalysts. TGA of the catalysts was carried out under an inert atmosphere. Weight loss was observed due to the removal of physically adsorbed H₂O and decomposition of CO₃²⁻ in the inter-layer galleries and OH⁻ within the
Figure A.2. The XRD patterns (a) and TGA curves (b) of the Fe-based and Fe-W-based LDH catalysts. TGA was carried out under a N$_2$ flow with a heating rate of 10 °C/min. Figures reproduced with permission from ref. 137, © 2015, Tsinghua University Press and Springer-Verlag Berlin Heidelberg.

brucite-like layers. The BET specific surface areas of the LDH catalysts were measured to be around 70 m$^2$/g.

CNTs were synthesized with Fe-based LDH catalyst and the growth temperature ranged from 700 to 1000 °C, typical temperature for CNT synthesis. After the in situ generation of Fe nanoparticles, the system was kept at the growth temperature for 40 min to synthesize CNTs.$^{151}$ Within this temperature range, CNTs have been obtained in all cases, while the carbon yield dropped from 120% at 700 °C to 10% at 1000 °C. Representative TEM images of CNTs grown at different temperature are shown in Figure A.3. With growth temperature below 800 °C, the products are MWNTs with 10-15 graphene layers and outer diameters around 20 nm. Their low-quality nature can be identified from the zoomed-in TEM images as their rough surfaces.
In contrast, the morphology of as-grown CNTs exhibits significant difference when growth temperature is above 850 °C. High-quality FWNTs with clean and smooth surfaces and uniform diameters are obtained with growth temperature between 850 and 1000 °C. These FWNTs have 2-4 layers of tubes and outer diameters around 4 nm.

To get more quantitative evaluation of the quality of the CNTs, Raman spectroscopy with an excitation wavelength of 633 nm was carried out on the as-grown samples without any post-synthesis purification. The representative spectrum is shown in Figure A.4a and all curves have been normalized to the G bands at ~1580 cm⁻¹. An obvious decrease in D band intensity, at ~1340 cm⁻¹, can be observed when the growth
temperature rise from 800 to 850 °C. The G/D ratio, defined as the ratio of G band intensity to D band intensity, increases from 2.3 to 15.5 as shown in Figure A.4b. These

Figure A.4. (a) Raman spectra of raw CNT samples grown for 40 min at 750, 800, 850, and 900°C with Fe-based catalyst. (b) G/D ratio of CNTs grown with Fe-based and Fe-W-based catalysts at different temperatures. (c) Growth temperature dependent carbon yield plot. The Raman spectra are normalized to G bands and the growth duration was 40 min for these experiments. Figures reproduced with permission from ref. 137, © 2015, Tsinghua University Press and Springer-Verlag Berlin Heidelberg.

results suggest a significant improvement in CNT quality with the increase of growth temperature, which is consistent with the transformation in CNT morphology from TEM measurement. The G/D ratio reaches the climax, 18.6, when the growth temperature further rises to 900 °C. The slight drop in G/D ratio with further increase of growth temperature can be explained by the adsorbed carbonaceous impurities on catalyst surfaces from the thermal decomposition, instead of catalytic decomposition, of ethanol. Therefore, high growth temperature, above 850 °C in the present system, is required for the synthesis of high-quality FWNTs.

However, the carbon yield of these high-quality CNT samples is low. As can be seen in Figure A.4c, a fast decline in carbon yield with increasing growth temperature is
observed. The carbon yield decreases by a factor of more than 10 at 1000 °C, when compared to yield of low-quality MWNTs grown at 700 °C. A clear discrepancy between CNT quality and carbon yield is observed in this system.

**A.3.2 Mechanism for low yield of high-quality CNTs**

The discrepancy between CNT quality and carbon yield is puzzling. Since from the point of view of reaction kinetics, high growth temperature, which is necessary to synthesize high-quality CNTs, should facilitate ethanol decomposition and increase the carbon deposition rate, leading to increased carbon yield. However, our observation contradicts this principle. Since the feeding rates of carbon precursor were kept the same for different growth temperature, this contradiction with reaction kinetics should come from the catalysts. Hence, to understand the discrepancy between CNT quality and carbon yield, two possible mechanisms have been proposed: 1) the amount of active metal nanoparticles at high growth temperature is smaller than the that at low growth temperature, leading to lower CNT growth rate at high temperature; 2) the catalyst is only active for a short period of time, lowering the overall carbon yield in the chosen growth duration.

