Effect of Secondary Metals in Gold Alloyed Nanoparticle Synthesis

by

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Class of 2019

A thesis submitted to the
faculty of Wesleyan University
in partial fulfillment of the requirements for the
Degree of Bachelor of Arts
with Departmental Honors in Chemistry

Middletown, Connecticut April, 2019
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Acknowledgments

My time at Wesleyan would not have been the same without the people that have guided and supported me along the way. I would first and foremost like to thank Professor Michelle Personick for accepting me into her lab during my freshman year and encouraging me to continue research. She has always been so patient and willing to share her vast expertise and knowledge and I could not be more grateful for my experience in her lab. I’d also like to thank all of my lab mates, past and present, including: Aidan, Haeyoon, Danny, Max, Tenzin, Abrar, Sonja, Leila, Melissa, and Sean. The long hours and moments of frustration in lab would not have been as bearable without the laughter and companionship of my lab mates!

I would like to thank my friends and housemates from Wesleyan for all of their love and support. Additionally, I would like to thank my life long friends from Pittsburgh who have always stood by me through thick and thin.

Most importantly I would like to thank my parents and brother for being catalysts in my education and love of science. To my parents, thank you for always encouraging me to pursue what makes me happiest and for showing me to value what is most important in life. To my brother, thank you for being not only a great sibling, but also a friend.

This thesis and all the research that went into it would not have been possible without the support of these people and many more! Thank you to all my professors and the rest of the Wesleyan community for giving me four incredible, life-changing years.
Abstract

Metallic nanoparticles have become a focus of research due to their many applications spanning various industries. One of their key applications is as catalysts in chemical reactions. Catalytic nanoparticles have the power to influence the products and reduce the amount of energy put into a reaction. The size, shape, and composition of nanoparticles greatly impact their catalytic capabilities. The arrangement of atoms on the surface of particles makes certain surface facets more favorable than others. Alloyed surfaces in particular are favorable due to their balance of stability and reactivity that constitutes an efficient catalyst. In this thesis, synthesis of alloyed bi- and tri-metallic particles is explored. All of the particles contain gold in combination with a reactive metal such as platinum or ruthenium. The ultimate goal was to combine the selectivity of gold with the reactivity of these secondary metals. Particles of Ir or Ru with Au were extensively studied to attempt to create particles of well-defined shapes with alloyed surfaces. The incorporation of these secondary metals proved difficult, however there are still possible alternate routes that should be pursued. Gold-silver particles were also focused on in the work of this thesis, specifically the shape-determining effect of platinum. It was found that seed-dilutions and temperature had more of a shape-determining effect than the Pt itself. The last system that was looked at was AuCu particles with the intent of reducing one layer of Cu on to Au. It was determined that Cu can deposit on Au, however these results are preliminary and the particles have not yet been tried as catalysts. Overall, the research for this thesis has lead to a deeper understanding of gold alloyed systems in seed-mediated nanoparticle synthesis with a future in catalysis.
Chapter I: Introduction

Research Motivation

Energy quite literally powers our modern global society. Without energy, everything would likely come to a halt: cellphones would be obsolete, cars would stall, and air-conditioners would break down. With the ever-growing world population and the emergence of more developed societies, the demand for energy is expected to be higher than ever before. A report from ExxonMobil estimates that by 2030 the global economic middle class will grow from 3 billion to more than 5 billion people.¹ This increase comes with improved living standards, and thus higher dependence on energy for things such as cars, electronics, and air-conditioning.¹ Specifically in the industrial sector, which includes construction, powering of factories, and the production of food, energy demand is expected to rise 20 percent. In particular, the chemical industrial sector is expected to see an even greater rise in demand at 40 percent.¹ With such a drastic increase in demand the next logical question is: how is this demand going to be met? What can be done to create more energy? One answer lies in catalysis.
In the simplest of terms, catalysis is a shortcut. In a chemical reaction, the energy required to make the reaction proceed as intended is known as the activation energy. The activation energy can be thought of as a large mountain to overcome, as seen in Fig. 1.1 as the physical snow-capped mountain.2 A catalyst is like a tunnel through the middle of the mountain; it is an easier route to the same end. The girl in the red car (see Fig. 1.1) does not have to put in nearly as much energy to get to the other side of the mountain in comparison to the physically exhausted mountaineer. In more scientific terms, a catalyst lowers the activation energy of a reaction by providing an alternate reaction pathway. This means that less energy is used to get the same product. An important factor of this is that the catalyst is not used up in the
reaction and instead only facilitates the completion. An example of catalysis is the catalytic converters found in modern vehicles. During use, car engines produce hazardous amounts of nitrogen oxides, carbon monoxide and unburned hydrocarbons. To reduce the amount of pollution released into the environment, catalytic converters, which usually contain a precious metal such as platinum, react with the pollutants to convert them into less harmful carbon dioxide, water, and nitrogen gas.\(^3\) This is just one example of everyday catalysis. The metal in these reactors is in the form of nanoparticles, which are highly unique catalysts and will be the focus of this thesis.

Catalysis is projected to be one of the key factors in meeting the expected demand for energy. Along with alternate sources (e.g. nuclear energy) and renewable sources (e.g. solar and wind), catalysts will provide more energy by creating more efficient processes for energy generation and chemical synthesis.\(^4\) The worldwide demand for natural gases and oils is not expected to decrease,\(^1\) so instead of eliminating these energy-intensive processes, the alternative is to make them more efficient. If catalysis is to be used to increase efficiency, it is crucial to understand how to form catalysts in order to create the best catalysts possible.

**Metallic Nanoparticles in Catalysis**

Nanoscience research spans a very wide berth of applications including, but not limited to, construction,\(^5\) agriculture,\(^6\) and medicine.\(^7\) The nanoscale holds many unique optical and electrical properties\(^8\) that have led it to become an area of significant research interest today. These unique properties can be attributed, in part, to the size limitation of the nanoscale itself. One particularly important feature for
The catalytic applications of nanoscale materials is their surface area to volume ratio. Due to their small size, this ratio is very high, which means that there is more surface area available for reactions (e.g. catalytic reactions) to take place, resulting in higher activity per unit mass and a more efficient use of expensive catalytic metals. This notable characteristic of nanoscale materials has led to increased interest in the catalytic properties of metallic nanoparticles. The variability of metallic nanoparticles makes them ideal catalysts; their shape, size, and composition are highly tunable and can be designed to make the perfect catalyst. In addition, catalysts in different physical states from the reactants, such as solid metallic nanoparticles in liquid reactant solutions, are known as heterogeneous catalysts. Due to their physical difference, heterogeneous catalysts are easy to separate from the products upon completion of the reaction, making nanoparticles even more attractive as catalyst.

