ABSTRACT

ORTIZ, NATHALIA. Gold Nanorods End-Capped with a Second Metal as Effective Photocatalysts. (Under the direction of Dr. Gufeng Wang).

The purpose of this dissertation is to develop novel nano-materials to solve some of today’s most challenging problems such as the need for clean environment and renewable energy. In specific, we propose to synthesize light-responsive nanoparticles that can utilize solar irradiation to catalyze chemical reactions such as hydrogen gas generation and the degradation of EPA priority toxic pollutants. To achieve this goal, gold nanorods (AuNRs) end-capped with a second catalytic metal were synthesized. AuNRs are especially of interest in serving as the substrate in these materials because they have tunable localized surface plasmon resonance (LSPR) wavelength ranging from visible to near IR, which allows us to use a large portion of the solar irradiation that cannot be effectively used currently. The reasons for selective decorating the catalytic metal at the AuNRs are two-fold: (1) to use the precious catalytic metals efficiently; and (2) to use the “hot” electrons generated in the LSPR process efficiently.

In Chapter 2, a synthetic approach was developed to selectively decorate the ends of AuNRs with a second metal. As a demonstration, Pd-end-capped-AuNRs were synthesized and its catalytic activity was demonstrated using a model reaction.

In Chapter 3, we evaluated the use of Pt- and Pd-end-capped AuNRs for the photo-degradation of EPA priority environment pollutant 4-nitrophenol. We demonstrated that these particles are excellent photocatalysts and can be used to effectively remove environmental pollutants in waste waters.

In Chapter 4, Pt-end-capped-AuNRs were synthesized and investigated as an effective photocatalyst for hydrogen gas production. We showed that photochemical reduction of Pt(IV) to
Pt metal mainly takes place at the ends of gold nanorods (AuNRs), suggesting that photon-induced hot electrons are generated, and/or localized in a time-averaged manner, at AuNR ends. These Pt-end-capped AuNRs showed high activity for hydrogen production under artificial white light, natural sun light, and more importantly, near IR light at 976 nm. This indicates that these particles are excellent in turning low energy photons to high energy hot electrons that can catalyze energetically unfavorable chemical reactions.

In Chapter 5, we explored the new approaches to extend the lifetime of the hot electrons generated in metal particles by orders of magnitudes so that the chemical yield of hydrogen gas can be enhanced. To achieve this, we investigated the composite particles between plasmonic AuNRs and ferroelectric materials, which possess a large remanent electric field that facilitates the charge injection and separation. Using near IR light, we demonstrated that hot electrons generated on plasmonic nanoparticles can be injected into ferroelectric materials and drive the photocatalytic reaction. The efficiency of using hot electrons for photocatalytic reactions is greatly enhanced, which improves the light-to-chemical energy conversion efficiency by about one order of magnitude for the same amount of Au particles being used. This new strategy may have a large impact on the design of future photocatalysts.

In Chapter 6, we evaluated the effectiveness of using photoelectrolysis of water as a realistic method to produce a clean and renewable fuel in replacing fossil fuels. Using Pt-end-capped AuNRs as the photocathode, we demonstrated that the particles can turn near IR light into chemical energy with a yield similar to those reported in the literature using visible light.
Gold Nanorods End-Capped with a Second Metal as Effective Photocatalysts.

by
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DEDICATION

This is dedicated to my mother, who has believed in me since kindergarten. Mami, you have taught me how to dream big, how to work hard, how to fight with grit to defend what I believe in. Most importantly, you taught me to love people, to embrace everyone with love, kindness and a big smile. To my wise father, who has come to the rescue every time I cried out for help: I can always hear you say, “Time will take care of everything. Be patient”.

To my loving husband and friend, Jonathan: You are my biggest fan; you never stop cheering me up and at all those moments when I wanted to quit, I am glad you were there to lift me up. To my beautiful daughter, Penelope: Grad school would never have been the same without you. Thank you for your smiles, eloquent phrases, your unconditional love and I am sorry for making you think that “Brickyards” = “Mama’s work again”. To my sisters and brother, Gaby, Any, Rebe, Jota, Gore, Caro, and mi Valita: I love you all with all my heart; you all have contributed greatly to the culmination of this journey and my life would be nothing without your love and support.

To her, the woman, the young girl, the young mother, the tough one, the construction worker, the painter, the care-giver, the interpreter, the class clown, the house cleaner, the foreigner, the wife, the curios one, the depressed one and the crazy one: Whatever role it is you play, one or all of them, you got all it takes. Do not let anyone tell you otherwise. Go out there, the world awaits. You CAN do it, I believe in you. I, a living proof, am telling you: It is possible!
BIOGRAPHY

Nathalia Ortiz, aka Nathalia Morales Valverde, was born in San Jose, Costa Rica on May 29, 1985. After graduating from high school in 2003, Nathalia spent 3 years taking care of her mother, who was recently diagnosed with Lou Gehrig’s disease. A year after her mother’s death Nathalia moved to the United States to pursue a degree in medicine, looking for answers to this devastating disease. Awaiting formalization of her immigration status, she endeavored into construction, carpentry and house-cleaning among other skilled jobs for a year.

Once established in Erie, PA she devoted her time to studies at Gannon University, where she received her Bachelor’s degree in chemistry, working full time as a certified nurse assistant at a local hospital and doing research with her undergraduate advisor, Dr. Carl Hultman. She realized that pursuing a degree in chemistry would give her the tools she had an ambition for, to reach a broader audience and help people in many different aspects, specifically using nanotechnology.

In 2013, Nathalia joined Professor Lin He’s research group, at North Carolina State University (NCSU), where she worked on the synthesis of stripped metallic nanowires, as a sensing mechanism for the detection of amyloid formation. A year later she moved to the research group of Dr. Gufeng Wang. She has been working with Dr. Wang, in the Department of Chemistry at NCSU, in the development of novel metallic nanoparticles with applications in pollutant treatment for environmental solutions, and as photocatalysts for renewable energy resources.
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1. **Ortiz, N.; Zoellner, B.; Janelli, T.; Tang, S.; Maggard, P.; Wang, G.** “Composite Ferroelectric And Plasmonic Particles For Hot Charge Separation And Photocatalytic Hydrogen Gas Production” Under revision and will be resubmitted


CHAPTER 1: An Introduction to Nanoparticle Design and Applications

1.1 Nanotechnology: Impact to National Technological Development

The development of nano-materials has been in the spotlight since the year 2,000 when the United States government called for research and development of nanotechnology-based activities. In 2017, the federal government allotted 1.4 billion dollars in the national nanotechnology initiative (NNI).\(^1\,^2\) The framework of this initiative focuses on five main areas or program component areas (PCAs): (1) nanotechnology signature initiatives, (2) foundational research, (3) nanotechnology enabled applications, devices and systems, (4) research infrastructure and instrumentation, and (5) environment, health and safety. Our novel research developments fall within areas 1, 2, 3, and 5, thus contributing to the attainment of the goals established by the NNI and the country’s technological development in general.

1.2 Metallic Nanoparticles and Localized Surface Plasmon Resonance

Metallic nanoparticles are the core of our studies because they exhibit optical characteristics of significance for the development of photocatalytic systems. In specific, we focus on gold nanoparticles (AuNP). In the nano-regime, AuNPs show unique optical properties such as strong absorption and scattering due to the localized surface plasmon resonance (LSPR), i.e., the collective oscillation of conduction electrons upon light excitation. The LSPR wavelength of a particle is highly dependent on the particle size, shape, and its environment. For rod-shaped AuNPs, i.e., gold nanorods (AuNRs), their plasmonic bands can be tuned in a controlled manner from visible to near IR region. Thus, they can serve as antennas to absorb solar energy at desired wavelengths. More interestingly, the decay of LSPR generates “hot” electrons, which refers to the electrons with an energy above the Fermi level. These hot electrons can be transported to the surface of the particles to participate in chemical reactions and turn photon energy to chemical
energy. Our goal is to combine AuNRs, which serve as the antenna, with a second catalytic metal to form a light-responsive catalyst that can drive different chemical reactions such as hydrogen gas generation and pollutant degradation.

![AuNRs Surface Plasmon Resonance](image)

**Figure 1.1.** Gold Nanorods Localized Surface Plasmon Resonance. (A) UV-VIS absorption spectrum of AuNRs. Two strong absorption bands are shown: the T-SPR and the L-SPR bands, which correspond to the collective oscillation of electrons along the transverse axis and longitudinal axis, respectively. (B) Collective oscillation of conduction band electrons upon light excitation. Particle size must be much smaller than the wavelength of light use to excited.

Among some of the very first known evidence of nanoparticles, the Lycurgus Cup, a Roman cup made of dichroic glass containing colloidal solutions of gold and silver nanoparticles, dates back to the 4th-century.\(^3,4\) It is unique in that it displays different colors when being
illuminated from the inside or the outside of the cup because of the LSPR-induced absorption and scattering of these nanoparticles. The theoretical understanding of how metal nanoparticles interact with light thus the coloration of the particles started in late 1800s and early 1900s. In 1908, the first complete solution describing the interaction between a spherical metal particle with electromagnetic field was introduced by Gustav Mie, thus named Mie solution or Mie theory. For gold nanospheres, one LSPR band was predicted, which is consistent with experimental observations. \(^5\)

Later, in 1912, Richard Gans published an expansion to Mie’s Theory for the ellipsoidal particles. Within its expansion, a depolarization factor is considered in solving the Maxwell equations, which incorporates the ratio between its length and width (i.e., the aspect ratio) of a given particle. Gans’ theory predicts two plasmonic bands, one corresponds to the collective oscillation of electrons along the short axis, i.e., the transverse mode SPR (T-SPR), and the other the collective oscillation of electrons along the long axis, i.e. longitudinal mode SPR (L-SPR). Note that we will use L-SPR to refer to the longitudinal SPR while LSPR is reserved for localized SPR throughout this document. The longitudinal SPR band is sensitive to the aspect ratio of the particle as well as many other factors such as the particle composition and dielectric environment. Thus, it gives us the opportunity to controllably tune the L-SPR band to the desired wavelength to serve as antennas for energy absorption (Figure 1).\(^5\)-\(^8\)

1.2.1 Au-Based Hybrid Nanoparticles

Because of their unique optical properties, AuNPs have been demonstrated to be useful in many fields such as therapeutic agents, optical imaging labels, biosensors, and surface enhanced spectroscopy, etc.\(^9\)
In this study, we mainly focus on the other property associated with LSPR: hot electron generation. After excitation, the LSPR can decay through multiple pathways such as LSPR dephasing, internal relaxation through electron-electron scattering, electron-phonon scattering, and energy dissipation into the environment.\textsuperscript{10-12} Studies show that the absorption of photons provides energy to the electrons through the LSPR process or inter/intra-band transitions. More importantly, the excited electron can reach an adiabatic equilibrium in the femtosecond time scale through electron-electron scattering, yielding “very hot” electrons, i.e., electrons with an energy much higher than the Fermi level. These high energy electrons can diffuse to the surface of the particle and participate in chemical reactions. Since they have very high energy, it is possible to use them to drive energy-unfavorable chemical reactions, e.g., hydrogen gas production, and turn photon energy into chemical energy. However, Au itself is an inert metal. Thus, a hybrid particle composed of Au and another catalytically active metal is preferred, in which the Au component harvests photon energy and turn it into high kinetic energy in hot electrons (and holes) while the other metal serves as the active center and catalyzes a specific chemical reaction.

In this design, we are especially interested in AuNRs as the substrate of the hybrid particle for several reasons: (1) the absorption band of AuNRs can be tuned in a controlled manner, which allows us to engineer the particle to work at desired wavelengths. (2) AuNRs have a large absorption cross section, which is important in absorbing diffusive natural solar light. (3) Most importantly, there is recent study indicating that AuNRs may convert low energy photons, e.g., photons in the near IR range, into very high energy hot electrons. This opens a new gate toward utilizing a large portion of solar energy that was deemed “useless” in the past.
Figure 1.2. Typical Gold Nanorods Synthesis: Seed-Mediated Growth Method. (A) Step 1: seed growth in the presence of a strong reducing agent and a surfactant (CTAB), yielding gold nuclei 1.5-3 nm in diameter. (B) Step 2: direct growth of gold nuclei into gold nanorods assisted by Ag⁺, CTAB, and the reducing agent (ascorbic acid).

However, so far, how the hot electrons are generated, and how they are distributed in terms of both energy and geological locations, are still not well understood and under intensive investigation. The general perspective is that the hot electrons may localize, in a time-averaged manner, at the ends of AuNRs, or, the “hot” spots where the largest electric field can be found using theoretical simulations.¹³⁻¹⁸ To best use these hot electrons, the most efficient way is to put the catalytic metal at places where the hot electrons tend to localize. This allows us to use both the metal and the hot electrons efficiently. In addition, putting the minimal amount of a second metal on the plasmonic particle will have the least interference with the LSPR and hot electron generation processes.

1.3 Synthesis of AuNRs End-Capped with a Second Metal

Based on above discussion, we set our goals as developing hybrid AuNRs end-capped with a second metal. However, selective decorating a nanoparticle is still challenging. We will adopt an “addition” approach and start from AuNR synthesis.
1.3.1 Synthesis of Gold Nanorods

Currently, the most used method in synthesizing AuNRs is the seed-mediated growth.\textsuperscript{19} This method was first introduced between 1999 and 2001 by two research groups independently: El-Sayed group and Murphy group.\textsuperscript{20-23} The seeded growth method involves two steps: (1) the growth of gold seeds, which are gold nuclei ranging in size from 1.5 nm – 3.0 nm; and (2) the directed growth of nuclei into gold nanorods in a special growth medium.\textsuperscript{19,24,25}

Figure 2. shows a schematic for the seeded growth method. This method is sometimes categorized as a soft template method since it may involve the surfactant micellar formation to shape the growth of the gold nanorods. Cetyltrimethyl ammonium bromide (CTAB) is the most popular surfactant used.\textsuperscript{26} Furthermore, introduction of an additional organic additive to the growth medium have demonstrated to lower the micellar surface charge, which in turn is more energetically favorable for the directional growth thus improving the shape of gold nanorods.\textsuperscript{27} Studies also have shown that using organic additives to the growth medium, the pre-reduction of Au(III) to Au(I) can take place more efficiently, which helps the AuNR growth. For instance, Liz-Marzan \textit{et al.} has shown that the pre-reductive step significantly increases the yield of AuNRs from \textasciitilde30\% to \textasciitilde100\%.\textsuperscript{28}

Once AuNRs are obtained, they serve as the substrate upon which a second metal at designated locations is added. However, the addition of a second metal usually leads to a randomized coverage on AuNRs, forming a core-shell structure. Full coverage of the AuNRs is detrimental to our purpose since the LSPR is damped. Thus, modification of the synthetic steps to limit the random overgrowth of the second metal on AuNRs is the key.
1.3.2 Overgrowth of a Second Metal on AuNRs

Great efforts have been paid to selectively decorate metallic particles with a second metal. Different approaches have been considered including: selective etching (subtraction), selective protection and overgrowth, and direct overgrowth at specific conditions (additions). For example, Guo et al. synthesized Ag-tipped-AuNRs in a three steps process: synthesis of AuNRs, synthesis of Au-core-Ag-shell particles, and selective etching of Ag using FeCl$_3$ (see Figure 1.3.A for schematic). Selective protection and overgrowth was developed by Wang et al., in which a silica shell is formed first either at the ends or at the middle of the AuNRs, leading to the reduction of the second metal only at unprotected locations on AuNRs (see Figure 1.3.B for schematic).

![Diagram A](image)

**A** Complete overgrowth of a silver shell on AuNRs, followed by selective etching of the silver shell from the core of the AuNRs initiated by the addition of FeCl$_3$. **B** Selective protection of either the core of the gold nanorods or the ends by a silica shell. Followed by selective overgrowth of a second metal at the unprotected areas. Images taken from references 30 and 32 respectively.

Recently, Majima et al. showed that by introduction of an additional organic modifier 5-bromo-sylicylic acid to the CTAB mixture, Pt or Pd tends to grow at the ends of the AuNRs.
This shows that by carefully selecting the organic modifier in the ligand, selective growth of a second metal on AuNR surface is possible. Therefore, we hypothesized that by introducing bulky organic modifiers, e.g., family of salicylic acid additives, to the growing medium, we can tune the CTAB ligand arrangement at the ends of AuNRs. Thus, the anisotropic growth of AuNRs and the selective overgrowth of a second metal can be achieved. This part of study is detailed in Chapters 2 and 3.

1.4 Hydrogen Gas Production

1.4.1 Solar energy conversion

Fossil fuel is yet the primary source of energy in the world. In United States, 81% of the total electricity generated (4.08 trillion kilowatt hours, kWh) is from fossil fuels; 9.0% from nuclear electric power and 10% of the total electricity generated comes from renewable energy resources, from which only 0.9% is from small scale-solar photovoltaics systems.34

The exhaustion of fossil fuels is inevitable. Thus, finding a renewable energy source is urgent. Solar energy is ideal in such a way that it is abundant and clean. However, solar irradiation is a very diffusive source. Thus, efficient using of the solar light is important to minimize the use of catalytic materials as well as to have the least impact on the environment, e.g., less land use for solar energy harvesting. In addition, solar irradiation reaching earth surface is not constant throughout the day and the year. Strategic design of conversion and storage of the energy must be considered to accommodate for these factors. Our initiative is to develop new materials that can convert solar energy in a sustainable way into chemical energy that can be used and stored, which meets the world’s energy demand.

Turning solar energy into chemical potential energy, e.g., that stored in hydrogen gas, is an ideal alternative to fossil fuels. Hydrogen gas generated from solar energy is a viable solution since
it is clean, has high energy density, and can be easily stored and transported. However, producing hydrogen gas from water using sunlight is an uphill process. Taking water splitting as an example, it has a thermodynamic Gibbs’ free energy change of 238 KJ/mol, corresponding to a standard potential of 1.23 V at pH = 0.0. Current semiconductor-based photocatalysts usually require photon energy to be larger than ~3.0 eV to drive the water splitting reaction efficiently. From the AM 1.5 solar irradiation energy distribution: 2.9 % UV (290 nm – 380 nm), 47 % Visible (380 nm – 780 nm), and 51 % IR (780 nm – 2500 nm), only a small portion of solar energy can be used using these materials for this purpose. Hence, maximally utilizing solar irradiation is the key in developing new materials to harvest solar energy and driving the water splitting reaction.

Water splitting involves two half-cell reactions; the reduction of hydrogen ions and the oxidation of the water molecules, each requiring a specific catalyst. In this study, we focus only on developing photocatalysts for the reduction of hydrogen ions: 2H⁺ + 2e⁻ → H₂. Plasmonic particles are ideal to serve this purpose because hot electrons are generated during the photoexcitation, which can be used in this reduction reactions. A hole scavenger, methanol, is utilized to deplete holes generated from the photoexcitation and drives the reaction continuously. Kandiel et al. demonstrated, through the using isotopic labeling, that the formation of molecular hydrogen is mainly from the reduction of H⁺ from water.

1.4.2 Semiconductor Photocatalysts

Exploring new photocatalysts that can convert solar energy into chemical energy is a rapid emerging field. Currently, semiconductors and semiconductor-based photocatalytic systems are the most used photocatalysts for this purpose. For example, titanium dioxide (TiO₂) remains among the most popular materials in hydrogen gas (H₂) production. In photocatalysis, the reaction consists of three primary steps: photoexcitation and the generation of electron (e⁻) and
hole (h\textsuperscript{+}) pairs; charge separation and transport to the catalyst surfaces; and electron transfer at the surface for driving a redox reaction. The photocatalytic efficiency is impacted by all three key factors: the amount of light absorption, the efficiency of charge separation, and the surface reaction rates.

The main advantages of semiconductors include high photo-reactivity, good stability over time, low cost, and environmentally friendly nature.\textsuperscript{43,44} However, semiconductor photocatalysts suffer from a few main drawbacks: low absorption coefficient, large energy gaps, and fast recombination hot charge carriers, which lower the chemical yield. By doping semiconductors with other ions can alleviate the first two problems\textsuperscript{45,46} but worsen the third one.

**Figure 1.4.** Scheme of Semiconductor and Composite Semiconductor-Plasmonic systems. (A) Energy diagram for a semiconductor system upon excitation. (B) Plasmon induced electron transfer from the gold nanosphere into the semiconductor conduction band. Images taking from references 47 and 42 respectively.
Composites made of semiconductors and plasmonic metal particles have been extensively studied to enhance the efficiency of current photocatalyst. Figure 4A shows a mechanism for charge transfer from a plasmonic particle into the semiconductor conduction band upon the excitation of the plasmonic metal particle.\textsuperscript{47} The addition of plasmonic nanoparticles to semiconductors have improved the performance of the photocatalysts in overall efficiency. For example, Mubeen \textit{et al.} designed an autonomous water splitting device, which contains a AuNR array on a TiO\textsubscript{2} thin layer.\textsuperscript{15} The transient population of hot electrons along the AuNRs will reach the conduction band of the semiconductor and further being transferred to the co-catalyst, where the reaction takes place.

Such a design sensitizes the semiconductor photocatalysts. However, current designs are still problematic in that the charge injection and subsequent charge separation are of low efficiency. The hot electrons have a higher tendency to flow back from the semiconductor to the metal because of the lower energy barrier from semiconductor to metal as compared to that from metal to semiconductor. In addition, the hot electrons tend to thermalize or recombine with holes before they reach the surface to catalyze the reaction in the semiconductor. How to overcome these problems is the key in designing new photocatalysts that have higher efficiency for photo-driven water splitting and hydrogen production.