To identify the reasons, CNT growth at 700, 850, and 950 °C for different growth duration was carried out and the results are plotted in Figure A.5. As we can see, the CNT growth rates at different temperatures are similar initially, but the carbon yield of samples grown at 950 °C levels off quickly at 15% after 5 min. Similarly, CNT growth stops after 20 min for samples grown at 850 °C. However, the carbon yield of samples grown at 700 °C linearly increases with growth duration until 60 min.
Interestingly, a recent study reported similar short catalyst lifetime in high-quality SWNT synthesis monitored by *in situ* thermogravimetric method. These results clearly suggest that the decreasing catalyst lifetime with increasing growth temperature is the main reason for the discrepancy between CNT quality and carbon yield.

With these results, we can speculate what happens during the CNT growth process: the active metal nanoparticles are in liquid phase or high-mobility solid phase according to the vapor-liquid-solid (VLS) mechanism for CNT and semiconductor nanowire growth. These nanoparticles may fuse into bigger particles via surface migration or Ostwald ripening, which are no longer active for CNT growth at certain temperature and cause growth termination. High growth temperature can facilitate this
Figure A.6. The TEM images of metal nanoparticles in CNT samples grown at 850 °C for 10 min (a) and 60 min (b) and at 950 °C for 3 min (c) and 60 min (d). Scale bar: 100 nm. Figures reproduced with permission from ref. 137, © 2015, Tsinghua University Press and Springer-Verlag Berlin Heidelberg.
aggregation process and lead to shorter catalyst lifetime. To prove this speculation, the size of metal nanoparticles in CNT samples grown at 850 and 950 °C with different growth duration was measured by TEM and representative images are shown in Figure A.6. As can be seen from the TEM images, the number of big nanoparticles increases with elongated growth duration. The size of metal nanoparticles increases slowly at 850 °C as quantitatively evidenced by their size distribution (Figure A.7a), which is consistent with the slow deactivation at this temperature. By contrast, big particles form shortly at 950 °C and the size distribution of metal nanoparticles after 5 min growth at this temperature is comparable to that after 60 min growth at 850 °C (Figure A.7), in agreement with the much faster deactivation of catalyst at 950 °C. This observation indicates that the deactivation of catalyst indeed comes from the aggregation of active metal nanoparticles.

Although lowering the growth temperature can elongate the catalyst lifetime, the improvement is limited due to the required minimum temperature to obtain high-quality CNTs. Other methods to suppress nanoparticle aggregation need to be developed to further elongate the catalyst lifetime. It has been reported that high melting-point metal, such as tungsten and molybdenum, can anchor active metal nanoparticles on catalyst surfaces by either forming alloy nanoparticles or constraining their movement.\textsuperscript{155-159} Therefore, we intercalated tungstate anions between the hydroxide layers to prepare FeMgAl-W LDH catalyst. CNT growth with this Fe-W-based LDH catalyst was carried out at 850 °C and 950 °C and the representative TEM images of these CNT samples are shown in Figure A.8a and b. High-quality FWNTs with smooth surfaces and high G/D
Figure A.7. Size distribution of active metal nanoparticles in CNT samples grown with different growth duration at 850 (c) and 950 °C (d). Figures reproduced with permission from ref. 137, © 2015, Tsinghua University Press and Springer-Verlag Berlin Heidelberg.

ratio were obtained (see Figure A.4b for Fe-W samples). More importantly, as shown in Figure A.8c, the catalyst lifetime of the Fe-W-based LDH is significantly elongated, leading to obvious improvement in carbon yield. When considering the cases with 40 min growth duration, the carbon yield of samples grown at 850 °C increases from 50% to 120% with the addition of tungsten, which is already comparable to the yield of low-quality MWNTs grown at 700 °C. This improvement is even more significant, from 15% to 80%, for the samples grown at 950 °C. Addition of tungsten in the catalyst is an effective method to elongate the catalyst lifetime and improve the yield of high-quality CNTs.
Figure A.8. Representative TEM images of CNTs grown for 40 min with Fe-W-based catalyst at 850 °C (a) and 950 °C (b). Scale bar: 100 nm, (inset: 20 nm). (c) Carbon yield evolution of CNT samples grown at 850 and 950 °C with Fe-based and Fe-W-based catalysts. Figures reproduced with permission from ref. 137, © 2015, Tsinghua University Press and Springer-Verlag Berlin Heidelberg.