**Figure 1.2:** Graphic demonstrating the Sabatier principle. Reproduced from reference 11.
The Sabatier principle (see Fig. 1.2) defines the ideal catalyst as one that binds tightly enough to the substrate to react, however not too tightly as to never let it go. Transition metal catalysts in particular, such as metallic nanoparticles, have been carefully designed to optimize this principle. As stated previously, the shape of a nanoparticle influences the catalytic properties of said particle. Catalytic activity, that is to say the rate of reaction, is one of these properties. The way atoms arrange themselves on the surface affects the number of atoms available for reactions. Atoms that are available in appropriate arrangements to catalyze a reaction are referred to as active sites, thus it follows that nanoparticles with more active sites are more catalytically active. An example of this can be seen in a study by Chen et al which focused on various gold surfaces and their catalytic activities in the oxidation of CO to CO$_2$. In Fig. 1.3 the blue bars represent the reaction rates based on total Au whereas the red bars represent the rate per active site. The different formations (shown at the top of Fig. 1.3) demonstrate drastically different levels of activity. The bilayer of Au film is much more active than the hemispherical Au particles both in terms of total Au and active sites (Fig. 1.3). This example clearly demonstrates the effect on catalytic activity from altering shapes, and thus active sites, of nanoparticles. This principle is applicable throughout all nanoparticle synthesis and can be altered to reflect the desired level of activity.
In addition to catalytic activity it is also very important to consider catalytic selectivity, which determines which products are formed. Much like activity, selectivity is dependent on the shape and more specifically the “facets”, or exposed faces, of the particle. As shown in Fig. 1.4, facets are determined by the arrangement of atoms on the surface. When the particles are grown from pseudospheres into shaped particles, different facets prevail to determine the ultimate shape. Selectivity is deeply dependent on shape as exemplified by the hydrogenation of benzene with catalytic platinum particles. Cubic particles catalyze the complete hydrogenation of benzene to cyclohexane whereas cuboctohedral particles catalyze both complete hydrogenation and partial hydrogenation of benzene (see shapes in Fig. 1.5). The different outcomes stem from the atomic interactions, which vary between facets. Cubic particles only have \{100\} facets whereas the cuboctohedral particles have \{100\} and \{111\} facets (see Fig. 1.4). Since the atoms are arranged differently on these facets, they interact differently with the substrate, thus promoting
distinct reactions. This is just one clear example of the powerful effects the shape of nanoparticles can have on the overall catalytic selectivity. A similar effect is also observed in particles of mixed composition.

**Figure 1.4:** (A) Depicts the arrangement of surface atoms for \{111\}, \{100\}, and \{110\} faceted particles. (B) Demonstrates the ultimate morphologies of particles with the facets shown in (A). Reproduced form reference 14.

![Figure 1.4](image)

**Figure 1.5:** Models of (A) cubic and (B) cuboctahedral particles. The benzene hydrogenation reactions below each structure represent results from reference 15, which demonstrated that cubic platinum particles catalyze the complete hydrogenation of benzene to cyclohexane, whereas cuboctahedral particles catalyze partial and complete hydrogenation of benzene.
Much like the catalytic effects caused by varying facets, the catalytic effect caused by multimetallic catalysts stems from the atomic level. The interactions between different metal atoms affects the active sites and can influence the selectivity and reactivity of the particle.\[^{16}\] There are many types of alloyed particles that can form, such as core-shell, mixed, and dilute alloys.\[^{10}\] Core-shell particles are comprised primarily of one metal in the center surrounded by a layer of a different metal. An example is gold-palladium core-shell particles, which, in a study by Mizukoshi et al.,\[^{17}\] were shown to have enhanced catalytic properties. In core-shell particles with a gold/palladium ratio of 1:4, the catalytic activity for the hydrogenation of 4-pentenoic acid was about three times higher than the equivalent 1:4 ratio of monometallic gold and platinum particles. The alloyed particles were significantly more active than the pure metals on their own, which demonstrates how the intramolecular bimetallic interactions were clearly the cause of the increased activity.\[^{17}\]

The ratio of metals incorporated in particles can vary from 50:50 to very dilute. Particles that have very low levels of one metal are known as single atom alloys (SAA), in which individual atoms of one metal are isolated on the less reactive host metal surface.\[^{18}\] SAA particles, also known as dilute alloys, are of particular interest for their unique catalytic ability to balance selectivity and activity. For example, when platinum atoms are in contact with each other, they bind strongly with each other, thus limiting their functionality as catalysts. However, when incorporated as a dilute alloy, this problematic binding is minimized and only the desired selective properties of platinum are observed.\[^{19}\] Dilute alloys such as these have been studied
mostly as catalyst for hydrogenation reactions, which are often limited by H₂ dissociation.\textsuperscript{18} Dilute alloys of metals such as platinum and ruthenium have been proven to be selective catalyst for H₂ dissociation. Copper is inert to H₂ dissociation, however when SAA of Pd are present on a Cu surface, the H₂ can dissociate on the Pd atom and spillover onto the Cu surface and desorb.\textsuperscript{18} In this case, the diluted Pd was able to enhance the heterogeneity of the particle. Another example of a SAA system is dilute Pd on Au particles, which are used as catalysts in oxidation reactions. These particles successfully combine the reactivity of Pd with the highly selective of Au.\textsuperscript{19} These are just a couple examples of the benefits to promoting the synthesis of dilute bimetallic catalysts and more will be explored in this thesis.

When considering core-shell bimetallic particles, the possibility of underpotential deposition (UPD) is very important to consider. UPD is a phenomenon in which a metal is able to reduce at a potential more positive than the potential at which bulk reduction would occur (see Fig. 1.6). This results in the formation of a monolayer; surfaces with monolayers are believed to have properties that differ greatly from bulk materials,\textsuperscript{20} much like the results observed in the aforementioned AuPd core-shell particles. The promotion of UPD is a focus of this research and will be discussed in more detail later on. While it is important to understand the catalytic implications that arise from the nanoparticles’ morphologies, the synthesis of the particles themselves is truly critical. It is through purposeful manipulation of the synthetic pathway that the physical characteristics can be designed.
Figure 1.6: Depiction of underpotential deposition and bulk reduction of copper on gold.