\subsection{1.5 Composite Ferroelectric-Plasmonic Nanoparticles}

Our hypothesis is that by combining plasmonic particles with ferroelectric materials, which possess large remanent internal electric fields, charge injection and separation can be efficiently achieved. Thus, the lifetime of hot electrons generated in the SPR process can be extended by orders of magnitudes thus the photocatalysis efficiency can be greatly improved.
1.5.1 Ferroelectrics

Ferroelectric materials have been extensively used in microelectronics, memory storage devices, temperatures sensors and switches, thin film capacitors and more. They characterize with a large, switchable polarization in the crystals. Perovskite type metal oxides are prominent ferroelectric materials. These materials are cubic structures in the form of $\text{ABO}_3$ (A represents a cation larger in size than B ion) following the cubic space group $\text{Pm3m}$. In the case of $\text{PbTiO}_3$, spatial interaction between lead and oxygen leads to a fix polarization within each unit cell. Further, rearrangement of individual atoms around the anion (negative oxygen) can be induced by either an external electric field or a temperature change, which causes the polarization direction to change and in turn stabilizes the crystal structure change. This process is reversible thus these materials have a switchable polarization.

More relevant to our efforts, studies have demonstrated that the remanent internal electric field in ferroelectric materials can help improve charge separation in photocatalytic system. This is possible through the coulombic attractions between the remanent filed with the electrons and holes. For example, Arney et al. evaluated the use of the ferroelectric $\text{PbTiO}_3$ for the photocatalytic reduction and oxidation of water; prominent results have been demonstrated because of this charge separation in the ferroelectric materials. Nonetheless, most ferroelectric materials, e.g. $\text{PbTiO}_3$, yet have very large band gaps (e.g., for $\text{PbTiO}_3 > 2.75$ eV, or, photon wavelength <450 nm), which limits their applications in solar energy conversion.

Here, we propose to combine AuNRs or Pt-end-capped-AuNRs with a ferroelectric material to form a composite photocatalyst. The AuNRs (or the hybrid AuNRs) will serve as the plasmonic antennas, which absorb light up to the near IR region and generate hot electrons. The
hot electrons can then be injected to ferroelectric materials and separated from holes efficiently. Thus, the hot charge carrier lifetimes can be greatly extended.

1.5.2 Composite PbTiO$_3$-Pt-AuNRs Systems

In this study, we use PbTiO$_3$ as the ferroelectric material. PbTiO$_3$ as a ferroelectric material will provide a large remanent electric field that facilitates charge separation. It also provides additional sites for the co-catalyst Pt on which hydrogen gas production will be carried out. By incorporating a semiconductor/ferroelectric material to our system, we expect the following: (1) efficient electron transfer from Pt-end-capped-AuNRs to semiconductor (here, PbTiO$_3$) through the Schottky barrier; (2) effective electron-hole charge separation, which extends their lifetimes.

Preliminary results are discussed in Chapter 4. It shows that this design works efficiently and can improve the hydrogen gas production rate by nearly one order of magnitude using the same amount of AuNRs. Knowledge gained from this research will help us better understand the underlying mechanism of hot-electrons charge generation and transport, and its involvement in fundamental chemical reactions taking place on the corresponding surface. Improvement in the design and efficiency of the photocatalytic materials is the long-term goal.
1.6 References


CHAPTER 2: Anisotropic Overgrowth of Palladium on Gold Nanorods in The Presence of Salicylic Acid Family Additives

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2.1 Abstract

We explored the use of salicylic acid (SA) and its derivatives 5-formyl salicylic acid (FSA) and 5-sulfo salicylic acid (SSA) as organic additives to cetyltrimethylammonium bromide (CTAB) in synthesizing gold nanorods (AuNRs) followed by palladium (Pd)-capping at the ends of AuNRs. In the AuNR synthesis step, SA family additives in the presence of low concentration of CTAB (50 mM) serve as both the pre-reducing agent and the cofactor in nanorod growth. At an optimum additive:CTAB ratio (0.1~0.2), AuNRs grow to the longest length. At low additive concentrations, the gold seeds do not grow. At high concentrations, the longitudinal growth of AuNRs is disrupted because the excessive additive disturbs the ligand structure, leading to more isotropic growth. In the Pd overgrowth step, Pd starts to grow from both ends for AuNRs synthesized at optimum additive:CTAB ratios. Feeding more Pd grows the particles into a core-shell structure, possibly because there lacks a tight ligand layer on Pd that favors the longitudinal growth. For AuNRs synthesized at high additive:CTAB ratios, Pd growth loses preference, showing randomized Pd nucleation on AuNR surface. Finally, the Pd-end-capped-AuNRs’ catalytic activity was tested using the resazurin reduction reaction. This study shows a new way to produce controllable deposition of Pd on AuNRs.


2.2 Introduction

Heterometallic nanostructures exhibit new characteristics compared to their monometallic counterparts, making them useful in the fields of electronics, catalysis, and biomedical applications.\textsuperscript{1-13} Especially of interests are gold nanoparticle (AuNP)–based hybrid heterometallic nanostructures. They show localized surface plasmon resonance (SPR) bands in the visible to the near IR range, which makes them strong absorbers for light. Hot electrons, \textit{i.e.}, electrons with energy above Fermi level, will be generated upon SPR excitation. The hot electrons can be subsequently transferred to the nanostructure surface to participate in chemical reactions, or thermally relax and heat the local environment. Thus, the plasmonic nanostructures can be used to photo-activate and/or boost the heterogeneous catalysis through the excitation of SPRs. For examples, AuNPs and AuNP-based nanostructures have been used in hydrogen production using solar source because of the properties mentioned above.\textsuperscript{14-18}

AuNRs have a tunable longitudinal SPR depending on their aspect ratios. By adding a second metal with specific catalytic activity on AuNR surface, we will be able to enhance or tune their chemical activity using selected wavelength. In addition, AuNRs with a large aspect ratio strongly absorb light in the near IR range, making them ideal receivers for solar emissions with low photon energy. Ideally, the second metal can be placed at the ends of the AuNRs because it is generally conjectured that the ends are where the hot electrons are distributed averagely. Moreover, putting the second metal at the ends has the additional advantages of consuming the catalytic materials economically, as well as little perturbation of AuNR SPRs.

However, so far, it is still challenging to selectively decorate the ends of AuNRs with a second metal. Great efforts have been devoted to the synthetic processes.\textsuperscript{2,3,19-23} To start, AuNRs are first synthesized using seed-mediated growth method in the presence of high concentration of
CTAB (100 mM) as the main surfactant.\textsuperscript{24,25} In the presence of small amount of silver Ag\textsuperscript{+} ions, Au seeds will have anisotropic growth rates at the corners and edges on the facets, leading to the formation of rod-shaped particles. However, further reduction of a second metal, \textit{e.g.}, Pd, will lead to isotropic growth and form a core-shell like structure.\textsuperscript{19} This is possibly because different metal ions have different sizes, affinity to the ligands, and growth conditions. As a result, the anisotropic growth is lost and the second metal is coated randomly on the AuNR surface.

Currently, there are three different approaches to synthesize AuNRs end-capped with a different metal: selective etching of core-shell particles, selective protection followed overgrowth, and direct overgrowth at selective conditions. For example, Guo \textit{et al.} used iron Fe\textsuperscript{3+} to laterally etch core-shell particles to produce Pd- and Ag-tipped Au nanorods. High catalytic activity of reducing p-nitrophenol to aminophenol as a model reaction has been reported for the tipped bimetallic nanoparticles.\textsuperscript{19} Similarly, Jing \textit{et al.} produced nanorice and nanodumbell bimetallic particles through site-selective surface etching of Ag-shell-Au-core nanocuboids. These new particles have high-index facets and show high reactivity.\textsuperscript{20} End-capped nanorods can also be synthesized by selective protection of AuNR surface using silica followed by the overgrowth a second metal.\textsuperscript{21}

Direct overgrowth of the second metal at selective conditions on AuNR ends is the mostly explored method to generate anisotropic particles. There are indications that by carefully selecting experimental conditions, anisotropic growth of a secondary metal can be achieved to a certain degree. For examples, highly preferential growth of Pt on the tips of AuNRs can be achieved by controlling the reduction conditions; the presence of silver ions was found to be highly dominant for the final particle structure.\textsuperscript{8,26} Using twinned gold decahedrons as seeds, Seo \textit{et al.} synthesized Ag-Au-Ag heterometallic nanorods in the presence of poly(vinyl pyrrolidine) (PVP).\textsuperscript{27}
Recently, Majima and co-workers showed that using 5-bromosalicylic acid (SA) as the additive, they can selectively deposit Pt and Pd on the ends of AuNRs. Salicylic acid and its derivatives have been used to facilitate AuNR growth in the low concentration of CTAB (50 mM) and tune AuNR geometry. It was found that SA family additives participate in the pre-reduction of Au(III) to Au(I), which helps the reduction yield of gold; they also serve as a growth cofactor that tune the compactness of CTAB bilayer at AuNR ends, facilitating the anisotropic growth of AuNR. Ye et al. compared a series of 11 SA family additives including amino-SA, methyl-SA, and bromo-SAs, etc. They found that while the hydrophobicity of the aromatic additive is important in the anisotropic nanorod growth, other factors such as the steric hindrance, chemical nature, and the CTAB-aromatic additive interactions delicately affect the particle growth.

Inspired by Majima’s work, we hypothesize that by tuning the size of the additive and its interactions with CTAB, we will be able to achieve anisotropic growth of a second metal on AuNR ends. In this study, we explored the use of salicylic acid (SA) and its derivatives 5-formylsalicylic acid (FSA) and 5-sulfosalicylic acid (SSA) as the additive for AuNR growth and Pd overgrowth, respectively. Acid forms of the compounds were used so there is minimal interference by other anions introduced in the acidification of the solution. We found that salicylic acid with a negatively charged side group (i.e. SSA) and a neutral hydrophilic side group (i.e. FSA) both assist the AuNR growth and the Pd overgrowth at the ends of AuNR. As a contrast, the presence of SA disrupts the longitudinal growth of AuNR. This suggests that the additional side group on SA plays an important role in the anisotropic growth of AuNR, possibly through sterically tuning the additive-CTAB interactions. In this study, Pd was used as the second metal because Pd is one of the most used metal catalysts. By combining Pd with AuNRs, we anticipate that these bimetal
heterostructures will serve as both a catalyst and a light absorber that has tunable light responsibility.

2.3 Results And Discussion

2.3.1 Synthesis of AuNRs in the presence of salicylic acid and its derivatives

In this study, we systematically evaluated the use of salicylic acid, FSA and SSA (Scheme 1), respectively, as the organic additives for the overgrowth of Pd at AuNR ends. First, we examined their effects on the synthesis of AuNRs using seed-mediated growth method because these nanorods will serve as the precursors in the Pd overgrowth.\textsuperscript{14,31,32} The synthesis involved growing the seeds in the presence of Ag ions and a surfactant, CTAB, at a high concentration (100 mM). Although the function of Ag ions is still under debating, it is generally accepted that Ag ions release surface tension within the surfactant layer at the edges and corners of the crystal facets by binding to the counter ions Br\textsuperscript{-}, leading to anisotropic growth speed on AuNR surface. Recently, it was found that using an organic additive or a mixture of surfactants, the growth of AuNRs can be tuned so that nanorods with large aspect ratio can be obtained.\textsuperscript{29,30,33} In addition, CTAB concentration can be reduced,\textsuperscript{30} or the Ag ions can be absent in the presence of the organic additive.\textsuperscript{24} The interaction between the organic additive and the surfactant is believed to reduce the micellar surface charge and is more energetically favorable for the growth process along the main axis. The molar ratio between the organic additive and the surfactant plays a key role in the final geometry, size, facet formation (morphology), and mono-dispersity of the AuNRs.

Here, all the three SA family organic additives showed concentration dependent impact on the yield and aspect ratio of the AuNR growth. Figures 2.1.A-C show the UV-VIS spectra of AuNRs synthesized at different additive:CTAB ratios for SA, FSA and SSA, respectively. All experimental conditions were the same except the additive concentrations. Low CTAB
concentration (50 mM) was used in all of the organic additive-assisted nanorod growth. The control experiment: AuNR growth in CTAB only (UV-VIS in Figure 2.2.B) used a high CTAB concentration (100 mM) because AuNRs barely grew in low CTAB solutions in the absence of the additive. The CATB-only nanorod grew to a limited length in the absence of organic additives (Figure 2.1.G).

**Scheme 2.1.** Schematics for the proposed CTAB-salicylic acid family additive interactions. (A) CTAB-SA interaction. (B) CTAB-FSA and SSA interactions.

For SA-assisted growth, the AuNRs started to grow in the presence of small amount of SA (SA 2.5 mM, or SA:CTAB = 0.05). The role of SA for pre-reducing Au(III) to Au(I) can be visually identified by the color loss of the gold solution after being added to the SA/CTAB mixtures. As
the SA concentration increased to 5.0 mM (SA:CTAB = 0.1), the nanorods grew to the longest length, with an aspect ratio of ~1:3, or the longitudinal SPR at 720 nm (Figures 2.1.A and 1D). Further increasing the SA concentration (SA:CTAB = 0.2), the ratio between the transverse SPR (T-SPR) and longitudinal SPR bands increased, indicating that the mono-dispersity became worse. This can be confirmed from the SEM image in Figure 2.1.E. When the SA:CTAB ratio was increased to 0.4, the longitudinal SPR band blue shifted, indicating that the aspect ratio of the nanorods became smaller. The SEM image (Figure 2.1.F) shows that the selective growth along the longitudinal direction was lost, possibly indicating that too much SA disrupted the CTAB layer and lead to the isotropic growth of the nanorods.

For FSA-assisted AuNR growth, low FSA:CTAB ratio (0.05) can also reduce a part of the Au(III) by visible color loss of the solution. Although all Au(III) were reduced after the addition of the excessive amount of ascorbic acid, there was nearly no detectable amount of nanorods formed (Figure 2.1.B). When the FSA:CTAB molar ratio was increased to 0.1 (5 mM FSA), the nanorods grew to the longest length, with a longitudinal SPR at 810 nm or an aspect ratio of ~1:4 (Figure 2.1.B). This suggests that FSA is important not only as a pre-reduction agent, but also as the growth cofactor for AuNRs. As FSA:CTAB ratio further increased, the nanorod anisotropic growth was partially lost (Figures 2.1.H-I), showing a blue-shifted longitudinal SPR wavelength (Figure 2.1.B).

Similar trend can be found for the SSA additive except that it required an even higher SSA:CTAB ratio (0.15) to start the nanorod growth. However, the nanorod can grow to an aspect ratio as large as ~1:5 (or longitudinal SPR at 870 nm, Figures 2.1.C and 2.1.J). Again, further increasing the SSA concentration grew the nanorod isotropically (Figure 2.1.K).
For these three organic additives SA, FSA, and SSA, first, it is immediately noticeable that all of them help the axial growth of AuNRs as compared to the CTAB-only nanorods. They show small difference in the starting growth concentrations but more importantly, they have different effects in promoting nanorod growth in the presence of low CTAB concentration (50 mM). Nanorods grown in the presence of SA have a smaller aspect ratio (1:3) and show more geometry heterogeneity. As a contrast, both FSA- and SSA-assisted growth give nanorods with larger aspect ratios and better quality in terms of particle size distribution. FSA-nanorods have a longitudinal SPR at 810 nm (aspect ratio 1:4), followed by SSA-nanorods at 870 nm (1:5) at optimal additive concentrations. The difference must come from the additional side group on the SA mother ring. The reducing capability decreases as the substitute group becomes more electron withdrawing. However, electron withdrawing is not the main reason for the different growth as all Au(III) are reduced to Au(I) in the excessive amount of ascorbic acid. Thus, it must be the interaction between the additive and the CTAB layer that tunes the AuNR growth. Here, the possible reasons include the polarity and size effects. Since a neutral and hydrophobic bromide group on the SA also promotes the AuNR growth,\textsuperscript{14,28} it is highly likely that the size of the side group strongly affect the longitudinal growth. The FSA and SSA molecules have a bulky side group so that they bind to the positively charged CTABs at the AuNR ends, creating more space in the CTAB layer that allows trafficking of gold ions for longitudinal growth (Scheme 2.1.B). As a contrast, the SA molecule has less steric hindrance so that it slips into the CTAB layer with little perturbation of the CTAB layer (Scheme 2.1.A).

Second, for all these three molecules, high concentration additives impair the elongation of the AuNRs. A careful examination of the SEM images (Figures 2.1.D-K) shows that the nanorods stopped growing in the long axis but kept growing in the short axis. It is possible that the
binding of the excessive additives disrupts the CTAB layer, leading to the loss of the anisotropic growth of the nanorods.

2.3.2 Pd overgrowth on AuNRs at optimal additive concentrations

We next studied Pd overgrowth on AuNRs grown in the presence of the organic additives. Since SA-nanorods show high poly-dispersity, we only focused on FSA- and SSA-assisted AuNRs. Special attention was paid to how the organic additive concentration influences the anisotropic growth of Pd on AuNRs.

Figure 2.1. Gold nanorod growth in the presence of SA, FSA, and SSA, respectively. (A-C) UV-VIS spectra. (D-K) SEM images. (A) Gold nanorods growth at different SA concentrations, (B) different FSA concentrations, and (C) different SSA concentrations. (D-F) Gold nanorods synthesized at SA:CTAB ratio 0.1, 0.2, and 0.4, respectively. The measured nanorod dimensions are: 32 ± 3 × 11 ± 2 nm, 42 ± 4 × 15 ± 2 nm, 30 ± 3 × 18 ± 2 nm, respectively. (G) Gold nanorods synthesized in the presence of CTAB only. (H,I) Gold nanorods synthesized at FSA:CTAB ratio of 0.2 and 0.4, respectively. The measured nanorod dimensions are: (H) 53 ±
$3 \times 13 \pm 1$ nm and (I) $41 \pm 6 \times 17 \pm 2$ nm. (J,K) Gold nanorods synthesized at SSA:CTAB ratio of 0.2 and 0.4, respectively. The measured nanorod dimensions are: (J) $65 \pm 5 \times 13 \pm 1$ nm and (K) $44 \pm 5 \times 23 \pm 2$ nm.

First, we examined Pd overgrowth on AuNRs synthesized at the optimal additive concentrations. Figure 2.2.A shows the Pd overgrowth on FSA-assisted AuNRs (10 mM FSA, or FSA:CTAB = 0.2) at different Pd:Au ratios. As the Pd concentration was increased, the longitudinal SPR band red-shifted first, indicating an increase of the aspect ratio of the particles due to Pd overgrowth. It suggests the selective growth of Pd at the ends of AuNRs. Here, the Pd:Au ratio is the theoretical molar ratio added into the growth solution assuming the reduction reactions are complete. Further addition of Pd damped the longitudinal SPR peak. Eventually, the longitudinal SPR peak blue-shifted, broadened, and further damped at high Pd concentrations, indicating the decrease of the aspect ratio and possibly the complete wrap up of the AuNRs by Pd. The same growing trend can be identified in the corresponding SEM images (Figure 2.2.C-E). At low Pd concentrations, Pd filled in the ends and corners of the AuNRs first, giving high reflectivity at both AuNR ends (Figure 2.2.CD). At high Pd concentrations, the particle grew into a cuboid shape, indicating a core-shell structure (Figure 2.2.E). Furthermore, elemental analysis shown in Figure 2.2.F also demonstrates the selective reduction of Pd at AuNR ends at a Pd:Au of 0.2. When the Pd concentration was increased to Pd:Au = 5:1, the overgrowth of Pd was complete and a core-shell particle formed (Figure 2.2.G).

Figures 2.2.B and 2.2.H-J show the UV-VIS spectra and the corresponding SEM images, respectively, for Pd overgrowth on SSA-assisted AuNRs. Similar trend can be found for Pd overgrowth on AuNRs synthesized at optimal SSA concentrations (SSA:CTAB = 0.2).

In summary, for both FSA- and SSA-AuNRs synthesized at optimal additive concentrations (additive:CTAB = 0.2), Pd first grew on the ends of the AuNRs, possibly for the
Figure 2.2. Pd overgrowth on AuNRs in the presence of optimal concentrations of SA family additives. (A,B) UV-VIS spectra of FSA- and SSA-assisted overgrowth of Pd on AuNRs, respectively. (C-E) SEM of Pd overgrowth on AuNRs in the presence of FSA with a Pd:Au ratio at 0.05, 0.2, and 5, respectively. FSA:CTAB ratio was 0.2. (F,G) EDX mapping of Pd and Au at Pd:Au ratio at 0.2 and 5, respectively. (H-J) SEM of Pd overgrowth on AuNRs in the presence of SSA with a Pd:Au ratio at 0.05, 0.2, and 5, respectively. SSA:CTAB ratio was 0.2.

The same reason that AuNRs elongated during the AuNR growth step. The additive-CTAB interaction favored a loose coating structure at the AuNR ends, which allowed the trafficking and subsequent reduction of Pd ions at the nanorod ends. However, the anisotropic growth of Pd was quickly lost, possibly because CTAB did not form a tight bilayer on Pd surface. The exposure of the Pd to the solution was demonstrated by its catalytic activity discussed in the later part of this manuscript. In the excess amount of Pd, it spread to the middle part of the nanorods, forming a core-shell particle.

2.3.3 Pd deposition on AuNRs synthesized at high and very high additive concentrations

For the AuNRs synthesized at higher organic additive concentrations, the preference of Pd growth at AuNR ends was gradually lost. Figure 2.3 shows the Pd overgrowth on AuNRs synthesized in the presence of 20 mM FSA and SSA (or, additive:CTAB = 0.4), respectively. The UV-VIS spectra show that the longitudinal SPR band red-shifted first, and then damped and blue-
shifted as Pd concentration was increased. This shows a similar trend as those nanorods synthesized at optimal additive concentrations, indicating that the overgrowth of Pd on AuNRs still started mainly from the ends. A close examination of the EDX images (Figures 2.3.B-C) discloses that at low Pd concentrations (Pd:Au = 0.125, and 0.25, respectively), Pd tended to distribute on the ends but also on the surface of the middle portion of the nanorod, indicating that Pd nucleation was relatively randomized. As Pd concentration was further increased so that Pd:Au over 1, the longitudinal SPR peak further blue-shifted and damped as expected: the excessive Pd covered the AuNRs completely and dampened AuNR SPRs.