A.4 Conclusion and outlook

In summary, low-quality MWNTs with high carbon yield can be synthesized at low growth temperature, while high-quality FWNTs with low yield can be synthesized at high growth temperature. The discrepancy between CNT quality and yield is proven to be originated from the aggregation of active metal nanoparticles and the resulting reduced catalyst lifetime at high growth temperature. By inclusion of tungsten in the catalyst to constrain the movement of metal nanoparticles, their aggregation can be suppressed to elongate the catalyst lifetime. The increased catalyst lifetime results in great improvement in the yield of high-quality FWNT, which is comparable to that of low-quality MWNTs. Based on the understanding of catalyst deactivation mechanism, other approaches to elongate the catalyst lifetime at high temperature, such as optimizing the gas feeding rates and catalyst composition, could also be developed. This understanding and the
demonstrated solution for low nanotube yield will make the large-scale production of high-quality CNTs more economical. It has both fundamental and practical importance to the research field.

Since the growth atmosphere is important to the synthesis of CNTs, further optimizations of the molar ratio between ethanol and H₂ could improve the quality and yield of CNTs grown with Fe-W-based LDH catalysts. The molar ratio between Fe and W in the catalysts is another critical parameter to investigate to obtain high-quality CNTs with high yield. Molecular-level understandings of the W-assisted elongation of catalyst lifetime are worthwhile for further in-situ electron microscopic and modelling investigations and could help the design of high-performance catalysts for CNT synthesis.
Appendix B: Controllable Synthesis of Rhodium Nanostructures for Plasmon-Enhanced Catalysis

B.1 Introduction

Rh nanocubes (NCs) with plasmonic resonances in the UV and visible regions have been demonstrated in Chapter 2. An edge length of larger than 60 nm is required to red-shift the resonant wavelength from deep UV of small Rh nanoparticles to visible region. However, this large size is undesired for catalysis due to low surface-to-volume ratio and associated lower number of active sites with the same weight of Rh metal. Therefore, Rh nanostructures with high surface-to-volume ratio and plasmonic resonance in the visible region would be promising candidates for plasmon-enhanced catalysis under sunlight light.

Au nanoshells (NSs) coated on spherical cores have been demonstrated to be a versatile platform for tunable the plasmonic properties of nanostructures. The resonant wavelength of metal NSs can be tuned by changing the material, size, and shape of cores and the thickness of metal shells. A hybridization model was proposed to understand the plasmonic properties of Au shells coated on SiO$_2$ cores.\textsuperscript{160} It can be seen as a hybridization of the plasmonic resonances of a large solid Au nanospheres with a cavity mode. With a thin layer of metal coating on SiO$_2$ cores, the resonant wavelength of the metal NSs can be red-shifted compared to the large solid nanoparticles. Hence, Rh NSs could be promising candidates for plasmon-enhanced catalysis under visible light.
Nanostructures with sharp tips can generate intense electromagnetic field and facilitate the production of hot electrons.\textsuperscript{44} Synthesis of Rh nanostructures with sharp tips could be a compelling strategy to improve their activities in plasmon-enhanced catalysis.

In this project, we develop methods to synthesize Rh NSs on SiO$_2$ cores and Rh tripods with sharp tips. The plasmonic properties of these Rh nanostructures are investigated by spectroscopic measurements, whose resonant wavelength can be tuned into visible region through the control of morphology.

\textbf{B.2 Experimental methods}

\textbf{B.2.1 Synthesis of Rh nanoshells}

The SiO$_2$ spheres were synthesized by a hydrolysis-condensation method.\textsuperscript{151} 50 ml ethanol (Koptec, 200 proof) was added to a 150 ml beaker with vigorous stirring, followed by adding 3.0 ml NH$_3$ (Fisher, 30\%). After ~5 min, 1.5 ml tetraethyl orthosilicate (TEOS, Acros, 98\%) was added dropwise to the solution. The transparent and colorless solution was stirred at room temperature for 6 h. 50 ul APTES (Acros, 99\%) was added dropwise to the solution and stirred at room temperature for another 2 h, followed by refluxing for 1 h. The product was washed with ethanol once. The white solid was dispersed in ~25 ml ethanol.