Metallic Nanoparticle Synthesis

The formation of particles varies greatly with the style of synthesis and the materials involved. Typically, metal salts are reduced using reducing agents, light, or electric current. Some examples of syntheses are polyol, electrochemical, and seed mediated. The general schematic for aqueous seed mediated synthesis, the synthesis used in this thesis, can be seen in Scheme 1.1. The formation of seeds occurs in a surfactant that functions as a capping agent. Common surfactants are cetyltrimethylammonium chloride (CTAC) or cetyltrimethylammonium bromide (CTAB) (Fig. 1.7). Sodium borohydride (NaBH₄) is a strong reducing agent that initiates the rapid nucleation of metal ions to form pseudo-spherical metallic seed
particles. The seeds are then added to a growth solution containing CTAB or CTAC, 
more metal salts, and a weaker reducing agent, ascorbic acid (Fig. 1.7). While the 
seed growth is rapid, the particle growth is a slower process due to the use of a 
weaker reducing agent. This slowed growth of the particles in the second step allows 
for the formation of organized facets rather than general nucleation into small 
spheres.

Scheme 1.1: Depiction of seed mediated synthesis using generic metal salts.
The pH and concentrations of numerous ions in the growth solution have a drastic impact on the final shape of the particles. Altering the pH, through the addition of acid/base, has a strong effect on the outcome of the synthesis since pH greatly influences the reduction potential of the ascorbic acid reducing agent. The same holds true for temperature, which can easily be changed by placing the reaction vial in a water bath or refrigerator. By altering the reduction potential of the reducing agent or metal ions in the growth solution, the nanoparticle formation can be sped up or slowed down to promote the formation of the desired product. Increasing the concentration of reducing agent has also been shown to have shape-determining effects, such as with gold nanoparticles. The additional reducing agent increases the rate of gold ion reduction, favoring increased kinetically controlled growth, leading to
higher energy \{100\} facets rather than thermodynamically favored \{111\} facets. This is also due in part to CTAB preferentially stabilizing \{100\} facets over \{111\}, therefore increased CTAB and increased reducing agent concentration promote the formation of cubes.\textsuperscript{21} Other factors that can be altered are the halide and metal ion concentrations.

When it comes to metal ion concentration, the concentration in the solution usually correlates directly to shape-control. Bimetallic gold-copper particles are a prime example of this phenomenon. When the amount of CuSO$_4$ in the system increases from 50.0 µL of 2.00 × 10$^{-3}$ M to 400 µL of 1.00 × 10$^{-2}$ M, the shape of the particles goes from cuboids to decahedrons.\textsuperscript{22} The copper ions preferably interact with \{111\} facets, thus retarding the growth of these facets and determining the final shape.\textsuperscript{22} Other concentrations in the growth solution that can be altered are halides, which are integral in CTAB and CTAC. Switching from one surfactant to the other can drastically affect the outcome of the synthesis, as will be discussed in this thesis. Other halides, such as iodide, have also been shown to have shape-directing properties when added in very small concentrations.\textsuperscript{23} All together, it is easy to see the infinite possibilities that can arise from varying the properties of the growth solution. The never-ending shapes, sizes, and compositions of metallic nanoparticles are what make them such a hot topic in research.

**Analytical Techniques**

Due to the nano-size of these particles, normal light microscopes cannot be used to visualize them. In lieu of a light source, electron microscopes are used to
image the nanoparticles. Scanning electron microscopy (SEM) focuses an electron beam on a sample and detects the height at which the electron is reflected. The resulting black and white image shows the surface features of the particles, with lighter spots being closer and darker spots being further from the electron source. Transmission electron microscopy (TEM) is also often used to image nanoparticles. TEM differs from SEM in that TEM measures the electrons that go through the sample rather than the ones that are reflected. This means that TEM images depict an outline or shadow of the particles. TEM images also have higher resolution due to the higher voltage used to accelerate the electrons.

In order to analyze the composition of the particles, two common techniques are used: Energy dispersive spectroscopy (EDS) and Inductively coupled plasma mass spectrometry (ICP-MS). EDS focuses a beam of electrons at the sample and measures the resulting x-ray emission, which is specific to each atomic element. ICP-MS, on the other hand, breaks down a sample into ions and separates these ions using mass spectrometry to identify the composition of the sample. To create a visual map of elemental composition X-ray photoelectron spectroscopy (XPS) can be used to further analyze particle composition.

**Thesis Overview**

This thesis focuses on three main metallic systems: gold-ruthenium/iridium, gold-silver-platinum, and gold-copper. Gold as a catalyst has been extensively studied and is known to be highly selective in hydrogenation reactions and carbon dioxide reduction reactions. The particles of gold with iridium or ruthenium were
synthesized with the intent of creating particles of well-defined shapes with alloyed surfaces. Ruthenium has recently emerged as a material of interest for its catalytic role in biomass related reactions. The term biomass refers to organic materials such as wood, crops, and animal waste. Biomass is a form of renewable energy since these materials store energy from the sun. The stored energy is converted to usable energy through conversion into biogas/biofuel, such as ethanol. Hydrogen gas is a form of biomass that can be difficult to store, however there are some chemical storage solution, such as ammonia borane (AB), that seem hopeful. In a catalyzed reaction, H₂ can be formed from aqueous AB and liquid water. Ruthenium particles stabilized on an activated carbon surface have been proven to be exceptionally active catalysts for this hydrolysis reaction. The particles are not only highly efficient, but also can be reused multiple times. Various other studies have been done on ruthenium catalysts, including bimetallic syntheses, such as that seen in this thesis. In a study by Zhang et al., stable ruthenium-copper catalysts were used three times before any significant degradation of catalytic activity was observed. These studies demonstrate the significance of ruthenium as a durable and active catalyst. In terms of iridium, there have also been plentiful studies on its catalytic capabilities. One such study examined iridium’s role as a catalytic enhancer by creating iridium-copper particles with a palladium shell. These core-shell particles demonstrated enhanced activity and stability when compared to monometallic palladium particles. Due to these past successes in catalysis, this thesis experimented with a novel approach to the incorporation of ruthenium and iridium in gold particles via seed-mediated synthesis.
The seed-mediated synthesis of gold-silver particles is a well-established system. Personick et. al\textsuperscript{30} demonstrated how increasing the silver concentration in the growth solution led to the particles morphology changing from \{111\} facets, to \{110\}, to \{310\}, and ending at \{720\} facets. Continuing from this basis, platinum and gold have also been studied closely. A study by Stone et. al\textsuperscript{31} looked briefly at PtAuAg particles, however the mechanism and relationship between these three metals was never fully explored. Here an attempt is made to understand the shape-determining factors of this growth mechanism.