**Figure 2.3.** Pd overgrowth on AuNRs in the presence of high concentrations of SA family additives. Additive:CTAB ratio was 0.4 for all figures. (A-C) FSA-assisted overgrowth of Pd on AuNRs. (D-F) SSA-assisted overgrowth of Pd on Au. (A,D) UV-VIS spectra at different Pd:Au ratios. (B,C) EDX mapping of Pd and Au at Pd:Au ratio at 0.125 and 0.25, respectively. (E, F) EDX mapping of Pd and Au at Pd:Au ratio at 0.25 and 0.5, respectively.
Similar trend can also be found for the overgrowth of Pd on SSA-nanorods synthesized at high SSA concentrations (Figures 2.3.D-F). When the additive concentration was further increased in AuNR growth, e.g., 33 mM FSA (or, FSA:CTAB = 0.67), AuNRs completely lost the preference for Pd nucleation at the ends. The AuNRs grew into a core-shell structure directly at medium Pd: Au ratio of 0.4 (Figure 2.4).

**Figure 2.4.** Pd overgrowth on AuNRs in the presence of very high concentrations of FSA. FSA:CTAB ratio was 0.67 for all figures. (A) UV-VIS. (B) EDX mapping of Pd: Au 0.4.

### 2.3.4 The effect of SA family additives on selective overgrowth on AuNRs

Above study shows that optimal amount of the SA family additives helps the selective growth at the ends of AuNRs for both Au and Pd. The difference between the overgrowth of Au and Pd is that Au can continuously grow on the AuNR ends and form a long rod at optimal additive concentrations; however, the anisotropic growth of Pd is quickly lost. This is possibly because the tight CTAB bilayer structure does not form on Pd surface. As a result, overfeeding Pd always grows the nanorod into a core-shell particle.

As the additive concentration increases in the Pd overgrowth step, the selective overgrowth is gradually lost. It is likely that excessive additive disrupts the CTAB layer so that the Pd
nucleation is randomized on the surface of the particle, which later grows into a thick Pd coating in the excess amount of Pd. It is possible that such randomized Pd nucleation also happens for the nanorods synthesized at optimal additive concentrations. However, since the overgrowth is kinetically controlled, most Pd is localized at the ends of AuNRs when Pd is limited.

For FSA- and SSA-assisted AuNRs, they show little difference in the selective overgrowth of Pd at the ends of AuNRs. Thus, although one of the additives is charged while the other is not, the interactions between the additive and the CTAB layer are similar for the two types of additives. They both favor a coating structure that allows Pd to diffuse into the coatings and deposit on Au surface (Scheme 1B).

2.3.5 Catalytic Reduction Reaction of Resazurin

Finally, the catalytic activity of both types of Pd-end-capped AuNRs using FSA and SSA as additives was tested through the model reduction reaction of resazurin into resorufin (Figure 2.5.A). Resazurin reduction in the presence of aliphatic amines is an extensively used method for cell viability test, bacterial growth, etc.\textsuperscript{34} The reduction of resazurin to resorufin can also take place in the presence of hydrazine as the reducing agent; however, the reduction rate is very slow in the absence of a catalyst. In the presence of a catalyst, e.g., small gold nanoparticles, the reaction rate can be enhanced greatly.\textsuperscript{35} Here, we used the Pd-end-capped AuNRs to catalyze this reduction reaction. Figure 5B shows an example of the UV-VIS absorption change as the reaction proceeds in the presence of a catalyst. Both types of Pd-end-capped AuNRs, FSA- and SSA-assisted, showed reactivity in this reaction. The reaction kinetics as measured using the material absorption are in Figure 2.5.C for FSA-assisted and in Figure 2.5.D for SSA-assisted AuNRs.
Both types of nanorods have a Pd loading of Pd:Au = 0.25. Both types of Pd-end-capped AuNR showed catalytic activity, suggesting that the catalytic metal Pd is exposed or partially exposed to the solvent.

**Figure 2.5.** Resazurin reaction kinetics catalyzed by Pd-end-capped AuNRs. (A) Reduction reaction of resazurin to resorufin. (B) An example of the UV-VIS spectra of the reactants and products in the reactions. (C,D) Reduction kinetics in the presence of FSA-Pd-end-capped-AuNRs and SSA-Pd-end-capped-AuNRs, respectively. Reactants: resazurin (7.85 μM) in the presence of hydrazine (175 μM) and Na₂CO₃ buffer at pH 10. Nanorods: FSA/SSA:CTAB 0.1, Pd:Au = 1:4.

As a contrast, the FSA-assisted or SSA-assisted AuNRs (no Pd coating) was tested as the control. FSA-assisted AuNRs showed some reactivity (Figure 2.5.C) while the SSA-assisted AuNRs showed negligible catalytic activity (Figure 2.5.D). These experiments showed that the catalytic activity was from the Pd coated on AuNRs.
2.4 Conclusions

We demonstrated that two new hydrophilic SA family compounds, FSA and SSA, can be used as additives in synthesizing AuNRs and Pd-end-capped AuNRs. In AuNR synthesis step, the SA family additives serve as both the pre-reducing agent and the growth co-factor. At optimal additive:CTAB ratios, AuNRs grow to their longest lengths. At high additive:CTAB ratios, AuNRs loses anisotropic growth possibly because of the disruption of the CTAB layer by the excessive additive.

The FSA- and SSA-assisted AuNRs show selective overgrowth of Pd at their ends. For AuNRs synthesized at optimal additive concentrations, Pd has a high preference to grow from the ends of the AuNRs. However, the selective growth of Pd on the AuNR ends is quickly lost as more Pd is reduced, possibly because CTAB does not form a tight layer on Pd surface. Feeding more Pd will grow the particle into a core-shell structure. For AuNRs synthesized at high additive concentrations, Pd growth is randomized on AuNR surface. The nanorod will grow into a core-shell particle directly. This study gives a picture of kinetic controlled Pd overgrowth on the ends of AuNRs synthesized with SA family additives.

2.5 Experimental

2.5.1 Chemicals

HAuCl$_4$·3H$_2$O (99%), NaBH$_4$ (99%), AgNO$_3$ (99%), H$_2$PdCl$_4$ (>99%), ascorbic acid (99%), CTAB (99%), SA, FSA, SSA, and concentrated HCl were purchased from Sigma Aldrich and used as received.

2.5.2 Preparation of gold seeds

In a typical seed synthesis, 10 mL of 0.5 mM HAuCl$_4$ solution was gently mixed with 10 mL of 0.2 M CTAB solution. Then, 600 µL of 10 mM freshly made NaBH$_4$ was introduced to the
solution and mixed at drastic stirring for 2 minutes. The final solution was left undisturbed for 30 minutes prior to use.

2.5.3 Preparation of AuNRs

AuNRs were synthesized following a modified procedure by Zheng et al. For CTAB-only nanorods, proper amount of CTAB was prepared to reach a concentration of 100 mM in the growth solution. In SA-family derivative-assisted nanorod growths, the CTAB concentration was 50 mM while the SA-family derivatives varied from 1.0 mM to 50 mM. Then, 1.92 mL of 10.0 mM AgNO₃ was added to 100 mL growth solution. After keeping the mixture undisturbed for 15 minutes, 100 mL of 1.0 mM H₄AuCl₄ was mixed with the growth solution at medium stirring speed for 15 min. Then, at drastic stirring condition, 512 µL of 0.1 M ascorbic acid was added to the solution within 30 seconds. At the same stirring speed, 320 µL previously synthesized gold seeds was added and the solution was kept being stirred for an extra 30 s. The final solution was left untouched for 12 hours at room temperature. The same procedure was applied to all salicylic acid family derivatives with varied additive:CTAB ratios.

2.5.4 Overgrowth of Pd on AuNRs

To overgrow Pd on AuNRs, 10-mL of as synthesized AuNR solution was used. For different Pd loadings, H₂PdCl₄, HCl, and ascorbic acid were added in fixed proportions. For example, for a Pd:Au ratio at 0.2, 40.4 µL of 0.10 M HCl was added to the Au solution under mild stirring condition, followed by 100 µL of 0.010 M H₂PdCl₄ and 573 µL of freshly prepare 0.10 M ascorbic acid. The final solution was left undisturbed for 8 hours at room temperature.

2.5.5 Electron Microscopy

All electron micrographs were taken at the Analytical instrumentation facility (AIF). SEM and S/TEM images were collected using an FEI Verios 460L field emission scanning electron
microscope (FESEM). TEM images were collected using a JEOL 2000 electron microscope. SuperX Energy Dispersive Spectroscopy (EDX) was done using Aberration Corrected STEM-FEI Titan 80-300.
2.6 References


CHAPTER 3: Effective Photocatalytic Degradation of EPA Priority Toxic Pollutant 4-Nitrophenol with Pd-End-Capped Gold Nanorods

Manuscript in preparation
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3.1 Abstract

4-Nitrophenol (4-NP) is a priority toxic pollutant classified by the U.S. Environmental Protection Agency. Removal of 4-nitrophenol is challenging due to their high stability. Current industrial solutions include time-consuming microbial degradation and/or solid-phase extraction. We propose to use a special design of hybrid metallic particles: gold nanorods (AuNRs) end-capped with a catalytic metal for photocatalytic degradation of 4-nitrophenol. Such a special design allows us to use both hot electrons generated in the surface plasmon resonance (SPR) process and the catalytic metal efficiently. Two types of particles were tested: Pt-end-capped-AuNRs (Pt-AuNRs) and Pd-end-capped AuNRs (Pd-AuNRs). Pd-AuNR photocatalyst shows higher reactivity, indicating the importance of the catalytic center of the photocatalytic reactions. Upon near IR light irradiation, 4-nitrophenol degradation rate increased by 45 time under the Pd-AuNRs catalysis. Compared to Pd-Au core-shells, the Pd-end-capped-AuNRs showed a reaction rate ~5 times larger when the same amount of Pd was used, indicating the effectiveness of the catalyst design. Finally, we show that this reaction can take place efficiently under natural sunlight when catalyzed by the Pd-AuNRs. This study shows the effectiveness of Pd-AuNR particles in photocatalytic reaction and opens up a new way in designing photocatalysts.
3.2 Introduction

Nitrophenols are commonly used in many synthetic processes for dyes, pharmaceuticals, pesticides, and explosives, etc. Large quantities are daily handled and disposed into main water streams.\(^1\) In specific, 4-nitrophenol (4-NP) has been identified as a priority environment pollutant by the environmental protective agency (EPA) due to its high adverse impact on the aquatic lives and human health.\(^2\) The EPA has set a standard of 1.0 mg/L of phenols for their safe discharge into the surface wasters in the industrial effluents.

Current industrial treatment of the waste water includes microbial decomposition and/or solid-phase extraction, which are slow, expensive, and sometimes inefficient.\(^1,3,4,5\) Semiconductor-based photocatalysts have been tested to improve the degradation speed of nitrophenols. TiO\(_2\) is among the most used catalysts because of its low cost, high stability, and good reactivity. For example, Chen et al. demonstrated the effective degradation of 4-NP using a TiO\(_2\) suspension irradiated with 365 nm light.\(^6\) In addition, TiO\(_2\) has been used in combination with metals or inorganic or organic sensitizers to enhanced its light absorption especially in the visible range.\(^7-9\) These semiconductor-based photocatalysts have shown great promises in efficiency when irradiated with high energy photons especially in the UV range. However, their efficiency is low for the light in the visible to near-infrared (NIR) range, which makes up the most solar irradiation power.

As an alternative, metal micro- and nano-particles have been tested as the catalyst for the degradation of nitrophenols in the presence of a reducing agent.\(^10-13\) The most studied metals are Pd and Pt because of their excellent catalytic activity. Especially, bimetallic nanocatalysts, either hybrids or alloys, have been studied recently because they provide more opportunities to optimize their activity by adjusting the charge transfer between the different metals, local coordination
environment, and surface elemental distribution, etc. In addition, the amount of expensive catalytical metals Pd and Pt can be reduced. The other metals used together with Pd or Pt include Ag, Au, Fe, and Cu, etc.\textsuperscript{14-17} These catalysts showed improved reactivity in nitrophenol reduction reactions. The most relevant study to this work is that Rong \textit{et al.} synthesized gold nanorods decorated with platinum islands and studied their catalytic activity of the degradation of 4-NP. However, its photocatalytic activity was not reported.\textsuperscript{18}

Recently, we developed a method to synthesize AuNRs end-capped with a second metal and proposed to use these particles as photocatalysts. The AuNR substrate shows excellent absorption in the visible to near IR wavelengths because of its localize surface plasmon resonance (LSPR), i.e., the collective oscillation of conduction electrons upon light excitation. More importantly, hot electrons are generated in this process and can be transported to the catalytic metal surface to catalyze desired chemical reactions. It is generally believed that hot electrons are localized in a time average manner at the ends of the AuNRs. Thus, by controlling the synthetic condition of the AuNRs we can selectively overgrowth a catalytic metal, that is suitable for the degradation of 4-nitrophenol, at the ends of the AuNRs, and efficiently use the catalytic metal. As well as the hot electrons generated by light.\textsuperscript{19-23}

So far, there has been only a limited number of studies using bimetallic heterostructures as photocatalysis, largely because of the challenges in synthesizing these hetero-metallic structures at the nanoscale.\textsuperscript{24} The published studies include the “palladium tipped AuNRs” for formic acid dehydrogenation,\textsuperscript{25} and “Pt-end-capped AuNRs” for hydrogen gas production. In this study, we tested the photo-reactivity of AuNRs end-capped with Pd and Pt, respectively, under the SPR excitation conditions. We showed that such a catalyst design provides a useful new method for photocatalysis including the removal of environmental pollutants such as 4-NP.
3.3 Results and Discussion

3.3.1 Optimization of the Catalysts

We have shown that by changing the composition of the AuNR growth medium (FSA:CTAB ratio), we can control the aspect ratio of the AuNRs. However, changing the FSA fraction also has an impact on the over-growth of the second metal on the ends of AuNRs. To gain further control over the LSPR wavelength while keeping the FSA fraction constant, we optimized the AuNR growth conditions by modifying the pH of the AuNRs growth medium. Shown in Figure 3.1.A, UV-VIS absorption spectra of the synthesized AuNRs with a fixed FSA;CTAB ratio of 1:5 demonstrate a red shift of the L-SPR band associated with the pH increase in the growth medium. SEM images confirm the aspect ratio difference of these AuNRs, which ranges from 3.5 to 5.0 as the pH is decreased from 2.3 to 1.4. The resulting gold nanorods have an L-SPR wavelength of 800 nm, 860 nm, 900 nm, and 920 nm, respectively. See Table S3.1.

![Figure 3.1. Synthetic optimization AuNRs. (A) UV-VIS and (B-E) SEM images of AuNRs synthesized at pH 2.3, 1.9, 1.8, and 1.4, respectively. Corresponding aspect ratios are 3.5, 4.0, 4.2, and 4.5, respectively. Scale bars: 50 nm.](image-url)
Furthermore, selective overgrowth of the second metal Pd or Pt, at a molar ratio to gold of 1:5 (5 being gold), was achieved by guiding the reduction of the salt of the metal (H₂PdCl₄ or H₂PtCl₆, respectively) utilizing the bulky organic modifier FSA within the surfactant packing layers. We have recently demonstrated that a 5:1 mixture of cetyltrimethylammonium bromide (CTAB) to 5-formyl salicylic acid (FSA) provides a stable soft template for the selective reduction of the second metal (Pd or Pt) mainly at the end of the gold nanorods.²¹ SEM images in Figures S3.1.F and S3.1.G show the selective addition of the second metal at the ends of the AuNRs for both short (SPR 800 nm) and long AuNRs (SPR 960 nm). This supports that AuNRs synthesis in a more acidic environment leads to the growth of a higher aspect ratio nanorod without significant impact on the further reduction of the second metal.

In the case of the synthesized AuNRs with CTAB-only growth medium, the addition of Pd showed no selectivity and the Pd appeared to cover the AuNRs randomly. A 1:1 Pd to Au loading formed a complete core-shell structure (Figure S3.1.E).

### 3.3.2 4-Nitrophenol Degradation in the absence and presence of light

The effectiveness of the 4-NP photocatalytic degradation was evaluated using the long AuNRs (L-SPR = 920 nm) end-capped with Pt or Pd, respectively. The Pd- or Pt- loading was 1:5 (5 being gold). To best take advantage of the SPR process and avoid the confusion of the direct excitation of the molecules, a near IR light source emitting at 976 nm was used.

The reaction progress can be monitored by measuring the absorption spectra of the reaction mixtures including 4-nitrophenol, the product, and the nanocatalysts (Figure 3.2.A). The peak absorbance at 400 nm corresponds to the 4-nitrophenolate, while the absorption at 300 nm is contributed by the 4-NP and the product together (Figure 3.2.B). The concentration of the AuNRs in solution was 7.3 x 10⁷ particles/mL, whose absorbance is negligible in the UV-VIS spectrum.
To study the reaction kinetics, the peak absorbance at 400 nm were monitored and plotted against the reaction time. We first tested the activity of the catalysts in the dark. Figure 3.2.C shows the reaction kinetics of the solution in the presence of the long Pd-AuNRs, short Pd-AuNRs, long AuNRs-only, and no particles, respectively. The total number of particles used in the solution was $7.3 \times 10^7$. 3.3 µmol of NaBH$_4$ was used. All reactants and catalyst concentration were similar to those reported in the literature. The reaction rates also fell in the same order of magnitude of those reported in the literature using other metallic particles, with a half lifetime of the material 4-NP to be 1800 seconds.

**Figure 3.2.** Degradation of 4-nitrophenol in the presence of catalysts. (A) The chemical reaction. (B) UV-VIS spectra of the degradation kinetics using Pd-End-Capped-AuNRs as the catalyst. (C) Reaction kinetics in the dark for long AuNRs, short Pd-AuNRs, AuNRs-only, and no particles, respectively. (D) Reaction kinetics in the presence of 976 nm light (2.0 W/cm$^2$) for long Pd- AuNRs and no particles, respectively, under the same conditions except the light.
As a contrast, in the absence of metal particles, the solution kept stable for long time (hours) and no observable reaction can be detected in the first two hours. Similarly, AuNRs-only particles also showed negligible reactivity. However, an initial increase of the absorption at 400 nm was observed for the solution containing AuNRs. This increase is assigned as the signal amplification of adsorbates on gold nanoparticles, which has been previously explained as the increase of the AuNP optical cross section in the presence of the adsorbates.\textsuperscript{22} These experiments showed that the Pd-AuNRs are excellent catalysts even in the absence of the light.

When we turned on the 976 nm light under the same experimental conditions, the reaction rates increased drastically and finished in seconds (Figure 3.2.D). The reaction rate, with a halftime of 40 seconds, increased by 45 times in the presence of the near IR light with an irradiance of 2000 mW/cm\textsuperscript{2}. The reaction was so fast that its kinetics was challenging to measure. In order to capture the photocatalytic kinetics, we lowered the concentration of NaBH\textsubscript{4} by 3.3 times. The original NaBH\textsubscript{4} concentration was labeled as “high” while the NaBH\textsubscript{4} concentration was labeled as “low”.

3.3.3 4-Nitrophenol Degradation Kinetics under near IR light irradiation

We next tested the catalytic activity of AuNRs-only, Pt-AuNRs and Pd-AuNRs in the presence of low NaBH\textsubscript{4} concentration under 976 nm near IR light irradiation. All particles have an absorption plasmonic band > 900 nm (Figures S3.1). As seen in Figure 3.3.A, in the presence of 976 nm light irradiation (at 2000 mW/cm\textsuperscript{2}), both Pd- and Pt-AuNRs showed excellent photocatalytic activity. As a contrast, in the absence of the metal particles but in the presence of light, there is no observable reaction in the first 3600 seconds. In the presence of light and under the low reducing agent concentration, the photocatalytic reduction proceeded with a half lifetime of ~80 seconds for Pd-end-capped-AuNRs, and ~300 seconds for Pt-end-capped-AuNRs,
respectively. The rate of degradation of 4-NP utilizing Pd is ~4 times that of the rate for Pt-based hybrid particles. Interestingly, AuNRs-only particles also showed reactivity when being irradiated but with a much slower reaction rate (900 s half lifetime). This difference shows that the reaction center is important to the catalytic reaction in addition to the hot electron generation. Since Pd-AuNRs showed the highest reactivity, we focused on the photocatalytic activity of Pd-AuNRs in the following studies.

We then compared the photocatalytic reactivity of the long and short Pd-AuNRs. Figure 3.3.B shows the reaction kinetics for the long Pd-AuNRs, short Pd-AuNRs, and core-shell Pd-AuNRs, respectively. The long Pd-AuNRs have a higher reaction rate (~120 seconds half lifetime) than the short Pd-AuNRs (~220 seconds half lifetime), possibly caused by the larger SPR absorption of long Pd-AuNRs.

The core-shell particles show a similar reactivity as compared to that of the long Pd-AuNRs (~210 seconds half lifetime). However, considering that the core-shells contains 5 times more Pd in the solution, the reaction rate per mol of Pd is ~5 time lower than that of the end-capped particles. This shows that the catalyst design is important in the efficiency of using the hot electrons generated in the SPR process. Our previously reported studies illustrated that the reduction of Pt salt mainly happened at the ends of AuNRs. Thus, localization of the catalytic metal at the ends of AuNRs apparently can use the hot electrons most efficiently, yielding a higher reaction rate.24
Figure 3.3. Photocatalytic degradation activity. (A) Reaction kinetics for long Pd- and long Pt-end-capped-AuNRs, respectively. (B) Reaction kinetics for the long-, short-, core-shell Pd-AuNRs, and AuNRs-only, respectively. The low concentration of NaBH₄ was used and the irradiation of 976 nm light was 2.0 W/cm².