The Rh seeds were spherical particles synthesized by a fast-injection method discussed in Chapter 4. 25 mg PVP (M.W. \(\approx\) 55,000, Aldrich) was dissolved in 5.6 ml EG (J. T. Baker) in a 20 ml glass vial and stirred in an oil bath at 160 °C for 30 min. 12 mg 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 product was washed by DI-water/acetone for three times and dispersed in 10 ml ethanol. 0.5 ml SiO₂ sphere solution and 4.5 ml Rh seed solution were mixed in a 10 ml centrifuge tube and shaken for 2 min to decorate the Rh seeds on SiO₂ spheres.

The overgrowth of Rh NSs used a polyol reduction method. 4.9 ml EG, 12.5 mg PVP, 0.1 ml 0.1 M HCl (ACS, Fisher) in EG solution, and 0.5 ml decorated seed solution were added to a 20 ml glass vial and stirred in an oil bath at 160 °C for 1 h. 3.8 mg RhCl₃ hydrate dissolved in 2 ml EG was injected into the light brown reaction mixture at 1 ml/h. After injection, the reaction mixture was stirred for another 30 min and washed with DI-water/acetone for three times. The precipitate was dispersed in 20 ml ethanol.

**B.2.2 Synthesis of Rh tripods**

Rh tripods were synthesized by a polyol reduction method. 54 mg KBr and 2.0 ml EG were added to a 20 ml glass vial and stirred in an oil bath at 160 °C for 50 min. 40 ul 0.1 M KOH (Alfa Aesar) in EG solution was added to the solution and stirred for another 10 min. 5.9 mg RhCl₃ hydrate and 12.5 mg PVP dissolved in 2 ml EG was injected into the colorless solution at 2 ml/h. The injection was paused for 15 min after adding 20 μl of the precursor. The reaction mixture was stirred for another 10 min after injection and washed with DI-water/acetone for three times. The precipitate was dispersed in 20 ml ethanol.
B.2.3 Material characterization

TEM images were collected by a FEI Tecnai G² Twin operating at 200 kV. The TEM samples were prepared by dispersing the catalysts in ethanol with sonication and depositing on a copper grid coated with a carbon film (Ted Pella, 01813). The thermal stability of Rh nanostructures was investigated by impregnating on inert Al₂O₃ nanoparticles and observed with TEM. Ultraviolet-visible extinction spectra were obtained on an Agilent Cary 50 spectrometer.

B.3 Results and discussion

B.3.1 Morphology and optical properties of Rh nanoshells

The synthetic steps of Rh NSs are shown in Figure B.1. SiO₂ spheres with diameters of 80~120 nm were synthesized by the hydrolysis and condensation of TEOS in an ethanol solution. The hydroxyl-terminated hydrophilic surface of SiO₂ spheres was functionalized with APTES to convert into amine-terminated hydrophobic surface (Figure B.2a). By mixing an ethanol suspension of SiO₂ spheres and an ethanol suspension of small Rh spheres in a tube, Rh seeds were decorated on the surface of SiO₂ spheres (Figure B.2b). This decoration process is enabled by the specific bonding between amine terminal groups on SiO₂ spheres and metal surface.

Rh NSs grown from Rh decorated SiO₂ spheres were synthesized by a HCl-assisted slow-injection method. Without the addition of HCl, Rh can be deposited on SiO₂ spheres but free Rh nanoparticles that unattached to SiO₂ spheres were also observed from TEM (Figure B.3b), probably due to the strong reducing power of EG that enable homogeneous nucleation of Rh nanoparticles during the synthesis. By adding HCl
to lower the reducing power of EG,\textsuperscript{162} Rh can be deposited on Rh decorated SiO\textsubscript{2} spheres without unattached Rh nanoparticles (Figure B.2c). However, different from Au that can form a continuous shell on SiO\textsubscript{2} spheres, the synthesized Rh NSs are composed of ~5 nm Rh nanoparticles densely packed on the surface of SiO\textsubscript{2} spheres. This densely packed layer of Rh nanoparticles also implies that new Rh seeds were generated on the surface of SiO\textsubscript{2} spheres during the synthesis. Rh NSs synthesized with one-fourth of Rh precursor in the standard HCl-assisted method resulted in a loosely packed Rh nanoparticle layer on the surface of SiO\textsubscript{2} spheres (Figure B.3b), due to inadequate amount of Rh precursor to form a compact layer of Rh nanoparticles.