To carry on multimetallic syntheses with gold, the final focus of this thesis is gold-copper particles. AuCu particles have been shown to participate as catalysts in renewable energy related reactions. Thiol-capped AuCu particles selectively reduce CO\textsubscript{2} to CO, thus converting a harmful fossil fuel emission into a molecule of diverse applications, such as production of methanol and hydrocarbons.\textsuperscript{32} The research of this thesis centers itself on understanding the growth mechanism of gold-copper core-shell particles. As a whole, this thesis presents an in-depth view of the growth of multimetallic gold-containing nanoparticle syntheses. By gaining more insight on the growth mechanisms of these particles, they can more easily be tuned to create catalysts for whatever the desired application may be.
Chapter II: Methods

Materials

The following chemicals were purchased from Aldrich: potassium hexachloroplatinate $\geq 99.9\%$, sodium borohydride $99.99\%$, cetyltrimethylammonium chloride 25 wt. % in water, silver nitrate $99.9999\%$, and ruthenium (III) chloride hydrate $99.98\%$. Cetyltrimethylammonium bromide of $\geq 99\%$ purity was purchased from Sigma. L-ascorbic acid of $\geq 99\%$ purity was obtained from Sigma-Aldrich. Tetrachloroauric acid trihydrate $99.99\%$, iridium (III) chloride hydrate $99.8\%$, sodium bromide $99.99\%$, potassium bromide $99 + \%$, sodium hydroxide $99.99\%$, and Puratonic copper nitrate $99.999\%$ were all purchased from Alfa Aesar. Hydrochloric acid was purchased from Fluka. The SEM used for imaging was a Hitachi SU5000 field-emission scanning electron microscope. The EDS incorporated in the SEM was an AMETEK EDAX Octane Pro-A. The ICP-MS used for elemental analysis was a Perkin Elmer ICP-MS Elan DRC-e.

Nanoparticle Synthesis

Seed Particles

All the particles were synthesized following a seed-mediated synthesis. All solutions were prepared using $18.2\Omega$ pure water. The platinum seeds were synthesized by combining 10 mL of 0.1M cetyltrimethylammonium bromide (CTAB) and 0.75 mL of 0.01M $K_2PtCl_6$ in a 20 mL vial with a stir bar. The solution was placed in a 60°C water bath with spinning for 5 minutes. Then 1.3 mL of 0.01M sodium borohydride was injected rapidly and the solution was left to heat with
stirring for two more minutes until the solution was clear and light brown in color. The vial was removed from the heat, covered in Parafilm with a small slit cut in it, wrapped in aluminum foil, and left undisturbed for two hours. The gold seeds were synthesized in a very similar manner, but at room temperature. In a 20 mL vial, 10 mL of 0.1M cetyltrimethylammonium chloride (CTAC) was combined with 20 μL 1M HCl and 250 μL 0.01M HAuCl₄ • 3H₂O and stirred for one minute. In the same vial, 600 μL 0.01M NaBH₄ was rapidly injected and stirred for an additional minute until the solution was a brownish-red color. The vial was covered in the same way as the platinum seeds and left undisturbed for two hours.

*Ruthenium/Iridium-Gold Particles*

In a 20 mL vial, 10 mL of either 0.1M CTAC or CTAB was added followed by 650 μL of 0.01M RuCl₃ hydrate or IrCl₃ hydrate, 200 μL HAuCl₄ • 3H₂O, and 420 μL 0.1M of L-ascorbic acid. The vial was heated for five minutes at 60°C. After heating, 50 μL of 10x diluted gold seeds were added. The seeds were diluted in either CTAB or CTAC depending on which surfactant the growth solution made of. The solution was swirled to mix immediately and placed in a 40°C water bath for 48 hours. In syntheses with acid or base added, HCl and NaOH respectfully were added after the addition of gold.

*Gold-Silver Particles from Platinum Seeds*

In a 20 mL vial, 10 mL of either 0.1M CTAC or CTAB was added. The following amounts were added specifically in the follow order: 200 μL 1M HCl, 500
\( \mu L \) 0.01M HAuCl\( _4 \) • 3H\( _2 \)O, 100 \( \mu L \) AgNO\( _3 \), and 100 \( \mu L \) 0.1M ascorbic acid. The solution was swirled and 100\( \mu L \) of 1000x diluted seeds were added. The seeds were diluted in either CTAB or CTAC accordingly. For some of the syntheses, the vial was heated at the specified temperature for five minutes before the addition of the seeds. The growth solution was left undisturbed at room temperature (unless otherwise specified) for three hours.

**Platinum-Gold-Silver Particles**

In a 20 mL vial, 10 mL of 0.1M CTAB were added followed by 600 \( \mu L \) K\( _2 \)PtCl\( _6 \), 200 \( \mu L \) 0.01M HAuCl\( _4 \) • 3H\( _2 \)O, 100 \( \mu L \) AgNO\( _3 \), and 100 \( \mu L \) 0.1M ascorbic acid. The solution was swirled and heated to either 40°C or 60°C for five minutes in a water bath. Upon removal from the heat, 100\( \mu L \) of 100x or 1000x diluted gold seeds in CTAB were added. The growth solution was left undisturbed at 40°C for three hours to 24 hours depending on the experiment at hand.

**Gold-Copper Particles**

The gold-copper particles were prepared in the same manner as the gold-silver particles synthesized in CTAC, however without the addition of silver nitrate. These Au-only particles were spun down, washed once with water, and resuspended in 10 mL 0.1M CTAC. A second growth period then began after the addition of 200 \( \mu L \) 1M HCl, 100 \( \mu L \) AgNO\( _3 \), various ratios of 0.01M HAuCl\( _4 \) • 3H\( _2 \)O and 0.01M CuNO\( _3 \), and 100 \( \mu L \) 0.1M ascorbic acid. The particles were left to grow at room temperature for 30 minutes.
**Characterization**

*Scanning Electron Microscopy*

The entirety of the imaging was conducted using Scanning Electron Microscopy (SEM). At the completion of the reaction the vial was vortexed and a 1 mL aliquot was removed and put in a 1 mL eppendorf tube. The particles were spun down at 7k rpm for five minutes, the supernatant was discarded, and approximately 1 mL of 18.2Ω pure water was added. To resuspend the pellet, the vial was vortexed and sonicated if necessary. This washing process was repeated once more. Upon discarding the supernatant of the second wash, approximately 0.1 mL of water was added and the pellet resuspended. A silicon wafer was cut into pieces and labeled with identifying symbols for each sample. Using a micropipette, a 2 µL drop of each sample was placed on the plate. The plate was placed in a desiccator until the liquid had all evaporated and imaged within 24 hours of plating. While imagining with the SEM, if elemental analysis was done, the EDS incorporated in the microscope was used.