3.3.4 Influence of Near IR Irradiation on 4-NP Catalytic Photodegradation Rates

To evaluate the ability of Pd-End-Capped-AuNRs to utilized low energy photons and convert them to high energy electrons, we studied the reaction rates as a function of irradiance.
Figure 3.4. Photocatalytic degradation of 4-nitrophenol at various photo flux. (A) Kinetics using different irradiance of 2.0 W/cm², 1.5 W/cm², 975 mW/cm², and 670 mW/cm², respectively. (B) Reaction rate as a function of irradiance. Long Pd-End-Capped-AuNRs were used.

Figure 3.4.A shows the reaction kinetics at 4 different light powers using on the long Pd-End-Capped-AuNRs. The irradiance used were 2.0 W/cm², 1.5 W/cm², 975 mW/cm² and 670 mW/cm², respectively. Interestingly, the 4-NP degradation rate showed a straight line (Figure 3.4.B), indicating the linear relationship between the photon flux and the reaction rate. This observation is consistent with our earlier reported H₂ production on Pt-AuNRs, which also showed a linear relationship. However, why this happens is still under investigation because it is inconsistent with the prediction based on Fermi-Dirac model of the hot electron energy distribution.
3.3.5 Reaction Order with Respect to Catalyst Concentration

The reaction rate as a function of the catalyst concentration was also studied using the long Pd-End-Capped-AuNRs. All experiments were carried out using the same type of particles (Pd-AuNRs with a Pd:Au ratio of 1:5). Figure S3.2 shows the reaction rate as a function of catalyst concentration, which showed a straight line. This indicates that this is a first order reaction with respect to the catalyst concentration, in which simple collisions between the particle and the material molecule can cause the reaction.25

![Graph showing reaction rate as a function of catalyst concentration.](image)

**Figure 3.5.** Photocatalytic degradation of 4-NP using natural sun light. Long Pd-End-Capped-AuNRs was tested. The natural sun light was measured to be ~260 mW/cm² during the ~60 min experiment.

3.3.6 Photocatalytic Degradation of 4-NP using solar irradiation

Finally, the photocatalytic activity of the long Pd-End-Capped AuNRs was tested using natural sun light. Figure 3.5 shows the 4-NP degradation kinetics over time, with a half reaction time of ~120 seconds. The solar irradiance was measured to be 260 mW/cm² on average over a 60 minutes period. The entire solution was irradiated, whereas for near IR light experiments, only a 1/5 of the solution was irradiated. Compared to the measurements in the dark, there is a degradation
rate enhancement of 20 times, demonstrating high photocatalytic activity using natural sun light. A control experiments using no particles showed no catalytic behavior. This shows that the particles can use the natural sun light to catalyze the reaction.

3.4 Conclusions

Two hybrid metallic particles, Pt- and Pd-end-capped AuNRs were synthesized, characterized, and tested for their photocatalytic activity to decompose 4-nitrophenol in the presence of a reducing agent. We showed that hot electrons generated in the near IR light excited SPR process can be effectively used to catalyze the reaction in these particles with a special design. The degradation shows a first order reaction with respect to the irradiation power and the catalyst concentration. Between Pd and Pt, Pd-based photocatalyst shows higher reactivity, indicating the importance of the catalytic center of the photocatalytic reactions. Finally, we showed that this reaction can be catalyzed by natural sun light. This study demonstrated the effectiveness of hybrid bimetallic plasmonic particles in photocatalytic reactions and opens a new avenue in designing photocatalysts.

3.5 Experimental

3.5.1 Synthesis of Catalysts

Anisotropic gold nanorods (AuNRs) capped with a second metal are synthesized in a multistep process. This process entails the synthesis of gold seeds, preparation of the growing media and AuNRs growth, and capping of the AuNRs with a second metal. This entire synthetic process is adapted from procedure previously studied. Gold Seeds were prepared first by gently mixing 5.0 mL of 0.5 mM HAuCl₄ solution and 5.0 mL of 0.2 M CTAB solution. Next, 600 µL of 10.0 mM freshly made NaBH₄ was added. The solution was mixed at 1200 RPM for 2 minutes and left undisturbed for 30 minutes prior to use. LSPR-tunable-AuNRs: AuNRs with various
aspect ratios were synthesized as follows: a 100 mL growing medium solution containing 10.0 mM 5-FSA and 50.0 mM CTAB was prepared (clear), 1.92 mL of 10.0 mM AgNO₃ was added to the growing medium and left undisturbed for 15 minutes. Next, a 100 mL solution of 1.0 mM HAuCl₄·6H₂O is added to the growing medium and stirred at 400 RPM for 90 minutes (pale yellow). To promote growth variation (different aspect ratios) a 1.0 M HCl solution was added drop wise to lower the pH to 1.6, see Table S3.1 for other pH values explored, and for summary of experimental conditions, Table S3.2. Then, 512 μL of 0.10 M ascorbic acid was added to the solution and mixed at 1200 RPM for 30 seconds.

Lastly, maintaining the same stirring rate, a 320 μL aliquot of the previously synthesized gold seeds was added. The final solution is left undisturbed for 12 hours at 30 °C. **CTAB only AuNRs** (use to synthesize Core-Shell-AuNRs): the same procedure is followed with two exemptions: the growing medium contains 100 mL of 0.1 M CTAB, not FSA, and there is no addition of HCl step. **End-Capped-AuNRs:** selective localization of a second metal (M) at the end of the gold nanorods can be done by taking a 10.0 mL aliquot of the previously synthesized **LSPR-tunable-AuNRs** is place in a glass vial under stirring at 400 RPM. Following, set amounts of HCl, H₂PtCl₆ for Pt and H₂PdCl₄ for Pd, and Ascorbic Acid were added. See table S2 for details. Briefly, for a Pd:Au ratio 0.2, 40.4 μL of 0.10 M HCl was added. Next, 100 μL of 10.0 mM H₂PdCl₄ were added and stirred for 10 minutes. Lastly, 573 μL of 0.10 M Ascorbic Acid was added dropwise.

The final solution is left undisturbed for 8 hours at 30.0 °C. **Core-Shell-AuNRs:** Complete coating of the AuNRs with a second metal can be done by using the as synthesized **CTAB only AuNRs**. In a 1 to 1 molar ratio of M:Au, to ensure full coating, the procedure is as follows: place 10.0 mL aliquot of as synthesized **CTAB only AuNRs** in a glass vial and stirred at 400 RPM, 404 μL of 0.10 M HCl were added, followed by 1000 μL of H₂PdCl₄, the solution is stirred for 10
minutes. Lastly, 5.73 mL of 0.10 M ascorbic acid was added dropwise. The final solution is left undisturbed at 30.0 °C for 8 hours. **Pd Only Particles:** nucleation of pd only nanoparticles were done by mixing 2.5 mL of 10.0 mM solution of H$_2$PdCl$_4$, 2.5 mL of 0.2 M CTAB at 400 RPM. Next, 10.0 mM solution of NaCl was added dropwise, the solution is stirred for 15 minutes. Lastly, 2.5 mL solution of freshly prepared 0.1 M NaBH$_4$ was added under stirring at 1200 RPM. The final solution was left undisturbed for 4 hours.

All synthesized particles underwent a centrifugation/cleaning step to remove unreacted ions and excess of surfactant in solution. This cleaning step involves centrifugation of the particles at 17 G for 3.0 minutes three times. All synthesized particles are suspended to their original volume with high grade deionized water.

### 3.5.2 Catalyst Characterization

All the catalyst structural characterization was performed at the Analytical Instrumentation Facility (AIF) using a FEI Verios 460L field emission scanning electron microscope (FESEM). Optical characterization and kinetics studies were done using a Shimadzu UV-VIS 2600 spectrometer.

### 3.5.3 Catalyst Evaluation

Photodegradation of 4-Nitrophenol (4-NP) was carried out in a polycrimide cuvette. A total volume of 3.0 mL of aqueous solution containing 20 µL of 10 mM 4-nitrophenol, 100 µL of the synthesized catalyst and 100 µL of 10.0 mM NaBH$_4$, unless otherwise noted (high concentration experiment 330 µL of 10.0 mM NaBH$_4$). Activation of the catalyst is done utilizing natural solar irradiance with an average power measured at 220 ± 40 mW. A 976 nm irradiation from a continuous wave laser (MDL-III, Dragon lasers), with a set power at 670 mW, 975 mW, 1575 mW vents.
and 2000 mW. The total illumination area was 1.0 cm$^2$, with only 1/5 of the solution being illuminated. All power measurements were done using a Coherent PowerMax P30 power meter.
3.6 References


3.7 Associated Content

Figure S3.1. Catalytic Material. (A) UV-VIS. (B-G) SEM images of synthesized AuNRs. (B-D) Gold nanorods. Measurements of the long axis are as follows: CTAB-only AuNRs: 32 ± 15 nm; short AuNRs: 42 ± 8 nm, long AuNRs: 57 ± 11 nm. (E-G) AuNRs modified with Pd. The long axis: 45 ± 16 nm, 51 ± 13 nm and 61 ± 9 nm respectively. The reported numbers were average from 25 particles. Scale bars: 50 nm.
Figure S3.2. Reaction rate as a function of catalyst. Catalyst concentration $7.3 \times 10^7$ particles/mL.
Table S3.1. Optimization of pH of the growing medium. LSPR and aspect ratio of the corresponding AuNRs.

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<th>Aspect Ratio</th>
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Table S3.2. Synthetic conditions for Pd-End-Capped-AuNRs.

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<th>0.1 M Ascorbic Acid (mL)</th>
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</tr>
</tbody>
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CHAPTER 4: Harnessing Hot Electrons from Near IR Light for Hydrogen Production Using Pt-End-Capped-AuNRs

The following work was reprinted with permission from: Nathalia Ortiz, a Brandon Zoellner, a Soung Joung Hong, a Yue Ji, a Wang Tao, a Yang Liu, b Paul Maggard, a,* and Gufeng Wang a,*

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4.1 Abstract

Gold nanorods show great potential in harvesting natural sun light and the generation of hot charge carriers that can be employed to produce electrical or chemical energies. We show that photochemical reduction of Pt(IV) to Pt metal mainly takes place at the ends of gold nanorods (AuNRs), suggesting photon-induced hot electrons are generated, or localized in a time-averaged manner, at AuNR ends. To use these hot electrons efficiently, a novel synthetic method to selectively overgrow Pt at the ends of AuNRs has been developed. These Pt-end-capped AuNRs show relatively high activity for the production of hydrogen gas using artificial white light, natural sun light, and more importantly, near IR light at 976 nm. Tuning of the surface plasmon resonance (SPR) wavelength of AuNRs changes the hydrogen gas production rate, indicating that SPR is involved in hot electron generation and photo-reduction of hydrogen ions. This study shows that gold nanorods are excellent for converting low energy photons in to high energy hot electrons, which can be used to drive chemical reactions at their surfaces.
4.2 Introduction

Molecular hydrogen is an ideal chemical energy carrier that is clean, has high energy density, and can be conveniently transported and stored.\textsuperscript{1-6} Using solar energy to produce hydrogen from water is one of the most attractive yet challenging reactions in converting solar energy into chemical energy.

Photocatalysts are needed to drive hydrogen gas production from sunlight. The photocatalysis reaction consists of three primary steps: photoexcitation and the generation of electron (e\textsuperscript{-}) and hole (h\textsuperscript{+}) pairs; charge separation and transport to the catalyst surfaces; and electron transfer at the surface for driving a redox reaction. The photocatalytic efficiency is impacted by three key factors: amount of light absorption, efficiency of charge separation, and surface reaction rates. In addition, the required photon energy for splitting water and generating hydrogen gas must be greater than the thermodynamic difference between the water reduction and oxidation potentials, i.e. \textasciitilde1.23 eV at room temperature.\textsuperscript{7,8} About 70\% of photons from solar irradiation have an energy greater than the required value.\textsuperscript{1} For most current semiconductor-based photocatalysts, e.g., TiO\textsubscript{2}, the band gap is too large, \textasciitilde3.0 eV, thereby reducing the fraction of the “useful” photons from solar irradiation.\textsuperscript{9}

Recently, the surface plasmon resonance (SPR) effect of plasmonic nanoparticles, e.g., Au nanoparticles (AuNP), has been investigated for its utility for driving heterogeneous photocatalysis.\textsuperscript{10-12} SPR can be described as the collective oscillation of conduction band electrons excited by light. At the SPR wavelength, the optical cross-sections of the particles are greatly enhanced, allowing efficient light absorption. This is very important for solar light harvesting as the photon flux from the sun is a fairly diffuse energy source, with an intensity on the order of
magnitude of ~100 mW/cm². Using Au or Ag nanoparticles as antennas, the efficiency of light absorption can be greatly improved.

More importantly, high energy “hot electrons” are being generated during the SPR process in plasmonic materials, which can participate in the chemical reactions on the particle surface. Hot electrons refer to the electrons with energy above the Fermi level.¹⁰,¹³ There are many studies showing that for noble-metal nanoparticle catalysts, as well as their hybrid systems with semiconductors, the catalytic activities are greatly enhanced by illumination at their SPR wavelength(s).¹³-²³ How the catalytic reactivity is enhanced on the plasmonic nanoparticle surface in the presence of light irradiation is still under intense investigation, and likely varies case-by-case. Generally, it is viewed that SPR can enhance photon-driven chemical reactions through two possible mechanisms: (1) the photothermal effect, i.e., the reaction is thermally activated or expedited by the hot lattice induced by electron-phonon scattering;¹⁴-¹⁶ and more interestingly, (2) “hot” charge carrier-induced reaction. In this latter pathway, the coherent electron oscillation induced by the oscillating electric field at SPR frequency is quickly damped to form electron-hole pairs.²⁴,²⁵ The hot charge carriers can then be transferred to the metal surface and the adsorbate molecules directly or indirectly, inducing the chemical reactions.¹⁰,¹³,²⁶ Especially, the excited electron gas in the nanoparticle initially would adiabatically establish an equilibrium with a mean temperature of several thousands of degrees. Thus, high energy hot electrons (photon energy larger than that at the SPR frequency) are produced in the SPR process even when the particle is excited by low energy photons.¹² The production of high energy hot electrons makes it possible for many reactions with a high activation energy barrier to move forward.

While AuNPs themselves are not active photocatalysts, it is thus necessary to integrate a second type of metal, e.g., Pt, into the plasmonic nanostructures to facilitate hydrogen gas
generation. The most frequently used metal for hydrogen formation is Pt.\textsuperscript{19,23,27} Ideally, depositing the Pt metal selectively over the surface areas where hot electrons are generated and/or distributed will be most effective. This also most efficiently utilizes the precious metal and causes minimal interference or damping of the SPR within the plasmonic nanostructures.

However, how the hot electrons are generated and distributed in the plasmonic particle, as well as how they are transported to surface and participate in chemical reactions, still has not been clearly elucidated. Note here that “distribution” means the time averaged distribution, as the hot electrons are very shortly lived and highly dynamic under an oscillating external electric field. It is generally conjectured that the hot electrons are more likely to be generated, and/or distributed, at the “hot” spots – where the near-field electric fields are greatly enhanced (e.g., the ends of gold nanorods). There are experiments suggesting this is the case, though controversy exists as there has not been conclusive evidence. For example, it has been shown that the photoluminescence hot spots correlate with the photochemical reaction hot spots on gold particle surface.\textsuperscript{25} However, the surface site reactivity may also be affected by the surface defects and lattice structures.\textsuperscript{28} The complexity of the problem shows that there is still much yet to be understood regarding the generation and distribution of hot electrons.

In this study, the reductive hot spots on gold nanorods (AuNRs) under light illumination were investigated, as well as depositing Pt at the hot spots for the purpose of hydrogen gas production. AuNRs are especially useful because they have tunable SPR wavelengths from visible to near IR ranges.\textsuperscript{29-31} By tuning the SPR wavelength to \(~\text{1000 nm}\) or longer, a highly tunable system is obtained that can efficiently use low energy photons to generate high energy hot electrons for hydrogen gas production.
4.3 Results and Discussion

4.3.1 Photochemical reduction of Pt(IV) on AuNRs

To determine the locations of the reactive hot spots under photo-illumination, the photon-induced reduction of Pt onto the AuNR surface was performed. The AuNRs were synthesized using our recently established method: a cetyltrimethylammonium bromide (CTAB) and 5-formyl-salicylic acid (FSA) mixture (FSA:CTAB = 1:5) was utilized as the capping ligands in seed-mediated growth. The resulting nanorods have an aspect ratio of ~4 and an SPR wavelength at 830 nm (SEM image in Figure 4.1.A). Since the tight packing of the ligands on AuNRs plays an important role on the growth of AuNRs and the overgrowth of a second metal on AuNRs as will be discussed in the next section, the particles were then cleaned 3 times using DI water to remove as much ligands as possible from the AuNR surfaces.

Figure 4.1. Photo-reduction of Pt on AuNRs. (A) SEM image for AuNRs before photo-reduction. (B) After photo-reduction of Pt metal. (C) EDX mapping of Pt photo-reduced on AuNRs with a theoretical Pt:Au ratio of 1:5. Scale bar: 10 nm. EDX Images taken by Dr. Yang Liu.
Results show that after cleaning, the overgrowth of chemically reduced Pt on cleaned AuNRs lost directionality and only yielded block-like particles with a uniform layer of Pt on AuNR surface (Supplementary Figure S4.1). This indicates that the tight packing of the ligands over the AuNR surface is lost and most of the particle surface is exposed to the solvent after washing.

The cleaned AuNRs were then exposed to artificial white light (280-950 nm, 800 mW/cm²) in the presence of H₂PtCl₆. Methanol was used as the sacrificial agent for the oxidation half reaction. After irradiation under white light for 6 hours, the particles were then characterized by SEM and EDX. As shown in the SEM images, the ends of the AuNRs changed from a round shape to a more flat, slightly expanded shape with greater reflectivity, indicating that Pt was deposited onto the AuNR ends (Figures 4.1.A-B). EDX images show the presence of Pt metal, which is predominantly deposited at the AuNR ends (Figure 4.1.C; for the longitudinal Pt distribution of an example, see Supplementary Figure S4.2).

As a contrast, in the absence of light illumination, the mixture of AuNRs, methanol, and Pt salt remained stable for a long time (months) in the dark, indicating that the Pt reduction requires light irradiation. Also, Pt reduction potential is more negative than that of Au both in the absence and presence of Cl⁻. Thus, the galvanic replacement reaction (i.e., Au metal oxidized and Pt reduced) is not spontaneous. In another control experiment, a Pt(IV) salt solution with the sacrificial agent methanol being illuminated under the same conditions showed no UV-VIS change after 6 hours, indicating Pt salt will not be reduced in the absence of AuNRs.

These experimental results confirm that: (1) Pt was photo-reduced at AuNRs due to the hot electrons generated in the SPR excitation of AuNRs; and (2) the photo-reductive sites were localized at AuNR ends, indicating that hot electrons are more likely distributed (in a time-average manner) at the AuNR ends.
4.3.2 Pt-end-capped-AuNRs synthesis

To more efficiently utilize the hot electrons, Pt metal was selectively overgrown onto the AuNR ends using a new protocol developed in our lab. Currently, the selective decoration of AuNRs with a second metal is still challenging. \(^\text{31}\) Recent developments include the addition of organic modifiers to alter the packing of the main surfactant (CTAB) on different locations of the AuNRs so that anisotropic overgrowth can be achieved. \(^\text{27,32}\) We recently have shown that using salicylic acid derivatives 5-sulfo- and 5-formyl salicylic acids, the aspect ratio of gold nanorods can be controlled, as well as for selectively depositing Pd on the ends of the AuNRs. In this study, we found that using FSA as the organic modifier with a slightly tuned procedure, Pt can be selectively overgrown over both ends of AuNRs.

![Figure 4.2. Pt overgrowth on gold nanorods synthesized in the presence of 0.2 molar ratio of FSA:CTAB. (A-F) Regular AuNRs with different Pt loadings. (A) UV-VIS. (B-F) SEM images. Scale bars: 50 nm. The Pt:Au ratio was 0.05, 0.1, 0.2, 0.5 and 1.0, respectively. (G-M) High ASR AuNRs with different Pt loadings. (G) UV-VIS. (H-M) SEM images. Scale bars: 50 nm. The]
Pt:Au ratio was 0, 0.05, 0.1, 0.2, 0.5 and 1.0, respectively. The measured uncapped AuNRs are $(41 \pm 8) \times (10 \pm 2)$ nm for Figure 4.1.A and $(55 \pm 5) \times (11 \pm 1)$ nm for Figure 4.2.H, respectively.

Figures 4.2.A-F show the UV-VIS spectra and SEM images of as synthesized Pt-end-capped AuNRs with different Pt loadings. It is clear that un-capped AuNRs show normal rounded end shapes. As the Pt was reduced, a granular Pt coverage can be identified on the AuNR surface. The nanorods show slightly expanded ends with more reflectivity (Figure 4.2.B vs. 4.1.A), indicating Pt was selectively deposited on to the ends of AuNRs. As the Pt:Au ratio was increased to 0.5, the nanoparticles become dog-bone shaped particles (Figure 4.2.E). The UV-VIS shows that the longitudinal SPR started from ~830 nm for un-capped particles, and gradually shifted to the red end (>1000 nm) and damped, possibly indicating the increase of the aspect ratio (ASR) of the particle and the damping by Pt on AuNR SPR. The damping by Pt is expected in the presence of the added Pt-Au interface. At a Pt:Au ratio 1:1, the SPR peak blue shifted back to 900 nm as the deposition of Pt grows toward the middle portion of the nanorod, leading to a smaller ASR.