Although the Rh NSs are not continuous shell on SiO\textsubscript{2} spheres, this compact layer of Rh nanoparticles forms a high number of plasmonic “hot spots” between the gap of adjunct nanoparticles. These hot spots could generate intense electromagnetic field and liberate hot electrons for chemical reaction, benefitting the application in plasmon-enhanced catalysis.

\textbf{Figure B.1.} Schematic representation of synthesis of Rh NSs.
Figure B.2. TEM images of amine-functionalized SiO$_2$ spheres (a), Rh seed decorated SiO$_2$ spheres (b) and Rh NSs (c). Scale bar: 100 nm. (d) UV-vis spectra of Rh NSs in an ethanol dispersion.

The UV-vis spectra of Rh NSs show a broad absorption throughout the UV and visible regions, in which two peaks are observed around 430 and 500 nm (Figure B.2d). This is distinctly different from the plasmonic properties of single Rh nanoparticle with
Figure B.3. TEM images of Rh NSs with one-fourth of Rh precursor as in the standard method (a) and without the addition of HCl (b). Scale bar: 100 nm.

size of 5 nm, which should have resonances in deep UV region. The red-shift of resonant wavelength into visible region indicates the coupling between adjunct Rh nanoparticles. By changing the size of SiO$_2$ spheres and the amount of Rh precursor added in the synthesis, the plasmonic properties of Rh NSs could be tuned for specific applications.

B.3.2 Morphology and optical properties of Rh tripods

Rh tripods were synthesized with similar conditions as the slow-injection synthesis of Rh cubes discussed in Chapter 2. However, KOH was added in the synthesis of Rh tripods to induce the change of morphology from cubic nanoparticles to tripods. Briefly, KOH and KBr were co-dissolved in EG and heated in an oil bath before the injection of Rh precursor and PVP into the reaction mixture. The morphology of as-synthesized Rh tripods is shown in Figure B.4a. These tripods have three arms with
length of ~15 nm arranged with a C3 symmetry. The cross-section of these tripods is flat as revealed by tilting the TEM stage to different angles. A small number of Rh cubes were also observed in the Rh tripod sample. UV-vis spectrum of these Rh tripods shows a resonant peak ~370 nm (Figure B.4b), close to previous simulations of Rh tripods with similar size.77

We propose two possible mechanisms for the KOH-assisted synthesis of Rh tripods. First, KOH could increase the reducing power of EG and accelerate the reduction of Rh precursor. The faster reduction of Rh precursor leads to the formation of Rh tripods. Second, KOH may react with the Rh precursor to produce rhodium oxides and hydroxides. The presence of rhodium oxides and hydroxides results in the formation of Rh tripods. To understand the growth mechanism and improve the morphological purity of Rh tripods, more experiments should be carried out.

Since the reducing power of EG also depends on the reaction temperature, tuning the reaction temperature and the concentration of KOH could reveal the role of Rh reduction rate in the synthesis of Rh tripods. Monitoring the particle morphology with different amount of Rh precursor could show the evolution of Rh tripods and provide insights of the growth mechanism. High-resolution TEM and electron diffraction measurements of Rh tripods can show their exposed crystal facets to deduce the growth mechanism.
B.3.3 Thermal stability of Rh nanostructures

The thermal stability of Rh NSs and tripods were investigated by supporting on inert Al₂O₃ nanoparticles that allows thermal treatment and TEM observation. Rh NSs calcined in air at 350 °C converted the compact layer of Rh nanoparticles into a continuous shell with rough surface (Figure B.4a). The Rh nanoparticles at high temperature could partially melt and the high surface energy of small Rh nanoparticles could induce the form of a continuous Rh shell. Thermal treatment is also a simple method to converted the Rh NSs into continuous shells.