*Inductively Coupled Plasma Mass Spectrometry*

ICP-MS preparation was similar to the process used for SEM plating. A 1 mL aliquot of the sample was removed and placed in a 1 mL eppendorf tube. The particles were then centrifuged for 15 minutes at 14.7k rpm and washed once. After spinning down again, exactly 1 mL of water was added and the pellet was resuspended. Exactly 1 mL was transferred to a 15 mL falcon tube and digested with 2 mL of aqua regia (3:1 HCl:HNO₃, use with extreme caution, this is a very strong
acid). The particles were usually digested within an hour, but were often left overnight to be sure. The sample was diluted with 18.2Ω pure water to bring the total volume to exactly 7 mL and analyzed by the ICP-MS instrument.
Chapter III: Ruthenium and Iridium on Gold Particles

Platinum alloyed nanoparticles have proven to be especially viable catalysts for oxygen reduction in fuel cells.\textsuperscript{33} Due to this promising application, there is a push for more research into different platinum alloys. This led to the synthesis of nanoparticles of platinum with gold or silver being studied extensively.\textsuperscript{31} Building upon this work, a similar approach was taken swapping platinum for ruthenium or iridium, to attempt to create gold and ruthenium or iridium alloyed particles. Ruthenium and iridium have been studied as catalysts in fuel cells much like platinum alloys.\textsuperscript{34} The goal was to synthesize shaped particles with surfaces of alloyed RuAu or IrAu to be used as catalysts.

The initial synthesis as described in the Methods section proved not highly successfully in achieving the desired particles. The IrAu particles were polymorphous and ranged from approximately 20 to 50 nm in diameter. The RuAu particles did not have a very defined shape and the surfactant proved difficult to remove before imaging. In addition, when analyzed by EDS, there was no significant ruthenium metal present. Despite the growth solution containing over three times more ruthenium ions than gold, gold was the only metal detected by EDS. The same observation was made for the iridium-gold system. In an attempt to incorporate more Ru and Ir into the surface of the particles, the pH was adjusted through an acid gradient. In theory, changes in the pH should increase the rate of reduction of Ru and Ir, thus encouraging their reduction on gold. \textit{Fig. 3.1} compares the RuAu particles with 0 \textmu L and 40 \textmu L of 1M HCl. It can be seen that some of the particles with no added acid have some defined shapes such as bipyramids and rods (\textit{Fig. 3.1A}). In the
particles with acid though, any shape-control is completely lost and only amorphous blobs form (Fig. 3.1B). This demonstrates that lowering the pH of the growth solution does not enhance the particle formation, but rather hinders it. The same acid gradient was applied to the IrAu synthesis however no significant change was observed.

![Figure 3.1: Ruthenium and gold nanoparticles with (A) 0 µL and (B) 40 µL 1M HCl (scale bar = 500 nm).](image)

Continuing to determine the effect of pH on growth, a gradient of base was also tested. Since decreasing the pH proved to change the rate of reduction such that a negative effect was observed, it was thought that creating a more basic solution might have the opposite effect on the rate of reduction. Bench top pH test strips were used to measure the pH of the growth solution. The normal pH of the growth solution was about 2, however increasing the pH to 5 through the addition of 0.1 mL of 0.1M NaOH proved much too dramatic. A color change was observed immediately upon heating the growth solution before adding the seeds. This color change is indicative of rapid metal reduction, likely that of gold which has a higher reduction potential than ruthenium or iridium. Smaller changes in pH were attempted by adding less base but
the system appeared to be very sensitive to base and was difficult to manipulate in small increments. Since changes in pH were not proving very effective, alterations of other factors were focused on.

As previously described, changes in temperature alter the reduction rate of metal ions and reducing agents. It is generally observed that reactions at higher temperatures proceed more rapidly. When looking at the effect of temperature during the incubation of the particles, the reaction was only run for 24 hours rather than 48. Looking at Fig. 3.2 it is easy to see that the particles incubated at a higher temperature (Fig. 3.2B) were much larger and have well defined facets. It is likely that the particles incubated at 40°C (Fig. 3.2A) have these facets, however their extremely small size made it difficult to determine using SEM. Regardless of the size and shape of the particles, EDS analysis still failed to detect iridium in these particles. A similar temperature effect was observed in the RuAu synthesis and no ruthenium was present in any sample.

Figure 3.2: IrAu particles incubated at (A) 40°C and (B) 50°C for 24 hours (scale bar = 500 nm).
Seed particle dilution is an easily manipulated property and very influential to the growth of the particles. When seeds are more diluted, there are less nucleation sites for particles to grow from. If there is an increased ratio of metal ions to seeds, larger particles would be expected to form. This theory is easily confirmed by looking at Fig. 3.3. The particles grown from 10x diluted seeds are about 30 nm in diameter, the 100x diluted sample average about 50 nm, and lastly the 1000x diluted seeds produced huge particles of just over 100 nm. From these images, it is obvious that more dilute seeds lead to larger particles. Beyond changing the amount of seeds added to the growth solution, the type of metallic seeds was also changed. Platinum seeds 100x diluted produced RuAu and IrAu particles of over 100nm. They were most comparable in size and shape to the particles growth from 1000x diluted gold seeds (Fig. 3.3C).

**Figure 3.3:** IrAu particles incubated for 24 hours with (A) 10x, (B) 100x, and (C) 1000x diluted Au seeds (scale bar = 500 nm).