**Table 4.1.** Theoretical and experimental Pt:Au ratios for the high aspect ratio Pt-end-capped AuNRs.

<table>
<thead>
<tr>
<th>Nominal Molar Pt:Au</th>
<th>Theoretical weight %</th>
<th>Experimental weight %</th>
<th>Standard deviation (%)</th>
<th>Experimental Molar Pt:Au</th>
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<tbody>
<tr>
<td></td>
<td>Au</td>
<td>Pt</td>
<td>Au</td>
<td>Pt</td>
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<tr>
<td>1:20</td>
<td>95.4</td>
<td>4.6</td>
<td>95.8</td>
<td>4.2</td>
</tr>
<tr>
<td>1:10</td>
<td>91.0</td>
<td>9.0</td>
<td>91.4</td>
<td>8.6</td>
</tr>
<tr>
<td>1:5</td>
<td>83.4</td>
<td>16.6</td>
<td>84.0</td>
<td>16.0</td>
</tr>
<tr>
<td>1:2</td>
<td>66.6</td>
<td>33.4</td>
<td>72.7</td>
<td>27.3</td>
</tr>
<tr>
<td>1:1</td>
<td>50.0</td>
<td>50.0</td>
<td>70.6</td>
<td>29.4</td>
</tr>
</tbody>
</table>
To investigate the utilization of low energy photons in the near IR range, the synthetic procedures were tuned in order to synthesize AuNRs with a higher aspect ratio (ASR~5, or SPR 880 nm). This was achieved by adjusting the pH of the AuNR growth solution to 1.2 using a small amount of HCl. It has been demonstrated that nanorods with a larger ASR can be synthesized at low pH conditions. The remaining procedures of end-capping Pt on AuNRs were kept the same. Figures 4.2.G-M show the UV-VIS and SEM images of AuNRs with higher aspect ratios. The SEM images show that under acidic condition, AuNRs grew longer, giving an ASR of ~5. Similarly, during the Pt overgrowth stage, Pt was also deposited at the ends of AuNRs, forming a dog bone-like shape. The UV-VIS spectra reveal that the longitudinal SPR starts at 880 nm and quickly red-shifts to ~1000 nm at Pt:Au ratios of 0.05~0.2. Increasing the Pt:Au ratio to 0.5~1, the SPR further shifts to ~1200 nm. Damping of the longitudinal SPR was also observed for these relatively longer rods.

In the particle synthesis, the nominal Pt:Au ratio was calculated assuming that all the metal ions were reduced in both the AuNR growth and the Pt overgrowth steps. To check whether this is true, we first estimated the Au reduction efficiency by comparing the actual particle concentration with the theoretical particle concentration assuming 100% reduction of Au ions. Practically, the estimation was done using SEM imaging. The as synthesized particle solution was concentrated by a factor of 2.86 (1.0 mL to 350 μL). 1 μL of the concentrated solution was dropped to the silicon substrate to form a circle with a diameter of 1.6 mm. The particles were imaged, which gives a surface concentration of ~1050 particles per μm² (Supplementary Figure S4.3). That gives a concentration of $7.4 \times 10^{11}$ particle/mL in the solution, which is similar to the theoretical concentration ($7.6 \times 10^{11}$ particle/mL) if we assume Au is 100% reduced. This is consistent with
the literature reports that Au will be nearly 100% converted to nanoparticles under similar conditions.\textsuperscript{35} Thus, it is reasonable to assume that all Au is reduced.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.jpg}
\caption{H\textsubscript{2} gas production kinetics under artificial white light and natural sun light irradiation. (A) Artificial white light irradiation provided by a Xe lamp at 280-950 nm with a power of 300 mW/cm\textsuperscript{2}. (B) Natural sun light irradiation. The sun light power varied between 190-260 mW/cm\textsuperscript{2}.}
\end{figure}

Next, we estimated the Pt and Au weight fractions using EDX imaging for clusters of particles (>20) and individual particles. Since we will focus on the hydrogen production under near IR light illumination, we only measured those high aspect ratio nanorods. EDX maps of individual nanorods are shown in Supplementary Figure S4.4. The Pt:Au experimental ratios are presented in Table 1. The average and standard deviation were from the measurement of clusters
containing > 20 particles. For low Pt:Au ratios (1:20, 1:10, 1:5), the Pt fraction is fairly consistent with the anticipated values. However, for high Pt:Au ratios, the Pt fraction is significantly less. The actual ratios are 1:2.66 for the nominal 1:2, and 1:2.4 for the nominal 1:1, respectively. Thus, the assumption that Pt is all reduced is only valid for low Pt:Au ratios (<1:5).

These results confirmed that Pt-end-capped-AuNR can be grown with different aspect ratios by tuning the synthetic protocols. To differentiate the two types of nanorods, the long nanorods are labeled as high ASR AuNRs while the short ones are labeled as regular AuNRs herein. For comparison, core-shell Pt-Au nanorods were synthesized using the conventional method where the growing medium contains only CTAB ligand. The Pt:Au ratio was 1:1 (Supplementary Figure S4.5). In the absence of the organic modifier FSA, the AuNRs are shorter; overgrowth of Pt on these shorter AuNRs leads to a core-shell type structure.

4.3.3 Photocatalytic activity and H₂ production

Next, the photocatalytic activity of both the regular and high ASR nanorods for hydrogen gas generation were investigated using artificial white light. Briefly, the Pt-end-capped-AuNRs were washed three times with DI water to remove excessive surfactants and unreacted ions in the solution. The nominal Pt:Au ratio was 1:10. Methanol (20% v/v) was used as the sacrificial agent. The particle solution was purged with N₂ and then irradiated under artificial white light from a Xe lamp (280-950 nm optically filtered, 300 mW/cm²). Each reactor contained 0.370 μmol Au and 0.037 μmol Pt.

Both samples show significant amount of gas being produced after light exposure and the hydrogen production was confirmed using gas chromatography for each run (for an example, see Supplementary Figure S4.6). The other half of the reaction is the oxidation of the methanol to
formaldehyde/formic acid, which was confirmed using Tollen’s test.\textsuperscript{36} No significant amount of CO\textsubscript{2} was detected in the product using gas chromatography.

Figure 4.3.A shows the hydrogen gas production from both the regular and high ASR Pt-end-capped-AuNRs. The error bars for the amount of hydrogen production were from 3 replicates. Both the regular and high ASR Pt-AuNR nano-catalysts showed significant activity over the first 20 min. The initial reaction rate was 8.1 and 7.1 H\textsubscript{2} molecules/Pt atom/min in the first 10 min for high ASR and regular Pt-end-capped AuNRs, respectively. Over ~40 minutes, each Pt atom produced ~150 H\textsubscript{2} molecules on average. For both regular and high ASR nanorods, their initial reaction rates and the total turnover numbers were similar, indicating their photocatalytic rates under white light are similar. Note that the initial reaction rate and the total H\textsubscript{2} production of our catalysts are comparable, or better than catalysts with similar structures in the literature. For example, Majima and coworkers reported producing ~2 \( \mu \)mol H\textsubscript{2} gas in a couple of hours with a similar Pt-tipped-Au nanorod catalyst (0.188 mg Au, Pt:Au = 1:3).\textsuperscript{27} Here, we are using 0.073 mg Au (Pt:Au =1:10) producing ~6 \( \mu \)mol H\textsubscript{2} gas in ~40 min.

The photon-driven catalytic activity of both regular and high ASR Pt-AuNRs was, however, lost after producing ~150 hydrogen molecules per Pt atom. There are several possible reasons that are responsible for this loss of reactivity. (1) The aggregation of the particles after reaction. Particle aggregation does occur, which can be identified by the partial loss of the solution color after reaction. However, it is only responsible for ~15\% of reactivity loss (See the UV-VIS in Supplementary Figure S4.7). (2) Surface morphological changes due to light illumination and local heating. Note that the initial.

Control experiments were also performed, including: (1) Pt-only nanoparticles; (2) Au-only nanorods; and (3) Pt-Au core-shell nanoparticles. Pt particles were produced by reducing Pt
salt using NaBH₄ directly. These have an average diameter of ~20 nm with different shapes (Supplementary Figure S4.9). The Pt nanoparticles showed little activity for producing H₂ gas upon white light illumination. The AuNRs with large ASR also showed activity in reducing H⁺ ions to hydrogen gas. However, their production rate and total cycles are not comparable to those of Pt-end-capped-AuNRs. It is possible that Au itself is not a good catalyst for producing hydrogen gas so that the production rate is low. As a consequence, their total cycle times are also limited before they are being damaged by light. Pt-Au core-shell nanoparticles were also tested, wherein the AuNRs were made using CTAB-only ligands and the Pt:Au ratio was 1:1 (Supplementary Figure S5). These particles showed low activity and the H₂ production rate is 0.4 H₂ molecule/Pt atom/min, ~20 times smaller than that of Pt-end-capped AuNRs per Pt atom per min. The low reactivity likely occurs because the damping of the SPR (Supplementary Figure S4.5.C) and the coating of the AuNRs surface by Pt so that the other half of the reaction, the oxidation of methanol, cannot proceed efficiently. These studies show that Pt-end-capped-AuNRs are active photocatalysts for transforming light into chemical energy, i.e., in the production of H₂.

4.3.4 H₂ production using solar light

The photocatalytic activity of the particles was also tested using natural sun light. Figure 4.3.B shows H₂ gas production versus time for the high ASR AuNRs (Pt:Au = 1:10). The error bars were again determined from 3 replicates. The experiments were carried out around noon, where the sun illumination power varied between 190~260 mW/cm². At this illumination power, the hydrogen gas production can be observed for the first 40 min. Again, the control (Pt-only particles) showed little activity in hydrogen gas generation. These experiments confirm that the nanoparticles are able to produce H₂ gas using natural sun light!
4.3.5 \textit{H}_2 \text{ production under near IR light illumination}

To determine whether these nanocatalysts can be driven by low energy photons in the near IR range for the production of \textit{H}_2 gas, coherent light from a 976 nm laser was used for the illumination. The laser was expanded to have an illumination area of \(\sim 1.0 \text{ cm}^2\), giving a power density of 2.0 W/cm\(^2\).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{\textit{H}_2 gas production kinetics under 976 nm light. (A) Regular vs. High ASR AuNRs. (B) High ASR AuNRs at different laser powers (2000, 875, and 250 mW/cm\(^2\), respectively). (C) Reaction rate as a function of illumination power. Pt:Au ratio was 1:10 for (A) (B) and (C). (D) High ASR AuNRs loaded with different amount of Pt.}
\end{figure}

Figure 4.4. A shows that both high ASR and regular AuNRs can produce hydrogen gas at high initial rates, 6.8 and 4.6 \textit{H}_2 molecule/Pt atom/min, respectively. The reaction rates seem to be
consistent with the absorbance of the particles: the high ASR Pt-end-capped AuNRs (LSPR = 1000 nm) have a higher absorbance at 976 nm than the regular ones (LSPR = 880 nm). This suggests that SPR is involved in the light absorption and hydrogen gas generation. Further, in the laser illumination experiments, the power density was 2.0 W/cm², 6.7 times higher than that of the white light illumination. However, the active production area in laser illumination was only 1.0 cm². As a contrast, under white light illumination, the whole solution was illuminated, which had a projection area of 10 cm², ~10 times larger than that of laser illumination. Thus, the overall hydrogen production rates using 976 nm and white light illumination were similar in the order of magnitude considering the production rate as a function of photon flux. We understand that the efficiency of hydrogen gas production is related to many factors including light absorption and hot charge carrier generation. Still, it is clear that it is practical to use near IR light for hydrogen production even though their photon energy is small.

To determine the process of how SPR is involved in the photocatalytic reaction, the laser power was tuned down from 2.0 W/cm² to 875 mW/cm² and then 250 mW/cm². The reaction rate also decreased, from 9.6 to 3.8 and then 1.2 H₂ molecules/Pt atom/min in the first 5 min (Figure 4.4.B). Thus, the initial reaction rate is linearly related to the illumination power (Figure 4.4.C).

The linear relationship possibly suggests that: (1) the chemical reaction, either the interfacial transfer of hot electrons from the nanoparticle to the reactant molecule or some photo-activated steps along the chemical reaction pathways, is the rate-limiting step for the hydrogen gas production, and (2) the Pt surface hot electron concentration is linearly proportional to the photon flux under our experimental conditions. (1) is highly likely considering that the generation and transport the hot electrons are very fast (on the fs to ps time scale). However, (2) is unexpected. Assuming that the instantaneous temperature of electron gas in metal particle upon light absorption
is dominated by the photon influx and increases linearly with respect to the illumination laser power, the total number of hot electrons exceeding a large threshold value would increase exponentially with respect to the temperature, or the photon flux, according to Fermi-Dirac distribution:

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}$$  \hspace{1cm} (1)

where $f$ is the probability an energy level is filled; $E_F$ is the Fermi level; $k_B$ is the Boltzmann constant; $T$ is the temperature. However, repeated experiments show a fairly linear relationship between the reaction rate and the photon flux. It indicates that the process of how hot electrons are generated and participate in surface chemistry is still a mystery. Indeed, there are many complicated processes including hot electron thermalization, establishing equilibrium with the gold crystal lattice, and being transported to Pt surface. Experiments aimed at elucidating these factors are currently underway. Nonetheless, this experiment corroborates both the tremendous potential and significant challenges of using hot electrons owing to their very short lifetimes. The effective separation of charge carriers generated in plasmonic metal particles represents a key future direction in designing metal-based photocatalysts.

As a final experiment, the Pt:Au ratio was varied in order to determine the optimum loading of Pt on AuNRs. Figure 4.4.D shows hydrogen gas production/Pt atom/min. These curves show that less Pt on Au nanorods favors the most efficient use of Pt in regard to both the photocatalytic rate and the total number of turnovers. However, using less Pt also reduces the absolute hydrogen gas production rate (H₂/min rather than H₂/Pt atom/min), which is unfavorable for mass production. Thus, the Pt:Au ratio of 1:10 was used throughout this manuscript unless specified.
4.4 Conclusions

To summarize, the photo-reductive sites were found to be located at the ends of AuNRs via the photodeposition of Pt metal onto the AuNRs. This finding suggests that hot electrons are generated, or localized in a timely-averaged manner, at the ends of AuNRs upon light excitation. A preparative method to selectively deposit Pt at the ends of AuNRs was developed in order to most efficiently utilize the photo-generated hot electrons at the active sites. These Pt-end-capped AuNRs showed significant photocatalytic activity for producing hydrogen gas under illumination by (1) artificial white light, (2) natural sun light, and (3) 976 nm light in the near IR region. Control experiments confirm that the SPR of AuNRs is involved in hydrogen gas production. Thus, tuning the particle SPR wavelength would allow the selective use of light at different wavelengths. Further, these findings show that gold nanorods are photocatalytically active, which can be driven by the capture of low energy photons to generate hot electrons, which can participate in chemical reactions for a variety of purposes. Yet, future challenges remain regarding the use of nanoparticle catalysts, most especially, the importance of long-term stability.

4.5 Experimental

4.5.1 Chemicals

HAuCl₄·3H₂O (99%), NaBH₄ (99%), AgNO₃ (99%), H₂PtCl₄ (>99%), ascorbic acid (99%), CTAB (99%), 5-formyl-salicilic acid (5-FSA), and concentrated HCl were purchased from Sigma Aldrich and used as received.

4.5.2 Particle synthesis

4.5.2.1 Preparation of gold seeds

In a typical seed synthesis, 5 mL of 0.50 mM HAuCl₄ solution was gently mixed with 5 mL of 0.2 M CTAB solution. Then, 600 µL of 10 mM freshly made NaBH₄ was introduced to the
solution and mixed at drastic stirring for 2 minutes. The final solution was left undisturbed for 30 minutes prior to use.

4.5.2.2 Preparation of regular AuNRs (aspect ratio ~4)

AuNRs were synthesized following our procedure previously reported. In short, a growth solution containing 10 mM 5-FSA and 50 mM CTAB is prepared. Then, 1.92 mL of 10.0 mM AgNO₃ was added to 100 mL growth solution. After keeping the mixture undisturbed for 15 minutes, 100 mL of 1.0 mM HAuCl₄ was mixed with the growth solution at medium stirring speed for 90 min. Then, at drastic stirring condition, 512 μL of 0.10 M ascorbic acid was added to the solution within 30 seconds. At the same stirring speed, 320 μL previously synthesized gold seeds was added and the solution was kept being stirred for an extra 30 s. The final solution was left undisturbed for 12 hours at room temperature.

4.5.2.3 Preparation of AuNRs with higher aspect ratio (aspect ratio ~5)

AuNRs with higher aspect ratio were synthesized following the same procedure for regular AuNRs except that 2.0 mL of 1.0 M HCl was added dropwise with stirring after HAuCl₄ has been introduced.

4.5.2.4 AuNRs end-capped with Pt

To selectively coat Pt on the ends of AuNRs with regular and higher aspect ratios, we adopted a procedure similar to our published work. Briefly, a 10 mL of as-synthesized regular and high aspect ratio AuNRs solution was used. For different Pt loadings, HCl, H₂PtCl₆, and ascorbic acid were added in fixed proportions. For instance, for a Pt/Au ratio of 0.1, 40.4 μL of 0.01 M HCl was added to the Au solution at 35 °C under mild stirring for 5 minutes, followed by the slow addition of 50 μL of 0.01 M H₂PtCl₆ in 5 min under mild stirring. Finally, 287 μL of freshly made 0.1 M ascorbic acid was added dropwise. The final solution was left undisturbed at
35 °C for 8 hours. The solution color changed from light reddish pink to light purplish, indicating the reaction had taken place.

4.5.2.5 Pt-only Nanoparticles

A 2.5 mL solution of 0.010 M H$_2$PtCl$_6$ was gently mixed with 5.0 mL of 0.2 M solution of CTAB at 35 °C. Slowly, 2.5 mL of 0.020 M NaCl was added and stirred for 15 minutes. Finally, 2.4 mL of freshly prepare 0.01 M NaBH$_4$ solution was added dropwise. The final solution was left undisturbed for 8 hours.

4.5.3 Electron microscopy

All electron micrographs were taken at the Analytical instrumentation facility (AIF). SEM and S/TEM images were collected using an FEI Verios 460L field emission scanning electron microscope (FESEM). TEM images were collected using a JEOL 2000 electron microscope. SuperX Energy Dispersive Spectroscopy (EDX) was done using Aberration Corrected STEM-FEI Titan 80-300.

4.5.4 Hydrogen gas production

The as synthesized particle solution was centrifuged at 17 G for 3 min, three times, to remove the surfactants and unreacted chemicals in the solution. The particles were then re-suspended in equal amount of deionized water before use. In hydrogen production, 1.6 mL particle solution was mixed with 1.0 mL of methanol and 2.4 mL DI water. The solution was then degassed by bubbling with nitrogen gas for 30 minutes. The solution was finally transferred to a quartz cell for irradiation. The quartz cell is connected to a thin, L-shaped tubing. The inside of the cell and tubing were purged with nitrogen has and a water droplet was used to seal the chamber. The volume change was read from the movement of the droplet in the horizontal segment of the L-shaped tubing. After the photoreaction, the volume of the produced gas was re-read after the whole
system was re-equilibrated at room temperature. The reported gas production volume was corrected for the temperature change during reaction.

4.5.4.1 White light irradiation

A high pressure Xe arc-lamp with power density of 300 mW/cm² (on the sample) was utilized. UV and IR long pass filters were applied to allowed only visible light (280-950 nm) to reach the quartz cell. The entire solution was irradiated and the solution was stirred throughout.

**Sunlight irradiation** The same photoreaction was done using natural solar light irradiation. The solar irradiation power varied from 190~260 mW/cm², as measured using a Coherent PowerMax P30 power meter. **980 nm irradiation** A continuous wave, 976 nm laser (MDL-III, Dragon lasers) was used in hydrogen gas production. The total output was set at 2000 mW, 875 mW, or 250 mW. The illumination area was ~1 cm². 1/5 of the solution was illuminated.

4.5.5 **Gas chromatography of the photoreaction products**

All gas chromatograms were taken using a SRI 8610C gas chromatograph with a 2.0 meter silica gel-packed column (1.0 mm internal diameter and 1/16th outer diameter), a thermal conductivity detector, and nitrogen as the carrier gas.