Rh tripods calcined in air at 350 °C retained the shape of tripods, but reduction under H₂ at 350 °C induced morphological change to nearly spherical nanoparticles (Figure B.5b). This change of morphology could be mediated by the adsorption of H₂ on the Rh surface that changes the surface energy of different crystal facets. Similar
adsorbate-induced morphological changes have been observed on CO adsorption on Pd nanoparticles.\textsuperscript{163}

These results show that the thermal stability of Rh nanostructures needs to be considered during the operation of catalytic reactions to take advantages of certain particle shape. The change of particle shape also affects the plasmonic properties of Rh nanoparticles, which needs to be characterized by diffuse-reflectance absorption spectroscopy. Other than gas-phase reactions, these Rh nanostructures could be used in liquid-phase reactions, which are generally operated at much lower temperature.

Figure B.5. TEM images of Al\textsubscript{2}O\textsubscript{3} supported Rh NSs calcined in air at 350 °C (a) and Al\textsubscript{2}O\textsubscript{3} supported Rh tripods reduced in H\textsubscript{2} at 350 °C (b). Scale bar: 50 nm.
B.4 Conclusion and outlook

In conclusion, a multi-step method to synthesize non-continuous Rh NSs on SiO$_2$ cores composed of compact agglomeration of small Rh nanoparticles is developed. The plasmonic resonance of Rh NSs is in the visible region due to the plasmonic coupling between adjunct nanoparticles, and the high surface-to-volume ratio feature required for catalyst is retained. The non-continuous Rh NSs can be converted into continuous NSs by a simple heating treatment. A KOH-assisted slow-injection method is developed for the synthesis of Rh tripods with plasmonic resonances in the near UV region. These Rh tripods with sharp tips can retain their shape in air at high temperature, but will change to spherical particles in H$_2$.

The size of SiO$_2$ cores and the amount of Rh can be tuned in Rh NSs to tune their plasmonic properties for specific applications. The proposed growth mechanism of Rh tripods needs to be proved with further experiments to synthesize Rh tripods with high purity. The activities of Rh NSs and Rh tripods in plasmon-enhanced catalysis will be investigated in model reactions, such as gas-phase CO$_2$ hydrogenation and liquid-phase degradation of organic pollutants.
References


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Biography

Place and Date of Birth

Beijing, People’s Republic of China
Dec. 24th, 1990

Education

20012~2017 Ph.D. (Chemistry)
Duke University, Durham, NC, United States

2008~2012 B. S. (Chemistry)
Tsinghua University, Beijing, People’s Republic of China

Publications


4. Jinghua Li, Keigo Otsuka, Xiao Zhang, Shigeo Maruyama, Jie Liu. Selective synthesis of large diameter, highly conductive and high density single-walled carbon
nanotubes by a thiophene-assisted chemical vapor deposition method on transparent substrates. *Nanoscale*, 2016, 8, 14156-14162.


**Presentations**

1. Xiao Zhang, and Jie Liu. Preferential Methane Production from Photocatalytic Carbon Dioxide Hydrogenation on Plasmonic Rhodium Photocatalysts. 
   **Oral presentation** at 2016 Materials Research Society Fall Meeting & Exhibit, Boston.

2. Xiao Zhang, and Jie Liu. Plasmonic Photocatalysis for Selective Carbon Dioxide Hydrogenation. 
   **Oral presentation** at 2016 Chemistry Department Graduate Research Symposium, Duke University.
   **Oral presentation** at 2016 Noble Metal Nanoparticles Gordon Research Seminar, South Hadley.  
   Poster presentation at 2016 Noble Metal Nanoparticles Gordon Research Conference, South Hadley.
4. Xiao Zhang, Fernando Moreno, Henry O. Everitt, and Jie Liu. UV Plasmonics based on Morphology-Controlled Rhodium Nanostructures.  
   **Oral presentation** at 2015 Materials Research Society Fall Meeting & Exhibit, Boston.
5. Xiao Zhang, Pan Li, Hongbo Zhang, Jie Liu. Understanding the Low Yield in the Synthesis of High-Quality Carbon Nanotubes.  
   Poster presented at 2015 MRS Spring Meeting & Exhibit, San Francisco.
6. Xiao Zhang, Pan Li, Hongbo Zhang, Jie Liu. Improved yield of high-quality few-walled carbon nanotubes with tungstate-intercalated layer double hydroxide catalysts.  

**Fellowships**