The last property that was manipulated was the surfactant. By switching the surfactant from CTAB to CTAC, the halide, bromide, is exchanged for another halide, chloride. While this may seem insignificant at first, it actually has a drastic
effect. When grown under the same exact conditions, the particles grown in CTAC (Fig. 3.4) demonstrate no shape-control. This clearly demonstrates that bromide must be a crucial shape-determining factor. To further investigate this effect, varied amounts of 1M NaBr was doped into the growth solution of particles grown in CTAC for 24 hours. Looking at Fig. 3.5A-C, the RuAu particles did not demonstrate any response to the added NaBr. The IrAu particles on the other hand showed dramatic changes in response to increased concentration of Br in the growth solution (see Fig. 3.5D-F). The increased Br concentration directly correlated to an increase in faceted particles of larger size. This suggests that Br is interacting with faceted surfaces promoting their growth. It is possible that a similar shape-directing effect could be observed in the RuAu system if the concentration of Br was increased even further. While these results are certainly intriguing, none of these particles incorporated significant amounts of neither ruthenium nor iridium. It could be possible that the level of Ru or Ir incorporated in the particles is so low that EDS could not detect it. ICP-MS, a more sensitive technique, might be able to determine the composition of these particles more precisely. Further exploration with other factors, such as incorporating other metals or halides, like copper or iodide, might prove useful in achieving the desired alloyed surface. Running the reaction at temperatures higher than 50°C could increase the rate of reduction of Ru and Ir. The ascorbic acid could also easily be swapped out for another stronger reducing agent, which may aid in the alloying process. While the ultimate goal is to synthesize RuAu and IrAu catalysts, efforts should be made to do so in an energy-efficient matter. The energy saved in catalysis should always exceed the energy put into making the catalyst itself.
Figure 3.4: IrAu particles grown in (A) CTAB vs (B) CTAC (scale bar = 500 nm).

Figure 3.5: SEM images of RuAu particles with (A) 100 μL, (B) 200 μL, and (C) 500 μL of 1M NaBr. The bottom row is IrAu particles with (D) 100 μL, (E) 200 μL, and (F) 500 μL of 1M NaBr (scale bar = 400 nm).
Chapter IV: Platinum Effect on Gold-Silver Particles

It has previously been mentioned that bimetallic platinum particle syntheses have been explored. On top of this, there has been research of trimetallic synthesis as well. In a study by Stone et al.\textsuperscript{31} PtAuAg particles were studied to determine the growth pattern. In the first ten minutes of synthesis, it was shown that concave cubes form initially, but later on in the growth process this shape is lost. These findings sparked an interest in the various shape-directing properties of gold, silver, and platinum when interacting with each other. To further explore this concept, the focus shifted to AuAg particles with low concentrations of Pt. When the growth solution is CTAC based, AuAg particles from Au seeds form concave cubes (CC). However, when switched to CTAB, the particles form tetrahexahedrons (THH) (\textit{Fig. 4.1}).\textsuperscript{35,36} Curiously, when the same conditions are followed using Pt seeds rather than Au seeds, CC are formed in both surfactants. The possible explanations for this difference were explored extensively.

\textbf{Figure 4.1}: AuAg (A) THH and (B) CC particles grown in CTAB and CTAC respectfully from Au seeds (scale bar = 500 nm).
In the aforementioned trimetallic synthesis of PtAuAg particles, K$_2$PtCl$_6$ was added directly to the growth solution at approximately a 3:1 ratio with HAuCl$_4$ and 6:1 ratio with AgNO$_3$. The addition of K$_2$PtCl$_6$ into the growth solution also brought with it the introduction of several new ions: potassium, platinum, and chlorine. All of these ions could be interacting in ways that alter the growth mechanism. Platinum, as an example, is much harder to reduce than gold, therefore the rate of reduction on the surface of the particle would be drastically different. Additionally, the growth solution in the trimetallic reaction was heated at 60°C before incubating for at least 24 hours at 40°C. This is a significantly warmer and longer growth period than the standard AuAg synthesis, which rest at room temperature for just three hours. The increase in temperature would increase the reduction rate of the metal ions and reducing agent, which would speed up growth significantly. The longer growth time also allows for the ions to rearrange into a more stable conformation, which might affect the morphology observed at the end of incubation. Lastly, the seed dilution used in the trimetallic synthesis used a seed dilution of just 10x, whereas the bimetallic methodology calls for 1000x diluted seeds. The effect of all of these varying factors will be investigated more closely to determine whether or not they are a significant shape-determining factor for concave cube formation. In other words, the characteristics of the PtAuAg synthesis were used to study the AuAg and Pt seed system in order to determine what was causing CC to form.
Figure 4.2: AuAg particles kept at room temperature (A) and 40°C (B) before the addition of 1000x diluted Pt seeds and incubated at room temperature for three hours (scale bar = 500 nm).

One of the most influential aspects of this reaction was the temperature throughout the growth process. By increasing the temperature of incubation, the rate of reduction was greatly increased. As shown in Fig. 4.2A, when AuAg particles grown from Pt seeds are kept at room temperature throughout the three hour growth process, the prevailing morphology appears to be THH. This is a stark comparison to the particles grown at 40°C (see Fig. 4.2B), which grew into polymorphic particles including CC, THH, and other faceted shapes. The particles incubated at an increased temperature were also much larger, at approximately 100 nm, whereas the particles grown at room temperature were approximately half this size at about 50 nm. The increase in size demonstrates how more metal reduced in the three hours of growth when the temperature was raised. It should be noted that the very small size of the particles grown at room temperature limited the quality of imaging. TEM imaging could be done to determine if these small particles have facets that just cannot be seen with the SEM.
Due to the success demonstrated by increasing the incubation temperature, the reaction vial was also heated before the introduction of the seed particles. The seeds function as a starting point for the particles to grow from; when they are present in solution they increase the rate of reduction by providing nucleation sites. This means that metal reduction does not rapidly occur until after the seeds have be introduced to the growth solution. By heating the reaction vial before the introduction of the seeds, the rate of reduction in the growth solution is increased and, in a sense, primed for the addition of seed particles. Fig. 4.3 depicts the difference observed when the growth solution is pre-heated to 40°C (Fig. 4.3A) vs. 60°C (Fig. 4.3B) while maintaining the incubation temperature of 40°C. The particles that were pre-heated to 60°C demonstrate more uniform morphologies, whereas the particles heated to just 40°C are a greater mixture of faceted particles. The consistency of the particles in Fig. 4.3B is more ideal for catalytic purposes since the reactivity and selectivity would be more consistent throughout a uniform sample. On the other hand, the energy required to heat the sample to 60°C takes away from the energy-efficiency aim. This highlights
an aforementioned delicate aspect of nanoparticle synthesis: energy-efficient catalysts must be synthesized in an energy-conscious manner. For this reason, pre-heating to just 40°C was kept as the standard condition.