4.5.6 **Photo-reduction**

The photo-reduction was carried out using an outer-irradiation type fused-silica reaction cell. The cell was irradiated for 6 hours with a 400W Xe Arc lamp. The lamp output was 280 nm ~ 950 nm with a power density of 800 mW/cm². The solution was composed of 5.0 mL of as prepare regular cleaned AuNRs, mixed with 49.3 µL of 0.01 M H₂PtCl₆ solution, 5.0 mL of methanol and diluted to a total volume of 30 mL with DI water. The solution was stirred throughout the entire reaction time.
4.6 References


Figure S4.1. Pt overgrowth on AuNRs having the FSA ligand removed. (A) Pt:Au ratio 0.2. (B) Pt:Au ratio 0.5. The AuNRs grew into a block like shape with a uniform layer of Pt. Scale bar: 50 nm.
Figure S4.2. Photo-reduction of Pt on AuNRs. (A) EDX map. Scale bars: 10 nm. (B) Longitudinal Pt distribution on AuNRs. 5-points average method was performed to smooth the raw data. Image taken by Dr. Yang Liu.
**Figure S4.3.** SEM image of AuNRs.
Figure S4.4. EDX maps of Pt-end-capped-AuNRs with the large ASR. The nominal Pt:Au ratio was (A) 1:20; (B) 1:10; (C) 1:5; (D) 1:2; and (E) 1:1, respectively. The experimentally Pt fractions are in Table 1. Scale bars: 20 nm. Image taken by Dr. Yang Liu.
Continue Figure S4.4.
Figure S4.5. Pt overgrowth on CTAB-only AuNRs. Nominal Pt:Au ratio 1:1. (A) SEM image. Scale bar: 400 nm. (B) Scale bar: 50 nm. (C) UV-VIS.
Figure S4.6. An example of gas chromatograph for H$_2$ production. H$_2$ production was checked at the end of experiments for all reported cases using different particles and different light sources. This specific case was from long rods with a Pt: Au ratio of 1:10, under the irradiation by 976 nm light. Due to the incomplete purging, oxygen was detected both before and after the photoreaction.
Figure S4.7. UV-VIS of Pt-end-capped-AuNRs before and after photoreaction under white light.
Figure S4.8. High-angle annular dark-field (HAADF) images for Pt-end-capped-AuNRs before and after photoreaction under white light. (A and B) Before exposure; (C and D) after the exposure of the artificial white light. The Pt:Au ratio was 1:5. Scale bars were 5 nm for (A) and (C); 2 nm for (B) and (D), respectively. Image taken by Dr. Yang Liu.
Figure S4.9. SEM images of Pt nanoparticles. (A) Scale bar: 300 nm. (B) Scale bar: 50 nm.
CHAPTER 5: Composite Ferroelectric and Plasmonic Particles for Hot Charge Separation and Photocatalytic Hydrogen Gas Evolution

Manuscript in preparation
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5.1 Abstract

Plasmonic nanoparticles are excellent light absorbers for harvesting solar energy, resulting in hot electrons that could potentially be utilized in photocatalytic hydrogen production. However, the lifetime of the hot electrons is short, and thus they typically cannot be used efficiently. Herein, we show that by combining plasmonic nanoparticles with a ferroelectric oxide, i.e., materials which possess a large remanent electric dipole moment, charge separation can be achieved and used to drive the photocatalyst. The efficiency of using hot electrons for photocatalytic reactions is greatly enhanced, and which improves the light-to-chemical energy conversion efficiencies by about one order of magnitude for the same amount of metal particles being used.
5.2 Introduction

Molecular hydrogen is an ideal chemical energy carrier that is clean, has a high energy density, and can be conveniently transported and stored.\textsuperscript{1-6} The use of solar energy to produce hydrogen from water is one of the most attractive yet challenging reactions in converting solar energy into chemical energy. To achieve hydrogen gas production from sunlight, photocatalysts are required. In general, a photocatalytic reaction consists of three steps: First, photoexcitation which leads to the generation of electron (e\textsuperscript{-}) and hole (h\textsuperscript{+}) pairs. Second, the electrons and holes must be separated and then diffuse to the catalyst surfaces. Third, the electrons and holes react with adsorbed electron acceptors and donors, respectively, to complete the photocatalytic reaction. Hence, the photocatalytic efficiency is predominantly affected by three main factors: amount of light absorption, charge separation efficiency, and surface reaction rates.

Semiconductors and semiconductor-based hybrid systems have been extensively studied and used as photocatalysts in hydrogen and/or oxygen production.\textsuperscript{7,8} The main advantages of these systems include low cost, environmentally friendly nature, relatively good stability in aqueous solutions, and high photocatalytic rates.\textsuperscript{9,10} In addition, tunability of their band gap can be achieved by doping the semiconductor with metal ions, which allows for visible light sensitization and broader absorption across the solar spectrum. However, one primary factor that limits the photocatalytic reaction efficiency for semiconductor-based photocatalysts is the fast recombination of the charge carriers (i.e., at the ns time scale). Owing to this fast charge recombination, the practical efficiency in converting solar energy to chemical energy is usually << 1%, while a minimum solar-to-hydrogen efficiency of ~10% is required for any system to be commercially viable.
The surface plasmon resonance (SPR) effect of noble metal nanoparticles, e.g. Au nanoparticles, has recently been integrated as a component of photocatalytic systems in order to absorb light in the visible to near IR range. SPR can be described as the collective oscillation of conduction band electrons excited by light. At the SPR wavelength, the optical cross-section of the particles is greatly enhanced, allowing efficient light harvesting. This is very important as the photon flux from the sun is a fairly diffusive energy source, with an intensity of ~100 mW/cm$^2$. Thus, using Au or Ag nanoparticles as antennas, the efficiency of light absorption can be greatly improved. More importantly, high-energy hot electrons are generated in the SPR process, which can participate in the chemical reaction on the particle surface. Herein, hot electrons refer to the excited electrons with energies above the Fermi level. Especially, the excited electron gas in the nanoparticle initially would adiabatically establish equilibrium with a mean temperature of several thousands of degrees. Thus, high energy hot electrons (i.e., photon energy larger than that at the SPR frequency) are produced in the SPR process even when the particle is excited by low energy photons. The generation of high energy hot electrons makes it possible for many catalytic reactions with high activation energy barriers to turnover at higher rates.

However, hot electrons in metallic particles are generally believed to have a very short lifetime in the femtosecond to picosecond time scale, which hinders their use in driving chemical reactions. In this study, we hypothesize that by combining plasmonic nanoparticles with ferroelectric (FE) particles, effective charge separation within the photocatalyst will be achieved, which cannot otherwise be accomplished in separate metal or semiconductor systems. Specifically, lead titanate (PbTiO$_3$) is selected as the ferroelectric material because of its large ferroelectric polarization and tunable conduction band energy that can be further used to facilitate charge separation and/or the injection of hot electrons. Significant promise has been shown for the
photocatalytic activity of PbTiO$_3$ powders with Pt co-catalyst. For example, Arney et al. showed that PbTiO$_3$ particles have high activities in the photocatalytic reduction and oxidation of water into H$_2$ and O$_2$, respectively.  

The ferroelectric semiconductor PbTiO$_3$ has been extensively studied for the last six decades.  

Ferroelectric materials are characterized by a polarization-dependent band bending mechanism, which lies close to the ferroelectric surface and promotes electron-hole pair separation. The large remanent electric field is considered to be a quite attractive feature for photocatalytic reactions such as water splitting.  

Generally, ferroelectric materials have been explored for their switchable polarization whose direction can be controlled by applying an external field. In many cases, concerted atomic-displacements that are driven by electronic phase transition result in the large permanent electric polarization. Furthermore, Streiffer et al. investigated ferroelectric materials within the nano regime, in which the formation of nanodomains within a given cell unit appeared to suppress polarization, leading to a constant electric field. Cai et al. also studied size-dependence switchable polarization of PbTiO$_3$ and concluded on the diminished activity of ferroelectricity within the nanoregime of PbTiO$_3$ powders. Thus, relatively larger particle sizes, e.g., micrometer sizes, are needed to sustain the ferroelectric behavior. For ferroelectric PbTiO$_3$, it has a bandgap size that falls at the edge of the visible range, at ~2.7 eV, and thus not absorbing light wavelengths longer than ~460nm.

In the current investigation described below, AuNRs and Pt-end-capped AuNRs (Pt-AuNRs) are used as the plasmonic particles to generate hot electrons. AuNR-based particles are especially of interest because they have tunable SPR wavelengths from visible to near IR ranges. By tuning the SPR wavelength to ~980 nm, we can selectively excite the AuNR particles and inject hot electrons to FE particles, while excluding the possibility of exciting the FE
particles directly. The new composite plasmonic-ferroelectric particles represent key new photocatalytic system that can achieve high efficiency in light absorption, electron-hole generation, and charge separation.

5.3 Results And Discussion

5.3.1 Flux synthesis of ferroelectric PbTiO₃ particles

The highly-faceted PbTiO₃ particles were synthesized in the form of either nano-particles (125~500 nm, NaCl flux) or micro-particles (1 ~ 5 μm, PbO flux). They are named as nano-ferroelectric (nano-FE) and micro-ferroelectric (micro-FE) particles, respectively. The resulting particles were characterized using scanning electron microscopy (in Figure S5.1 and Figures 5.1-5.3 together with impregnated AuNRs). Their crystalline structures were characterized by powder X-ray diffraction (Figure S5.2), which are consistent with expected XRD pattern. Their bandgap sizes were characterized using UV-VIS diffuse reflectance spectroscopy (Figure S5.3).

Scheme 5.1. Scheme of the proposed plasmonic-ferroelectric composite particle for hydrogen production. Ox: oxidant, e.g., H⁺ or a sacrificial oxidant in a model redox reaction; Red: reductant, e.g. H₂O, sacrificial agent, or other reductant in a model redox reaction; E_F: Fermi level.
5.3.2 AuNRs and Pt-end-capped AuNRs (Pt-AuNRs) synthesis

AuNRs and Pt-end-capped AuNRs were used as the plasmonic nanoparticles. To demonstrate the charge injection from plasmonic particles to the ferroelectric oxide, and to exclude the possibility that the excited electrons are generated by excitation of the ferroelectric particles directly, near IR light illumination at 976 nm was utilized and which has a significantly lower photon energy than the band gap of the PbTiO$_3$ at ~460 nm.

We recently showed that using 5-formyl salicylic acid as the organic modifier and by tuning the pH, AuNRs with different aspect ratios could be synthesized as well as their Pt-end-capped versions.$^{36,37}$ In this study, the “long AuNRs” (aspect ratio ~5) were mainly used, which has an SPR wavelength of 850 nm when unmodified and 920 nm after Pt-end-capping. The SPR wavelength better matches the light source output at 976 nm. The “regular AuNRs” (~4, SPR 810 nm unmodified, Figure S5.5), and Au nanospheres with a diameter of 40 nm (SPR 532 nm, Figure S5.6) were used as controls.

While the AuNRs themselves can absorb light and generate hot charge carriers, the motivation for investigating the Pt-AuNRs in addition to AuNRs were two-fold: (1) to compare the hydrogen gas production efficiency for Pt-AuNRs and composite Pt-AuNRs/FE-Pt particles; and (2) to achieve an optimal match so that the AuNRs and the ferroelectric particles will have enhanced surface contact to facilitate the charge separation. At a Pt:Au ratio of 1:10, the nanorod ends are slightly expanded and less protected,$^{37}$ which will provide specific contact points between the particles.
5.3.3  Charge injection from AuNRs to PbTiO₃: Photochemical surface reduction using near IR light

The fundamental hypothesis is that the hot electrons generated on plasmonic particles will be injected into ferroelectric particles owing to the permanent electric polarization. To test whether charge injection occurs, the photon-induced reduction of Pt(IV) onto the composite AuNR-FE particles was performed. The AuNRs particles (no Pt) were used and impregnated onto bare Micro-FE PbTiO₃ particles to avoid confusion with photo-reduced Pt. Before impregnation, the AuNRs were cleaned 3 times to remove excessive ligands on the particles. The suspension of the composite particles was then exposed to 976 nm near IR light in the presence of aqueous H₂PtCl₆ and methanol as the sacrificial agent. The near IR light was from a laser expanded to have an illumination area of ~1.0 cm², giving a power density of 2.0 W/cm².

After irradiation under 976 nm light for 30 minutes, the particles were then characterized by SEM. As shown in the SEM images, Pt islands emerged on FE particle surface, with most of them located within a distance of ~100 nm from the AuNRs (Figure 5.1). This is strong supporting evidence that the hot electrons are being injected from plasmonic particles to the FE particles, and which are driving the photochemical reduction of the Pt at the surfaces. Again, 976 nm near IR light has a photon energy well below the bandgap of the PbTiO₃, so that excited electrons will not arise from light absorption within the ferroelectric.

As a control, under the same conditions no Pt islands were found to deposit on the FE particle surface (Figure 5.1.B) in the absence of AuNRs. These experiments confirm the hypothesis that charge injection takes place from the AuNR to FE particles.
Figure 5.1. SEM images of the AuNR/FE particles after the photon-driven reduction of Pt islands onto their surfaces under irradiation by 976 nm light. (A) PbTiO$_3$ particles impregnated with AuNRs. Scale bar: 500 nm. (B) Control experiments for PbTiO$_3$ particles with no AuNRs. Scale bar: 1 μm. (C) Enlarged area in (A) to show the Pt islands. Scale bar: 100 nm. EDX scanning shows that a small area including AuNRs and surrounding Pt islands contains Pb: 60.8 ± 0.4%, Ti: 14.5 ± 0.2%, O: 18.9 ± 0.3%, Au: 3.5 ± 0.2%, and Pt: 1.4 ± 0.2%. As a comparison, the PbTiO$_3$ particles before Pt reduction contain Pb: 65.8 ± 0.3%, Ti: 16.2 ± 0.2%, and O: 16.3 ± 0.2%.

5.3.4 Photocatalytic H$_2$ production: Enhanced rates for composited AuNR and FE particles

The photocatalytic activities of the particles were investigated under irradiation in aqueous solutions for the reduction of water to H$_2$ for the composited plasmonic-ferroelectric particles. AuNRs alone are poor catalysts although they are excellent light absorbers and can result in the production of hot electrons from the excess photon energy. Our collaborative efforts have demonstrated that that by end-capping AuNRs with Pt they become highly active for the
production of hydrogen gas, even when being illuminated with near IR photons. The initial H₂ production rate (in the first 10 min) was measured to be ~0.26 μmol/min for ~0.4 μmol total Au, which compares very favorably among all AuNP-based metallic nanoparticles. This shows that they are efficient in absorbing low energy photons and converting them to hot electrons that can drive hydrogen production.

The composited Pt-AuNR/FE-Pt particle were similarly investigated for their photocatalytic activity for hydrogen gas production and compared to that for the Pt-AuNRs alone. The ferroelectric particles were first deposited with Pt islands (1 wt%) to serve as surface cocatalysts using a photochemical reduction reaction under white light illumination (Figure S5.7). Importantly, the cocatalyst islands serve to lower the kinetic barrier (i.e., overpotential) for hydrogen formation. The composite particles were synthesized using the well-known wet-impregnation methods and annealed together at a low temperature of 80 °C for surface attachment of the particles. Figures 5.2.A and 5.2.B show that the Pt-AuNRs were distributed evenly over nano-FE (average size ~125 nm) and micro-FE (average size ~1 μm) particle surfaces. The average loading of the AuNRs on the FE particles were consistent with the expected values (AuNR:FE ~0.6 for 125 nm nano-FE and ~280 for 1 μm micro-FE, respectively). The Pt-AuNRs with an aspect ratio of 5 and Pt:Au = 1:10 were used throughout unless specified.

The composite AuNR/FE particles, i.e., using either nano-FE or micro-FE particles, were suspended in a solution containing methanol for H₂ production and tested for their photocatalytic rates under 976 nm near IR light illumination. Both the nano-FE and micro-FE particles showed significant amount of hydrogen production after light exposure, which was confirmed using gas chromatography during each experimental run. The other half of the reaction is the oxidation of
the methanol to formaldehyde or formic acid, which was confirmed using Tollen’s test. No significant amount of CO₂ was detected among the product gases using gas chromatography.

Figure 5.2. Photocatalytic H₂ gas production on composite Pt-AuNR/FE-Pt particles. (A and B) SEM image of Pt-ferroelectric particles impregnated with Pt-AuNRs. (A) NaCl Fluxed PbTiO₃ particles; dimension: ~ 125 nm. Scale bar: 500 nm. (B) NaCl Fluxed PbTiO₃ particles; dimension: ~ 1 μm. Scale bar: 1 μm. (C) Hydrogen production on composite Pt-AuNR/micro-FE-Pt and Pt-AuNR/nano-FE-Pt particles. As a comparison, hydrogen gas production on Pt-AuNRs and Nano-FE-Pt particles are also shown.

The Pt-AuNR/nano-FE-Pt particles gave a H₂ production rate of 1.8 ± 0.3 μmol/min for a total of 9 runs using FE particles made from 3 different batches. In each experiment, a sample containing 16.0 mg FE, 0.8 μmol Pt on nano-FE, 0.40 μmol Au, and 0.040 μmol Pt on AuNRs were used. Figure 5.2.C shows a set of experimental data containing 3 replicates using the 125 nm FE particles. This rate is compared to that of the pure metallic Pt-AuNR particles. In order to make this an appropriate comparison, the total Au in both solutions (0.40 μmol Au) was normalized in order to compare the efficiency of using the hot electrons generated from the AuNR particles. This
result shows that the production rate was enhanced by a factor of 6.8, almost a full order of magnitude when the FE particles are present.

Similarly, the Pt-AuNR/micro-FE-Pt particles also show an enhanced H₂ production rate of 0.54 ± 0.3 μmol/min for 4 different experiments using the same amount of materials. Thus, the production rate is enhanced by 2.0 times for the Pt-AuNR/micro-FE-Pt composite particles. The rate for the micro-FE particles is lower, possibly because the total surface area of the micro-FE particles is much smaller (~10 times) than that of the nano-FE particles.

Note that in the composite particles, there was more Pt present over the composited particles’ surfaces. However, this is desired so that the photocatalytic rates are not limited by the inherent surface activities of the ferroelectric oxide or the AuNR’s, but rather, only by the efficiency of generation of hot electrons and the charge injection between the AuNR and the FE particle. The experimental design confirms a scheme that can distribute these hot electrons onto multiple cocatalyst islands that are exposed to the solution. Thus, their lifetimes are extended and the solar to hydrogen conversion efficiency is enhanced in this system design.

As a control experiment, the nano-FE-Pt particles (no AuNRs or Pt-AuNRs) were also tested under 976 nm illumination. Surprisingly, the Pt-nano-FE particles also produced hydrogen gas, but at a much smaller rate and the particles lost activity quickly. It is possible that the heating effect of the laser can also promote electrons from the valence band to the conduction band, and which can thermally drive the reaction. However, this process is very inefficient and the hydrogen production rate is low. Thus, these studies show that Pt-AuNRs can inject hot electrons to FE particles upon illumination; these hot electrons can participate in chemical reactions, e.g., producing H₂.
We also noticed that the photon-driven catalytic activity of the composite particles decreased over time and was lost after ~60 min. The possible reasons can be inferred from the observation of the sample solution: the composite particles would aggregate overtime so we are losing particles; the AuNRs may also detach from the FE particles. These effects require further planned investigations.

![Figure 5.3](image)

**Figure 5.3.** Photocatalytic H₂ gas production on composite AuNP/Pt-FE nanoparticles. (A, B, C) SEM images of the composite particles. NaCl fluxed FE particle size: ~500 nm. (A) With 40 nm Au nanospheres. Scale bar: 500 nm. (B) With regular AuNRs. Scale bar: 1 μm. (C) With long AuNRs. Scale bar: 300 nm. (D) Hydrogen production as a function of time for the respective types of composited particles.

5.3.5 SPR involvement in hot electron generation

To further support that the hot electrons are generated on the plasmonic nanoparticles and being transported to the FE particle surface to participate reaction, the Au nanoparticles were used with different aspect ratios *without* the Pt-end-capping. The photocatalytic activities were investigated for the nano-FE (average size 500 nm) impregnated with long AuNRs, short AuNRs,
and spheres (40 nm in diameter) using 976 nm near IR light illumination in aqueous solutions, as described above.

Shown in Figures 5.3.A-C, are SEM images of the composited particles with three different shapes for the gold nanoparticles, i.e., 40nm spheres, short nanorods and longer nanorods. Their photocatalytic activities for hydrogen production as a function of time is plotted in Figure 5.3.D. All of these composited particles showed activity in the first 20 min. The initial reaction rates were 1.3, 0.74, 0.010 μmol H₂ molecules/min for the same amount of FE particles in the first ~10 min for long AuNRs, regular AuNRs, and 40 nm Au nanospheres, respectively. The trend of the reaction rates is consistent with the absorbance of these particles at 976 nm: from the long AuNRs to regular AuNRs, the absorbance decreased by ~half and the production rate also reduced by half; for the Au nanospheres, the absorbance at 976 nm is almost negligible and the production rate also becomes 10 times smaller. These experimental results strongly support that the particle SPR is involved in the light absorption and hydrogen gas generation, and that the hydrogen production happens predominantly on the FE particle surface rather than on AuNR ends.

5.3.6 Composites using AuNRs or Pt-AuNRs?

Composite particles prepared from AuNRs/Pt-AuNRs (i.e., with or without the Pt end capping functionality) and nano-/micro-FE particles were investigated. Both of them can greatly enhance the H₂ production rate as compared to metallic particles only. Generally, for the same batch of FE particles, composites using Pt-AuNRs have a production rate 50~100% higher than those using AuNRs. The Pt-AuNR/nano-FE-Pt particles gave a H₂ production rate of 1.8 ± 0.3 μmol/min (9 runs using different FE particles) while the AuNR/nano-FE-Pt particles gave a rate of 1.0 ± 0.5 μmol/min (6 runs using different FE particles). This is possibly because the Pt end-capped AuNR provides better contacts between the particles and facilitates the charge transfer.
Figure 5.4 shows one example that both AuNR- and Pt-AuNR composites were prepared with the same batch of nano-FE particles with an average size of ~250 nm. The initial production rate was ~1.9 μmol H$_2$/min for Pt-AuNR/FE-Pt and 0.84 μmol H$_2$/min for AuNR/FE-Pt composites, respectively. In the experiments, the same amounts of materials were used as indicated earlier. The higher production rate is apparently not solely caused by the extra Pt on AuNR ends, which is only ~5% of the total Pt in the composites. More likely, Pt serves as a bridge between the AuNRs and the FE particles, thereby reducing the energy barrier for charge transfer. Thus, the Pt end-capping of the AuNRs is a key factor in the fully optimized composite particle system.

![Graph showing the comparison of photocatalytic H$_2$ production](image)

**Figure 5.4.** Comparison of the photocatalytic H$_2$ gas production on AuNR/FE-Pt versus AuNR/FE-Pt particles. Nano-FE: Prepared in a NaCl flux with sizes of ~ 250 nm.