![Figure 4.4: SEM image of AuAg particles from Pt seeds diluted (A) 10x, (B) 100x, and (C) 1000x (scale bar = 500 nm).](image)

As described previously in Chapter 3, the dilution of the seed particles can have a large impact on the size of particle morphology (see Fig. 3.3). A similar relationship between size and seed dilution as described with RuAu and IrAu particles is observe in AuAg particles from Pt seeds. Even more so, the shape of the particles also appears to be dependent on the seed dilution. The particles from 10x diluted seeds (Fig. 4.4A) are approximately just 60-90 nm in diameter. These small particles are varied in shape, however the majority of shapes seem to be CC and some THH. In
the 100x diluted sample (Fig. 4.4B) the particles are slightly larger, approximately 100nm, and are still a mixture of morphologies. These particles do seem to tend toward THH formation but cubic particles are still present. Moving on to the 1000x diluted seed particles, the ultimate nanoparticles are huge at approximately 200 nm or larger. A wide variety of shapes form under these conditions including smaller THH with diameters around 100 nm. Instead of cubic particles there are many other faceted particles. This evidence suggests that the lower dilution of seed particles does have a role in shape-determination, meaning that smaller particles tend toward CC formation more than larger particles. The PtAuAg particles from the Stone et al.\textsuperscript{31} study showed that after the first ten minutes of growth the particles were cubic, however this morphology was less prevalent later on in the growth process. This also supports that smaller particles favor cubic conformations, which is in agreement with what is demonstrated in Fig. 4.4. The size-dependence could be due to stability such that larger particles rearrange as they grow to form more stable morphologies, like those in Fig. 4.4C.

Seed dilution also proved to have a strong effect on the amount of platinum incorporated in the PtAuAg particles. Particles of 100x diluted and 1000x diluted Au seeds were analyzed through EDS. Table 4.1 presents the average elemental ratios for each metal in the final particles. From this data, it is clear that the particles from 100x diluted seeds incorporated approximately equal amount of Pt and Au, whereas the particles from 1000x diluted seeds incorporated almost twice as much Au than Pt. In terms of creating a dilute alloyed particle, this suggests the 1000x dilution is preferential to the 100x dilution, however that does not address the concern of CC
formation. The shape of the particles between the two dilutions did not appear to be significantly different, however the difference in incorporation of metal could give insight to the AuAg with Pt seeds system. To summarize what we know so far, lower dilutions create more cubic particles, and they also might incorporate more platinum as demonstrated by *Table 4.1*. There are a couple reasons that this may be observed.

If decreasing the dilution incorporates more platinum, and cubes are seen at lower dilutions, than it may be hypothesized that an increase in platinum incorporated in the particles creates more cubic particles. This could be because lower dilutions of seeds would correlate to more residual Pt in solution. Therefore if shapes are seen at lower dilutions, i.e. more Pt in solution, than the shape-control could be attributed to platinum incorporating in the particles. Another reason for this shape-control could simply be the smaller size. While this is not definitive proof of more Pt incorporated in the AuAg particles from Pt seeds, ICP-MS could be used in the future to definitively determine if that is indeed the case.

**Table 4.1**: Elemental composition percentages based on average calculations from EDS analysis of PtAuAg particles. The seed dilution was carried out in CTAB, despite the Au seeds being grown in CTAC.

<table>
<thead>
<tr>
<th>Seed Dilution</th>
<th>Pt</th>
<th>Au</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>100x</td>
<td>43.9%</td>
<td>34.7%</td>
<td>21.5%</td>
</tr>
<tr>
<td>1000x</td>
<td>32.1%</td>
<td>58.9%</td>
<td>9.0%</td>
</tr>
</tbody>
</table>
Figure 4.5: SEM image of PtAuAg particles with (A) 600 µL and (B) 200 µL of 0.01M K₂PtCl₆ pre-heated and incubated at 40°C for three hours.

If the residual platinum from the seed dilution were truly the cause of CC formation, than observing the effect of the concentration of platinum itself in solution in the synthesis of AuAg particles from Pt seeds could help explain the growth mechanism. To test this, the amount of Pt in the PtAuAg synthesis was altered. In this trimetallic synthesis the predominant metal in solution is platinum, followed by gold then silver. Particles synthesized at this ratio are shown in Fig. 4.5A. When the amount of Pt added was made equal to that of Au, there was less shape-control observed (Fig. 4.5B). The particles in both images were very small and inconsistent throughout. In both samples the solutions were cloudy and the SEM revealed many salt crystals. This implies that a large portion of the metal salts precipitated out rather than reducing to form particles. Due to this, the particles were not nicely dispersed throughout the samples and were very disordered in shape. While Fig. 4.5 seems to suggest that the increased concentration of platinum is having a positive effect on shape-control, these results were not strong enough due to the poor reactivity in the solution. To coax the metals into reducing, it may be necessary to increase the
incubation temperature and thus increase the rate of reduction. It could also be suggested to use $\text{Na}_2\text{PtCl}_6$, which is more soluble than the potassium form of the salt.

Continuing the focus on the platinum salt $\text{K}_2\text{PtCl}_6$, the potassium ions could be interacting with the metallic surfaces to alter the growth mechanism. To observe the effect of potassium on growth, the platinum was removed from the synthesis entirely in order to make sure it was not a confounding variable. To this end, gold seeds were used instead of platinum ones. Due to the importance of seed dilution as demonstrated in Fig. 4.4, the conditions were tested for both 100x diluted and 1000x diluted seeds. As the source of potassium, $\text{KBr}$ was used since there was already an excess of bromine in solution from the CTAB surfactant. This was also compared to $\text{NaBr}$, which would ensure that the additional Br was not responsible for any shape change, should one be observed. The results of this experiment are laid out in Fig. 4.6. Based on these images, there is no significant difference within the conditions of the same seed dilution. The particles from 1000x diluted seeds are THH (Fig. 4.6D-F), whereas the particles from 100x diluted seeds (Fig. 4.6A-C) resemble THH with more metal deposited on the ends, similar to a dumbbell shape. It is possible that the low concentration of added $\text{KBr}$ or $\text{NaBr}$ was not enough to observe a difference, however solubility issues can occur at high concentrations, which limited the concentration range that could be tested. With heating this problem could possibly be resolved, but this again brings up a conflict with energy efficiency.
Figure 4.6: AuAg particles from Au seeds (A-C) 100x diluted and (D-F) 1000x diluted. The growth solutions for (A) and (D) had no additional Br added, (B) and (E) had 10 µL of 0.01M NaBr, and (C) and (F) had 10 µL of 0.01M KBr (scale bar = 500nm).
Figure 4.6: AuAg particles from 100x diluted Pt seeds pre-heated at 40°C and incubated at 40°C for three hours with (A) 0 µL and (B) 200 µL 1M HCl added to the growth solution (scale bar = 500 nm).