5.3.7 Nano-FE versus Micro-FE PbTiO$_3$ Particles

The FE particles showed variability in their sizes according to whether the flux reaction involved their preparation within a PbO or a NaCl molten-salt. Though, the particles prepared in the NaCl flux were in the nanometer range (125~500 nm) while the particles prepared in the PbO flux were in the micrometer range (1~ 5 μm). Generally, the Nano-FE composites showed a higher
reactivity (1.8 ± 0.6 μmol/min, 9 runs with different FE particles) than the micro-FE composites (0.5 ± 0.3 μmol/min, 4 runs using different FE particles). For example, in Figure 5.2.C, the nano-FE particles (~125 nm) showed a reactivity of 1.9 μmol H₂/min while the micro-FE particles (~1 μm) exhibited a rate of 0.50 μmol H₂/min, where the error bars were from 3 replicates.

**Figure 5.5.** Photocatalytic H₂ gas production on composite Pt-Au/Pt-FE particles under 976 nm light. Nano-FE: PbTiO₃ nanoparticles prepared within a NaCl with sizes of ~250 nm. (A) Reaction kinetics as a function of illumination power; (B) Reaction rate as a function of illumination power.

There are two possible reasons for this difference: (1) the exposed crystallographic surface facets show different rates of reactivity, and/or (2) the nanometer-sized FE particles have a large surface area per gram of the particles so that their reaction rate is higher. Indeed, comparing the
total surface area of 200 nm cubes and 2000 nm cubes, the total surface area of the smaller particles is 10 times larger! Further investigations are planned to determine the impact of the particle surfaces and areas, as well as the loadings of AuNRs onto the FE particles.

5.3.8 Reaction rate as a function of illumination power

The above results demonstrate that the composite particles made of Pt-AuNRs and nano-FE-Pt particles exhibit high photocatalytic activities for the production of molecular hydrogen. To have a better understanding how SPR-generated hot electrons are involved in the photocatalytic reaction, the hydrogen production rate was measured as a function of the laser illumination power on Pt-AuNRs/Pt-nano-FE particles. Figure 5.5.A shows the reaction rates at different laser powers (2.0, 1.6, 0.98, and 0.25 W/cm²). As the laser power increases, the initial reaction rate increases from 0.28, 0.34, 0.65, to 1.5 μmol H₂ molecules/min. Thus, the initial reaction rate follows a non-linear relationship with respect to the illumination power (Figure 5.5.B). A quadratic function rate \( rate = 5.5 \times 10^{-7} I^2 - 1.9 \times 10^{-4} I + 7.6 \times 10^{-2} \) can satisfactorily fit the data, where \( I \) is the illumination intensity.

Interestingly, this observed quadratic relationship is in direct contrast to the linear rate ~ power relationship for the same hydrogen reduction reaction observed on Pt-AuNRs surface. In that case, it was suggested the chemical reaction, either the interfacial transfer of hot electrons from the nanoparticle to the reactant molecule or some photo-activated steps along the chemical reaction pathways, is the rate-limiting step for the hydrogen gas production; the surface hot electron concentration on Pt-AuNRs is linearly proportional to the photon flux under our experimental conditions. The second conclusion is, however, unexpected because the instantaneous temperature of electron gas in metal particle upon light absorption is dominated by the photon influx and increases linearly with respect to the illumination laser power. The total
number of hot electrons exceeding the Fermi level is linear. However, the total number of “high energy” hot electrons exceeding a large threshold value would increase non-linearly with respect to the temperature, or the photon flux, according to Fermi-Dirac distribution:

\[
f(E) = \frac{1}{\exp[(E - E_F) / (k_B T)] + 1}
\]

where \( f \) is the probability an energy level is filled; \( E_F \) is the Fermi level; \( k_B \) is the Boltzmann constant; \( T \) is the temperature. The linear rate~power relationship may be caused by the low activation energy of the hydrogen gas production reaction in the presence of methanol. Thus, even very low energy hot electrons can participate in the chemical reaction, giving a linear reaction rate ~ light intensity relationship.

In this case, a non-linear relationship is obtained, possibly suggesting that the metal-semiconductor Schottky barrier plays an important role in limiting the “high energy” hot electrons. That is, only when the hot electrons have an energy higher than the interfacial energy barrier can they be transferred to FE particle and then Pt island surface and participate in the chemical reaction. This energy barrier process will make the population of the hot electrons that participate in chemical reaction follow a non-linear relationship, whereas in the earlier case (Pt-AuNRs), hot electrons can directly diffuse to the metal surface so that the hot electron population will be linearly proportional to the light intensity.

5.3.9 Photocatalytic \( H_2 \) production under Sunlight

All the experiments described above have been performed under near IR light illumination at 976 nm. This wavelength was purposely selected in order to exclude the possibility that hot electrons are being generated from bandgap excitation within the FE particles directly. Thus, at 976 nm, all of the electrons participating in the chemical reactions are injected from the plasmonic AuNRs.
Figure 5.6. Photocatalytic $H_2$ gas production kinetics on composite Pt-Au/Pt-FE particles under natural sun light. Nano-FE: PbTiO$_3$ nanoparticles prepared within a NaCl flux with sizes of ~250 nm. Average solar illumination on the sample: ~100 mW/cm$^2$.

However, light in the entire UV-VIS-near IR spectrum can be used to generate hot electrons in plasmonic particles, as well as in the FE particles, and used to drive the photocatalytic reaction. To demonstrate this, the photocatalytic activity of the composite Pt-AuNR/nano-FE-Pt particles was tested under natural sun light in September, Raleigh, North Carolina, USA. Figure 5.6 shows $H_2$ gas production yield as a function of time. The experiments were carried out around noon, where the sun illumination power was measured to be ~245 mW/cm$^2$ orthogonal to the ray direction. Considering the incident angle of the solar rays, the illumination power on the sample was on the order of magnitude of ~100 mW/cm$^2$. At this illumination level, the hydrogen gas was produced with an initial rate of 0.54 μmol/min. These experiments confirm that the nanoparticles are practically useful in producing $H_2$ gas from natural sun light!

5.4 Conclusions

In summary, these investigations have demonstrated that by combining Pt-end-capped-AuNR and ferroelectric particles PbTiO$_3$, a new type of photocatalyst design can be obtained for
hydrogen gas production using light. It was hypothesized that the large permanent electric polarization of the FE particles could be utilized to extract hot electrons generated on a nearby plasmonic particle that is in contact with FE particle. Effective charge separation within the particle photocatalyst can be achieved, which greatly extends the lifetime of hot electrons and improves their efficiency in driving the chemical reaction.

Charge injection from the AuNRs to the FE particles was confirmed using near IR light using both the photodeposition of Pt islands as well as in hydrogen generation. The hybrid plasmonic-ferroelectric particle system significantly improved charge separation, thus the efficiency of using the photon generated hot electrons and catalyzing the reaction. It is also observed that using the Pt-AuNRs can reduce the Schottky barrier, thus further promotes the charge transfer. The outcome of this study is an effective photocatalyst system that takes advantage of a new fundamental mechanism that effectively separate electrons and holes generated in metal SPR process.

5.5 Experimental

5.5.1 Chemicals

HAuCl₄·3H₂O (99%), NaBH₄ (99%), AgNO₃ (99%), H₂PtCl₄ (>99%), ascorbic acid (99%), CTAB (99%), 5-formyl-salicilic acid (5-FSA), hydrochloric acid (HCl, concentrated), Methanol (99%) were purchased from Sigma Aldrich and used as received. PbO (99.99%) and TiO₂ (Anatase, 99.9%) were obtained from Alfa Aesar, Ward Hill, MA.

5.5.2 AuNP synthesis

5.5.2.1 Preparation of Au seeds

AuNRs were synthesized using the seed-mediated method following our procedure previously reported. In a typical seed synthesis, 5.0 mL of 0.50 mM HAuCl₄ solution was
gently mixed with 5.0 mL of 0.20 M CTAB solution. Then, 600 µL of 10 mM freshly prepared NaBH\(_4\) solution was introduced to the solution and mixed at drastic stirring for 2.0 minutes. The final solution was left undisturbed for 30 minutes prior to use.

5.5.2.2 Preparation of regular AuNRs (aspect ratio ~4)

A growth solution containing 10 mM 5-FSA and 50 mM CTAB was prepared (100 mL). Then, 1.92 mL of 10.0 mM AgNO\(_3\) was added. After keeping the mixture undisturbed for 15 minutes, 100 mL of 1.0 mM HAuCl\(_4\) was mixed with the growth solution at medium stirring speed for 90 min. Then, at drastic stirring condition, 512 µL of 0.10 M ascorbic acid was added to the solution within 30 seconds. At the same stirring speed, 320 µL previously synthesized gold seeds was added and the solution was kept being stirred for an extra 30 s. The final solution was left undisturbed for 12 hours at room temperature. The final total Au concentration was ~0.50 mM.

5.5.2.3 Preparation of long AuNRs (aspect ratio ~5)

Long AuNRs were synthesized following the same procedure for the regular AuNRs except that 2.0 mL of 1.0 M HCl was added dropwise with stirring after HAuCl\(_4\) has been introduced. The final total Au concentration was ~0.50 mM.

5.5.2.4 Preparation of Pt-End-Capped-AuNRs (Pt-AuNR; Pt:Au = 1:10)

To selectively coat Pt on the ends of AuNRs with regular and higher aspect ratios, the same procedure was adopted as reported in our published work.\(^{36}\) Briefly, 10 mL of fresh regular or long AuNRs solution was used. For Pt loading at a Pt:Au = 1:10, 40.4 µL of 0.010 M HCl was added to the Au solution at 35 °C under mild stirring for 5.0 minutes, followed by the slow addition of 50 µL of 0.01 M H\(_2\)PtCl\(_6\) in 5.0 min under mild stirring. Finally, 287 µL of freshly made 0.10 M ascorbic acid was added dropwise. The final solution was left undisturbed at 35 °C for 8 hours.
The solution color changed from light reddish pink to light purplish, indicating the reaction had taken place. The final total Au concentration was ~0.50 mM.

5.5.2.5 Preparation of Au spheres

Au spheres capped with CTAB were synthesized using the same seeds for AuNR synthesis. In a typical Au sphere synthesis, 10 mL of 0.50 mM HAuCl$_4$ solution was mixed with 10 mL of 0.20 M CTAB solution for 15 minutes. 1.0 mL of 6.0 mM cold NaBH$_4$ solution was then added under drastic stirring in 2.0 minutes. The final solution was allowed to age for 48 hours. The as synthesized AuNP were 40 nm in diameter.

5.5.3 Preparation of PbTiO$_3$

The flux synthesis of PbTiO$_3$ was performed by combining a stoichiometric mixture of PbO and TiO$_2$. The mixture was ground in acetone for 30 min before the addition of salt flux. For nano ferroelectric particles: NaCl salt flux was introduced in a flux-to-reactant molar ratio of 1:1; for micro ferroelectric particles: PbO flux was added in a flux-to-reactant molar ratio of 1:1. After grinding, the reactant mixture was placed inside alumina crucibles and heated to 1000 °C inside a box furnace in air for a reaction time of 1.0 h. The crucibles were cooled to room temperature inside the furnace. The resulting powder was first washed with deionized water to remove the flux, then washed briefly in 1.0 M HNO$_3$ to remove excess PbO flux, and finally dried overnight in an oven at 800 °C. Fine homogeneous yellow powders of PbTiO$_3$ were obtained in high purity, as judged from powder X-ray diffraction.

The FE particles showed variability in their sizes and H$_2$ production rates for each batch of synthesis. The nano-FE particles varied from 125 ~ 500 nm and the micro-FE particles varied from 1 ~ 5 μm, respectively. Each batch of FE particles were characterized using SEM. An appropriate comparison of photocatalytic rates was only performed when the same batch of particles was used.
5.5.3.1 *Pt deposition on PbTiO$_3$ through photo-reduction using white light (Pt-PbTiO$_3$)*

The ferroelectric particles were coated with 1% Pt islands (by weight) as surface co-catalysts using photochemical reduction. In a typical experiment, 300 mg of ferroelectric material was suspended in 15 mL solution containing 16% methanol (v/v) and 15.0 µmol of Pt salt (H$_2$PtCl$_6$). The photo-reduction was carried out using an outer-irradiation type fused-silica reaction cell. The cell was irradiated for 4.0 hours with a 400 W Xe Arc lamp. The lamp output was 280 ~ 950 nm with a power density of 800 mW/cm$^2$. The solution was stirred throughout the entire irradiation time. The final product was washed three times with DI water and re-suspended to a total volume of 15.0 mL of DI water. (Final concentrations: 20 mg/mL PbTiO$_3$; total Pt concentration ~1.0 mM.)

5.5.3.2 *AuNRs (or Pt-AuNR) impregnation onto PbTiO$_3$ (or Pt-PbTiO$_3$)*

The AuNRs (either with or without Pt-end capping) solution was pre-cleaned 2~3 times using DI water to remove excessive ligands and resuspended in the same amount of solution. 7.5 mL of the prepared PbTiO$_3$ or Pt-PbTiO$_3$ suspension was mixed with 7.5 mL of clean AuNR solution. The solution was then placed in a glass vial and heated to 80 °C, under constant stirring, overnight. The mixture dried up completely with the AuNRs adsorbed on PbTiO$_3$ or Pt-PbTiO$_3$ surface. The solids were stored for future use or immediately resuspended in DI water for H$_2$ production. For H$_2$ production, the solid was resuspended in 7.5 mL DI water and a part of the suspension was used in hydrogen production. (Concentrations: 20 mg/mL PbTiO$_3$; Pt on PbTiO$_3$ ~1.0 mM; total Au ~0.50 mM; Pt on AuNR ~ 0.050 mM.)
5.5.3.3 Photo-reduction of Pt on AuNR/FE composite using 976 nm light

To observe the charge injection from AuNRs to PbTiO₃, the 976 nm light photo-reduction was carried out on AuNR-PbTiO₃ composite. The AuNR was first impregnated onto PbTiO₃ using the same procedure for impregnating AuNRs onto Pt-PbTiO₃.

The photo-reduction was then carried out using an outer-irradiation type fused-silica reaction cell. 50 mg of AuNR-PbTiO₃ composite was added to 2.5 mL binary mixture containing 1.0 mg/mL Pt salt and 400 μL methanol. The cell was irradiated for 1.0 hour with a continuous wave, 976 nm laser (MDL-III, Dragon lasers). The total output was set at 2000 mW with an illumination area of 1.0 cm² (~1/5 of the solution was illuminated). (Concentrations: 20 mg/mL PbTiO₃; total Pt ~1.0 mM; total Au ~0.5 mM; Pt on AuNR ~0.05 mM. Note Pt was not completely reduced under this condition; a significant amount of Pt was still in the solution.)

5.5.4 Electron microscopy

Scanning electron microscopy (SEM) images were collected using an FEI Verios 460L field emission SEM (FESEM).

5.5.5 Photocatalytic Hydrogen Production

In photocatalytic H₂ production experiments, the impregnated Pt-AuNR/FE-Pt or AuNR/FE-Pt particles were re-suspended in DI water before use (Concentrations: 20 mg/mL PbTiO₃; Pt on PbTiO₃ ~1.0 mM; total Au ~0.50 mM). 800 μL composite particle solution was mixed with 500 μL of methanol and 1.2 mL DI water to form a 2.5 mL solution. The solution was then degassed by bubbling with nitrogen gas for 15 minutes. The solution was finally transferred to a quartz cell for irradiation. The quartz cell was connected to a thin, L-shaped tubing. The inside of the cell and tubing were purged with nitrogen for 15 minutes. A water droplet was used to seal the whole reaction chamber. The volume change was read from the movement of the droplet in
the horizontal segment of the L-shaped tubing. After the photoreaction, the volume of the produced gas was re-read after the whole system was re-equilibrated at room temperature. The reported gas production volume was corrected for the temperature change during reaction. (Total materials used in the reaction: 16 mg ferroelectric material, Pt on FE 0.8 μmol, ~0.4 μmol Au, Pt on AuNRs ~0.04 μmol). A continuous wave, 976 nm laser (MDL-III, Dragon lasers) was used in hydrogen gas production. The total output was set at desired power (2000 mW, 1575 mW, 975 mW, or 250 mW). The illumination area was ~1 cm². 1/5 of the solution was illuminated.

5.5.6 Gas chromatography of the photoreaction products

All gas chromatograms were taken using a SRI 8610C gas chromatograph with a 2.0 meter silica gel-packed column (1.0 mm internal diameter and 1/16th outer diameter), a thermal conductivity detector, and nitrogen as the carrier gas.
5.6 References


Figure S5.1. SEM images of ferroelectric particles used in the study. (A) NaCl-fluxed PbTiO$_3$ particles with a dimension of ~ 250 nm. Scale bar: 1 μm. (B) PbO-fluxed PbTiO$_3$ particles with a dimension of ~ 5 μm. Scale bar: 5 μm.
Figure S5.2. Powder X-ray Diffraction (PXRD) patterns of PbTiO$_3$ particles. (A) The theoretical PbTiO$_3$ PXRD pattern. (B) The PbO fluxed PbTiO$_3$ PXRD pattern. (C) The NaCl fluxed PbTiO$_3$ PXRD pattern.
**Figure S5.3.** Diffuse reflectance spectra of NaCl-fluxed PbTiO$_3$ and PbO-fluxed PbTiO$_3$ particles.
Figure S5.4. Long AuNRs used in this study. SEM of (A) AuNRs only, Scale bar 100 nm. (B) Pt-end-capped AuNRs. Pt:Au = 1:10. Scale bar: 200 nm. (C) UV-VIS.
**Figure S5.5.** SEM image and UV-VIS of short AuNRs. Scale bar: 300 nm.
Figure S5.6. SEM image and UV-VIS of 40 nm Au spheres. Scale bar: 150 nm.
Figure S5.7. Exemplary SEM image of Pt islands on ferroelectric particles deposited by photoreduction. NaCl-fluxed PbTiO3 particles with a dimension of ~ 250 nm. Scale bar: 100 nm.
CHAPTER 6: Enhancing Electrochemical Hydrogen Reduction Using Photon-Generated Hot Electrons from Pt-End-Capped-AuNRs

Manuscript in preparation
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6.1 Abstract

Photoelectrolysis of water is considered a realistic method to produce a clean and renewable energy in replacing fossil fuels. Current synthetic design of solar-activated electrodes aims at efficient light harvesting, charge separation, and carrier mobility. However, photoelectrodes that can use red to near IR light, a large fraction of solar irradiation, to catalyze the electrolysis of water are scarce due to the low photon energy of these lights. Herein, we evaluated the effectiveness of using Pt-end-capped-AuNRs as a cathode in photoelectrolysis of water. We demonstrated that these nanoparticles can turn near IR light into chemical energy with a yield similar to those of other current methods in using UV to visible light. To maximize the efficiency of using generated hot electrons from AuNRs, the loading of co-catalyst Pt on AuNRs was optimized. The robustness of particle-modified photocathodes was tested and they showed long term stability in the presence of high photon flux. This study provides new insight on using low photon energy near IR light in photoelectrolysis of water.
6.2 Introduction

The photo-catalyzed hydrogen evolution reaction (HER) and oxygen evolution reactions (OER) are yet challenging as means for water splitting. Utilization of solar energy to drive these fundamental reactions such as HER and OER for the production of chemical fuels that can eventually substitute fossil fuels is imperative. In specific, the production of hydrogen from water is significant because its main source is abundant and its process is clean, CO₂-free, and sustainable.

Water splitting requires photon energy equivalent to or larger than 1.23 eV, or the light having a wavelength shorter than ~1000 nm. In practice, the operational potential usually ranges between 1.7 eV - 1.8 eV (~685 nm) because of the overpotentials on the electrodes. Currently, most of the photoelectrolytic systems for water splitting are semiconductor based, which can only utilize high energy photons from UV to a part of the visible light. From the AM 1.5 solar irradiation energy distribution: 2.9 % UV (290 nm – 380 nm), 47 % Visible (380 nm – 780 nm), and 51 % IR (780 nm – 2500 nm), high energy photons only account for a fraction less than 50% of the total solar irradiation, while most of the photons on the low energy side are deemed “useless”. The development of photo-activated system that can take advantage of low energy photons is limited, though necessary.

As mentioned above, most of current photo-electrochemical systems are semiconductor based. For example, TiO₂ is one of the most used semiconductors since it is non-toxic and stable. However, its large band gap can only absorb UV light. Introducing plasmonic nanomaterials, such as gold nanoparticles, as the sensitizers can extend their absorption of light to lower energies. However, there are several shortcomings associated with current designs. (1) In cases where the light absorption relies merely on the nanoparticle, the system requires high loading of
nanoparticles, which blocks the reactive site on the semiconductor particles. (2) Matching the surface plasmon resonance absorption energy with the semiconductor band gap could enhance the light harvesting; however, this requires the doping of the semiconductor to decrease the band gap, which is unfavorable for charge separation thus the catalytic reaction. (3) Also, highly structured 3D systems are limited by the optical penetration depth and light diffusion length thus wasting the catalytic materials.\textsuperscript{34} (4) Lastly, semiconductors with small bandgaps such as Si, Cu\textsubscript{2}O and CdSe can match the plasmonic absorption. However, these semiconductors are known for their poor performance when used as photoelectrodes because they are vulnerable to corrosion, and in many cases, they require a sacrificial agent or the addition of co-catalysts.\textsuperscript{567}

In this study, we evaluated the performance of Pt-end-capped-AuNRs (Pt-AuNRs) based cathodes for the photoelectrolysis of water. These Pt-AuNRs have absorption bands in the red to near IR range of the solar spectrum. We hypothesize that these Pt-end-capped-AuNRs, upon near IR light excitation, will convert the low energy photons to high energy hot electrons thus can effectively use these near IR light that were deemed of less usefulness. The overall photo to current conversion efficiency from solar irradiation can be enhanced (Figure 6.1.B).

6.3 Results and Discussion

6.3.1 Fabrication of the Particles and the Photocathodes

Our earlier study has suggested that hot electrons are most localized in a time-averaged manner at the ends of AuNRs. In this study, to most efficiently use the hot electrons and the catalytic metal Pt, we used Pt-end-capped AuNRs deposited on a gold surface as the cathode (Scheme 6.1). The gold surface is used in this study since it is inert in nature, resistant to corrosion, non-reactive to oxygen species, and highly conductive. Pt-end-capped-AuNRs were synthesized following previously reported method.\textsuperscript{9} The resulting gold nanorods have an aspect ratio of ~ 4
(51 nm ± 4 nm × 12 nm ± 2 nm) and an SPR wavelength at 880 nm (Figure 6.1). The particles were then used directly for the Pt overgrowth. Figure 6.1 shows the UV-VIS spectra and SEM images of the synthesized Pt-end-capped-AuNRs with different Pt:Au ratios. The longitudinal SPR band first red-shifted to ~1000 nm and then blue-shifted, indicating that Pt is mostly deposited at the AuNR ends and the aspect ratio (ASR) of the particles increases for the Pt-AuNRs. The L-SPR band was damped with the excessive loading of Pt, consistent with the literature reports. The excitation source at 976 nm was used to match the Pt-AuNR plasmonic band.

Scheme 6.1. Schemes of the cathodes. (A) Schematic drawing of solar irradiation activation of the photocathode with hot electron generation. (B) Proposed schematic for hot electron generation and charge injection in the electrolytic reaction. Volmer-Tafel model was assumed.
Furthermore, the surfactant on these Pt-end-capped-AuNRs were stripped off by extensive wash of the particles using DI water. The particles (~$4.4 \times 10^7$ particles) were then deposited on the gold surface by drop casting method followed by annealing at 50 °C for 1.0 hour. The effective surface area of the electrode (bearing the particles) was measured to be 0.159 cm$^2$. Figure 6.2.A shows a typical SEM image of the electrode surface, on which a uniform, single layer Pt-End-Capped-AuNRs were present. Figure 6.2.B shows the schematic drawing of the electrolytic cell.

![Graph showing UV-VIS-NIR absorption measurements of AuNRs with Pt:Au ratios at 0.0, 0.1, 0.2 and 1.0 respectively](image1)

![SEM images of corresponding Pt-end-capped-AuNRs. Insets: zoomed view of individual AuNRs](image2)

**Figure 6.1.** Pt-End-Capped-AuNRs used in the electrode. (A) UV-VIS-NIR absorption measurements of AuNRs with Pt:Au ratios at 0.0, 0.1, 0.2 and 1.0 respectively. (B) SEM images of corresponding Pt-end-capped-AuNRs. Insets: zoomed view of individual AuNRs.
6.3.2 *Photoelectrolytic current*

To evaluate the photoelectrolytic activity of the prepared cathodes for the hydrogen evolution reaction (HER), chronoamperometry experiment was done. Figure 6.3.A shows the typical Faradic current of the cathode as a function of time when the near IR light source was turned on and off repeatedly. It is evident that there is photoactivation of the electrode upon light irradiation at 90, 270, 450 and 600 seconds.

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**Figure 6.2.** Modified Photocathode and the photo electrolytic cell. (A) SEM image of Pt-end-capped-AuNRs modified photocathode. The particles have a Pt:Au ration of 1:5. (B) Schematic set up for the electrochemical cell.

The absolute photocurrent was as high as 1.1 mA (6.9 mA/cm²) at a 976 nm light irradiation of 975 mW/cm². The slow kinetics upon the light’s on and off were observed, similarly to those
reported in the literature. The slow rise may be attributed to the reorganization of the charged surfactants and the slow mass transport to the electrode; the slow decay after the light being turned off may be a reflection of the depletion of electroactive species accumulated on the electrode during the photo reaction.

**Figure 6.3.** Photocatalytic activity of the particle-modified photocathode. (A) Step chronopotentiometry with 976 nm near IR light irradiation at 975 mW/cm² being turned on and off repeatedly. (B) Linear sweep voltammetry of the Au electrode in presence and absence of light, the Pt-End-Capped-AuNRs modified Au electrode in the absence and presence of light, respectively. The irradiation was 2,000 mW/cm² at 976 nm. The current measurements were from 3 measurements on the same electrode.

Furthermore, linear sweep voltammetry (LSV) was used for qualitative analysis of the photoelectrolysis. To yield the best photocurrent, the photo electrolytic conditions were optimized (Figure S.6.1). It shows that the photocurrent density increases as the pH decreases. To keep the electrolytic solution in a relatively mild condition, pH 3.0 was selected. The photocurrent also
increases as the electrolyte sodium sulfate concentration increases. Experimentally, the electrolyte concentration was selected to be 1.0 M as the photocurrent is no longer sensitive to the electrolyte concentration.

Next, we evaluated the net photocurrent generated by the Pt-AuNRs on the Au electrodes. The net photocurrent is the difference between the limiting current for the Pt-AuNRs modified electrode in the presence and the absence of the light. However, in our setup, the particles covered areas is only 0.16 cm² while the laser spot and Au electrode size are 1.0 cm². The increment of the current generated by the Au electrode also needs to be considered. Since the electrode area is much larger than the near IR light sensitive area (where the particles cover), the net photocurrent is defined as:

\[
    i_{net} = (i_{Electrode+Particles}^{Light} - i_{Electrode+Particle}^{Dark}) - (i_{Electrode}^{Light} - i_{Electrode}^{Dark})
\]

(1)

Figure 6.3.B shows the linear sweep voltammograms (20 mV s⁻¹) of the particles-modified electrode and the unmodified electrodes in the presence and the absence of light, respectively. The particles had a Pt:Au ratio of 1:1. The irradiance was at 976 nm with a power of 2,000 mW cm⁻². A net photocurrent density by the Pt-end-capped-AuNRs was recorded at 5.3 mA/cm². This increase in activity of H₂ reduction is apparently due to the activation of the photocatalysts, which turns near IR light to activated electrons that participated in the hydrogen reduction. The induced photon-to-current efficiency (IPCE) was estimated to be 0.65 %. This efficiency is similar in the order of magnitude to those from other current methods in using photons in the full solar spectrum. That being said, this is the first known to us reported photocathode that has such a high IPCE efficiency for near IR light.

In addition, the onsets (defined as the applied voltage reaching at a current density of 5.0 mA/cm²) for the reductive potential of hydrogen in the presence and absence of light were recorded.
and compared. For the Au-only electrode and the Pt-AuNRs modified Au electrode, the onset shifted by ~100 mV for the particles-modified electrode, indicating that the presence of Pt greatly reduces the over potential of hydrogen production. For the particles-modified electrode, the onset shifted from -4.0 mV for no light to -3.0 mV for with light. This indicates that Pt-AuNR particles converted photon energy to the electron kinetic energy that was used to overcome the energy barrier of the reaction. Thus, the apparent over-potential of the hydrogen production becomes smaller. This is described in Figure 6.3.B, which shows that light helped to promote the electrons to a higher energy level followed by the electrons being injected to the open orbital of H⁺ assuming the Volmer-Tafel mechanism dominates the HER reaction. Generally, it is believed that HER may involve two mechanisms. (1) The Volmer step, during which the adsorbed hydrogen ions receives an electron and forms the reactive intermediate, followed by the Tafel step, in which two reactive intermediates combine to form a hydrogen molecule. (2) The Volmer step, followed by the Heyrovsky step, in which a reactive intermediate combines with a H⁺ ion and receives an additional electron to form hydrogen molecule.¹²

6.3.3 Optimizing Pt Loading on AuNRs

To use the hot electrons efficiently, we increased the loading of Pt at AuNR ends. This is achieved by feeding more Pt salt in a stepwise manner described in the Experimental to ensure most of the reduced Pt were at the ends of AuNRs. The investigated loadings of Pt with respect to the total gold (Pt:Au molar ratio) was 0.1, 0.2, and 1, respectively (Figure 6.1.B). The effectiveness of Pt reduction has been evaluated in our previous publication, which shows that the actual Pt:Au ratio is consistent with the nominal Pt:Au ratio up to 1:1.

We then tested the activity of the cathode for HER reaction under an irradiance of 975 mW/cm² near IR light at 976 nm wavelength. Figure 6.4.A shows the net photocurrent density of
the electrode modified with particles at different Pt: Au ratios, indicated in the figure as the nominal molar ratio.

**Figure 6.4.** The effect of Pt: Au ratio on cathode activity. (A) Net photocurrent density vs Pt: Au ratio. (B) IPCE efficiency as a function of Pt: Au ratio. The error bars were from 3 measurements from same electrode.

With more Pt on AuNRs, the *net* photocurrent density increased in a linear manner, indicating we are using hot electrons more efficiently under current light irradiation condition (Figure 6.4.A). This is possibly because the total Pt surface area increases, allowing the electrode to use there SPR-generated hot electrons more efficiently.
The incident photon-to-current efficiency (IPCE) of the photocathodes was then evaluated based on the net photocurrent measured using the linear sweep voltammograms. Correspondingly, the IPCE efficiency also increases linearly with respect to the Pt:Au ratio (Figure 6.4.B). This indicates that at an irradiance at 975 mW/cm², we can improve the efficiency of using the hot electrons by using more Pt at the ends of AuNRs.

6.3.4 Power Dependence

It is unclear how the low energy photons were converted to high energy hot electrons by AuNRs. According to Fermi-Diract model, the number of hot electrons above a certain threshold increases non-linearly (expediting) with respect to the temperature of the particle. That is, if we assume the particle temperature increases linearly with respect to the irradiance, the number of hot electrons should increase non-linearly with respect to the irradiance. However, we have observed repeatedly (in H₂ production and 4-NP reduction) that chemical reaction rate increases linearly with respect to the irradiance.

To better understand how the low energy photons are converted to the hot electrons and being used in the electrochemical process, we varied 976 nm irradiance from 250 mW/cm², 650 mW/cm², 830 mW/cm² to 975 mW/cm². The particles with a Pt:Au ratio of 1:10 were used. Using the same electrochemical technique, linear sweep voltammograms were taken at various powers and the net photocurrent densities were recorded and plotted in Figure 6.5.A. The net photocurrent increases as the photon flux increases. F-statistic shows that a second order polynomial \( y = 3.61 \times 10^{-6}x^2 + 6.91 \times 10^{-4}x + 1.30 \) fits the data better than a linear relationship with a confidence level larger than 95% (the sum of the residual squared \( \chi^2 \) 0.09 for second order fitting vs. 0.27 for linear fitting. The second order response suggests that the photoreaction on the electrode involves the selection of high energy hot electrons, which is consistent with the
prediction based Fermi-Dirac model of hot electron energy distribution. This indicates that higher photon flux is more favorable in producing more hot electrons in unit amount time.

Figure 6.5. Power dependence of net photocurrent generation. (A) Net photocurrent vs photon flux. (B) IPCE % with respect to the photon flux. The error bars were from 3 replicates on the same electrode.

However, the IPCE efficiency showed a complicated pattern (Figure 6.5.B). At low photon flux, the IPCE efficiency was the highest, 1% at 250 mW/cm². It decreases quickly with respect to the photon flux to 0.75% at 650 mW/cm². Interestingly, the IPCE efficiency starts to increase again but slowly 0.8% at 975 mW/cm². The higher IPCE at lower photon flux reflects that with a fixed Pt surface area, although more hot electrons can be generated, the efficiency of using these hot
electrons drops. At a higher photon flux, the IPCE increase slightly caused by the non-linear net photocurrent–photon flux relationship.

6.3.5 White vs Near IR Irradiation

In order to assess the potential of the photocathode under natural sunlight irradiation, a white light source (Xe lamp) was used to simulate the solar irradiation. The Xe lamp output was tuned to have an irradiance of 275 mW/cm² and the cyclovoltammogram (CV) was recorded (Figure 6.6).

![Figure 6.6](attachment:figure6.6.png)

**Figure 6.6.** Cyclic voltammogram of the particles-modified electrode under near IR and white light irradiation. (Blue) Under artificial white light at 275 mW/cm²; (red) Under near IR irradiation at 250 mW/cm². Pt-AuNRs with a Pt:Au = 1:10 used in modifying the electrode.

As a comparison, the CV for the near IR source irradiation at 250 mW/cm² was also plotted. The same electrode was used on which Pt-AuNRs with a 1:10 Pt:Au ratio were applied. The white light provided a net photocurrent ~3.4 times of that under near IR light illumination. This indicates that although our electrodes are ideal for near IR light, they also work under natural solar light. The IPCE efficiency is higher under the white light, possibly because the white light has much
more high energy photons that can be turned into high energy hot electrons more more efficiently.

6.3.5 Stability

Finally, the stability of the particles-modified cathode was assessed by being exposed for a total of 16 hours under near IR light irradiation at 975 mW/cm$^2$. The cyclic voltammogram (0.2 V to -0.8 V vs RHE) was recorded during the whole time period (16 hours, 300 cycles). Figure 6.7.A shows a representative set of cyclic voltammograms (first 100 cycles) under light irradiation at 975 mW/cm$^2$. In contrast, the cyclic voltammogram for the same sample in the absence of light is shown in Figure 6.7.B. Furthermore, Figure 6.7.C demonstrates the net photocurrent defined in Equation 1 as a function of the scanning cycles. Over a period of 16 hours, the activity of the electrode only lost by 18.2 %, which shows the excellent stability of the electrode against high irradiance of near IR light (at 975 mW/cm$^2$).
**Figure 6.7.** Long-term stability of the electrode under irradiation. (A) First 100 CV cycles under near IR irradiation at 975 mW/cm$^2$. (B) Control CV of the same electrode in the absence of light. (C) The net photocurrent as a function of total CV cycles under 16 hours near IR irradiation at 975 mW/cm$^2$.

### 6.4 Conclusions

Pt-end-capped-AuNRs modified cathodes were tested for the photoelectrolytic hydrogen evolution reaction (HER) under near IR light irradiation. At optimized conditions, the IPCE efficiency can be as high as 1.5%, which is similar in the order of magnitude to current other methods in using the whole solar irradiation spectrum. Tuning the Pt:Au ratio can tune the IPCE efficiency, indicating that the HER reaction is limited by both the hot electron generation rate and the available Pt surface area. Finally, the stability of the photoactivated cathodes were tested. The cathodes only lost 18% activity over a 16-hour period under ~1000 mW/cm$^2$ irradiation. Overall,
this study shows that Pt-end-capped-AuNRs modified photocathodes can effectively convert low energy photons to chemical energies in photoelectrolytic reduction of hydrogen.

6.5 Experimental

6.5.1 Chemicals

HAuCl₄·3H₂O (99%), NaBH₄ (99%), AgNO₃ (99%), H₂PtCl₄ (>99%), ascorbic acid (99%), CTAB (99%), 5-formyl-salicilic acid (5-FSA), Na₂SO₄, sulfuric acid, and hydrochloric acid (HCl, concentrated) were purchased from Sigma Aldrich and used as received.

6.5.2 Pt-End-End-Capped-AuNRs Synthesis

The AuNRs were synthesized using our recently established method: a cetyltrimethylammonium bromide (CTAB) and 5-formyl-salicylic acid (FSA) mixture (FSA:CTAB = 1:5) was utilized as the bulky organic modifier in combination with a traditional seed-mediated growth. The resulting gold nanorods have an aspect ratio of ~ 4 (51 nm ± 4 nm x 12 nm ± 2 nm) and an SPR wavelength at 880 nm (SEM image in Figure 6.1.A). The particles were then used as prepared for Pt reduction. Briefly, the reduction of Pt with a loading of 1:10 (Pt:Au), 10 mL of as-synthesized AuNRs solution was used 40.4 µL of 0.01 M HCl was added to the Au solution at 35 °C under mild stirring for 10 minutes, followed by the slow addition of 50 µL of 0.01 M H₂PtCl₆ in 10 min under mild stirring. Finally, 287 µL of freshly made 0.1 M ascorbic acid was added dropwise. The final solution was left undisturbed at 35 °C for 8 hours. The solution color changed from light reddish pink to light purplish, indicating the reaction had taken place.

Step 2. To increase the loading of Pt to 1:1, 2:1 and 4:1 (Pt:Au) a second round of Pt reduction was done following the exact procedure scaling the values to the given loading.
6.5.3 Preparation of the Photocathode

Substrate preparation: The atomically thin gold substrate was fabricated following a previously published method. Briefly, a silicon wafer (test grade, University Wafers) was first cleaned in ethanol and dried with a stream of high purity nitrogen gas. The cleaned wafer was then coated with a 250 nm gold film, deposited with an Edward 306A resistive evaporator. Following, glass microscope slides were cut into 1 × 1 cm chips and sonicated in diluted Contrad 70 (Micro, Cole-Parmer), deionized water, and ethanol, each for 30 min, and dried under a nitrogen stream. The cleaned glass chips were subsequently affixed to a gold-coated wafer with two-part epoxy (Epoxy Technology) and cured at 150 °C for 1.75 h. The glass chips were then gently detached from the silicon wafer, which exposes a smooth gold film on the topside of the glass chip.

Pt-End-Capped-AuNRs Modified-substrate: A single layer of prepared slow-feeding Pt-End-Capped-AuNRs is used to modify the substrate using drop cast method. A net volume of 60 µL from a nanoparticle suspension with a concentration of 7.4 x 10^{11} particles/mL was cleaned using sonication for 3 times to remove the surfactant. The drop cast particles are then annealed at 55 °C for one hour. The final product is rinsed with a stream of deionized water to remove any immobilized particles.

6.5.4 Electron microscopy

Scanning electron microscopy (SEM) images were collected using an FEI Verios 460L field emission SEM (FESEM).

6.5.5 Photoelectrochemical Measurements

All electrochemical measurements were performed in a three electrodes cell, Pt-End-Capped-AuNRs-Modified substrate as the cathode, a Pt electrode as the anode and a Ag/AgCl reference electrode. The supporting electrolyte was 1.0 M Na_2SO_4 buffered to pH=3.0 with H_2SO_4.
degas with N₂. The potential of the electrode was controlled using a WaveNano Potentiostat/Galvanostat System from Pine Research Instrumentation. The reported values are normalized vs reversible hydrogen electrode (RHE) using \( E_{\text{RHE}} = E_{\text{Ag/AgCl}}^\circ + 0.059 \text{pH} + E^\circ_{\text{Ag/AgCl}} \). \( E^\circ_{\text{Ag/AgCl}} = 0.1976 \text{ V} \) at 25°C. *IS-Chronoamperometric* measurements were done at a constant potential of -0.25 V vs RHE, upon light irradiation intervals of 90 seconds, for a total period of 630 seconds. *Cyclic Voltammetry* measurements were done at a scan rate of 100 mV/sec forward cathodic scan. *Linear Sweep Voltammograms* were collected at a scan rate of 20 mV/s.

The photoelectrolytic activity was tested using a continuous wave, 976 nm laser (MDL-III, Dragon lasers). The total output was set at 2000 mW unless otherwise noted. In addition, white light measurements were performed using a 100 W Xe lamp expanded to with a power set at 275 mW, as measured using a Coherent PowerMax P30 power meter.
References


6.7 Associated Content

Figure S6.1. Optimization of the electrolytic conditions using linear sweep voltammogram. Electrode modified with Pt: Au (1:10) under 2,000 mW/cm² irradiance. (A) Optimization of pH at 1.0 M Na₂SO₄. (B) Optimization of the electrolyte concentration.
CHARPTER 7: Concluding Remarks

In summary, the investigations reported in this document demonstrate our interest in developing plasmonic materials that can effectively utilize solar irradiation, especially in the near IR region, to catalyzed fundamental chemical reactions for renewable energy and sustainable environment. A synthetic approach to selectively reduce a catalytic metal, Pd or Pt, at the ends of AuNRs was develop and tested to achieve this goal.

Furthermore, we showed two applications to take advantage of these special photocatalysts: the Pd-end-capped-AuNRs and the Pt-end-capped-AuNRs. The hybrid Pd-AuNRs showed excellent photocatalytic activity in degrading an EPA priority toxic pollutant, 4-NP, which confirmed out initial thought. Under the same concept, we showed that Pt-end-capped-AuNRs can effectively produce molecular hydrogen using light. Most importantly, these hybrid metallic catalysts are excellent in converting low energy photons to high energy electrons, which greatly extended our capability in using the whole spectrum of solar irradiation.

Above studies demonstrated great potentials of these novel hybrid metallic nanoparticles. They show great efficiency in harvesting solar emission and turn them into useful work. However, in order to produce commercially viable catalysts, continuous improvement of these catalysts are still needed in: (1) improving the chemical yield; and (2) improving the long term stability of these particles.

To further improve the efficiency of these photocatalyst, we worked with Dr. Maggard and hypothesized that by combining our plasmonic particles with a special semiconductor, i.e., the ferroelectric material that has a large remanent polarization, we can achieve efficient charge injection and separation of the hot charge carriers generated in the plasmonic particles during the SPR process. Thus, the lifetime of these charge carriers can be extended by orders of magnitude
so their efficiency of use can be greatly enhanced. Our preliminary data using Pt-end-capped-AuNRs and PbTiO$_3$ composites showed promising results. Further studies are being carried out in our labs in order to: (1) understand the charge injection and separation; and (2) optimize these systems and maximize the photon to hydrogen conversion efficiency. Efforts are also being made toward commercializing these particles.

Lastly, most of current nanoparticle catalysts show excellent reactivity but suffer from low stability, e.g., particle aggregation. One way to overcome this problem is to lay these particles down on the surface. By doing so, we lose a part of reactivity but gain stability. In this effort, we tested electrochemistry of these particles when deposited on an electrode as a first step. These particles retained excellent photocatalytic activity. In addition, their stability is greatly enhanced. This study shows a practical solution in solving nanoparticles’ stability problem and may be the ultimate design in using high reactive nanoparticle catalysts.