The final aspect looked at as a possible source of shape-control was pH. A significant difference between the trimetallic PtAuAg synthesis and the AuAg particles from Pt seeds was the amount of acid added to the growth solution. In the synthesis of trimetallic PtAuAg particles there was no additional acid, whereas the bimetallic AuAg synthesis had 200 µL of 1M HCl, correlating to an overall concentration of 0.02M. It is clear from Fig. 4.6A that the low pH obtained from the additional HCl is crucial for shape-control for the bimetallic system. By lowering the pH, the rate of reduction is slowed to allowed for stable, well-faceted particles to form (Fig. 4.6B). At increased pH, the shape-control is completely lost, as seen in the random, spikey particles in Fig. 4.6A. It is interesting that the PtAuAg synthesis produces shaped particles despite the lack of shape-controlling acid. This indicates that the platinum in solution, or the potassium incorporated in that metallic salt, are likely filling this shape-stabilizing role that acid plays in the bimetallic synthesis.

Another possible explanation for the shape difference could lie in crystal structures of each element. Both gold and platinum have face centered cubic (fcc)
lattices, however gold has a lattice constant of 4.08Å whereas platinum has a lattice constant of 3.92Å. The strain caused by this mismatch is 4.08%. In comparison to the lattice mismatch between silver and gold (silver is fcc with a lattice constant of 4.09Å), which is less than 1% strain, 4.08% is a lot of stress. The strain cause by this strong mismatch could be a possible driving force for shape-determination. The rate of diffusion, which represents the rate at which distinct metals bond with each other, could also be in effect here. The difference in diffusion of Au on Pt vs. Pt on Au could make the alloying process much more difficult due to the conflicting rates. A final hypothesis for shape-control could be related to the extreme sensitivity of the system to small changes, especially changes in temperature. Therefore variations in the time of year or the weather could result in dramatic changes. While all experiments were carried out in the same room, the environment of the laboratory undoubtedly varied from time to time.
Chapter V: Gold-Dependent Copper Deposition

In a study by Personick et al.\textsuperscript{30} it was determined that gold particles with varying amounts of silver on the surface could be synthesized through promotion of underpotential deposition. Here, copper is substituted for silver in an attempt to create gold particles with a monolayer of copper on the surface. Gold is known to be highly selective in oxidation reactions\textsuperscript{32} whereas copper has been shown to be very active in similar reactions.\textsuperscript{38} One downside to Cu though is its rapid rate of oxidation. A solution to stabilizing Cu and protecting it from oxidation is by alloying it with another metal such as Au.\textsuperscript{38} In order to create particles with an alloyed AuCu surface, it first must be determined if copper has the ability to underpotentially deposit on a gold surface. To this end, gold-only particles were synthesized as described in the Methods section. After washing and resuspending these particles in surfactant, ratios of copper and gold salts with reducing agent were added. The intention was to determine if small amounts of copper were depositing on the surface and how much, if any, gold would need to be present to facilitate UPD. In order to determine the elemental composition of these particles, ICP-MS was used. ICP-MS essentially vaporizes the sample into ions and determines how much of each element is present. Table 5.1 displays the ICP-MS data for AuCu particles. For the samples with ratios of Au:Cu ranging from 1:1 to 1:5, the percentage of copper incorporated into the particles was less than 1\% which is likely not significant enough to support there being a full layer of Cu deposited on the surface. In the sample with no gold, however, there is just over 1\% of copper in the particles. While this still is not definitive proof of a monolayer of copper, it does support the theory that copper can
deposit on a gold surface without gold ions being present. As a means of confirming this theory, elemental mapping through X-ray photoelectron spectroscopy (XPS) could prove powerful in determining if Cu is truly depositing only on the surface as hypothesized. The catalytic capabilities of these particles should then be explored in hydrogenation or oxidation reactions.

Table 5.1: ICP data of AuCu particles with varying ratio of Au:Cu salts in the growth solutions. The copper amount was consistently kept at 250 µL of 0.01M CuNO₃ while the amount of HAuCl₄ was varied according to the desired ratio. HCl and ascorbic acid were added in the same concentrations as the gold particle synthesis.

<table>
<thead>
<tr>
<th>Au:Cu in growth solution</th>
<th>Cu (ppm)</th>
<th>Au (ppm)</th>
<th>Cu:Au in particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:1</td>
<td>6.55E-03</td>
<td>0.572</td>
<td>1.15E-02</td>
</tr>
<tr>
<td>1:1</td>
<td>6.56E-03</td>
<td>5.48</td>
<td>1.20E-03</td>
</tr>
<tr>
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<td>6.51E-03</td>
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<td>1.46E-03</td>
</tr>
<tr>
<td>1:3</td>
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<td>4.91</td>
<td>1.76E-03</td>
</tr>
<tr>
<td>1:5</td>
<td>7.49E-03</td>
<td>3.74</td>
<td>2.00E-03</td>
</tr>
<tr>
<td>1:0</td>
<td>8.77E-05</td>
<td>3.69</td>
<td>2.38E-05</td>
</tr>
</tbody>
</table>
Chapter VI: Conclusion and Future Work

With the demand for energy consistently increasing, the search for energy-efficient solutions has led scientists to the realm of nanoparticle synthesis. When it comes to nanomaterials, the variety in shape, composition, and functionality are truly endless. As catalysts in chemical reactions, nanoparticles can be used to make these reactions more efficient by lowering the activation energy and/or selectively producing only the desired products. Designing catalysts for specific functions requires in-depth knowledge of their synthetic pathways, which has been the focus of this thesis. The attention for this research narrowed in on three gold alloyed systems: Ru/IrAu, AuAg with Pt, and AuCu particles. All of these systems were carefully explored resulting in an enhanced understanding of how these metals interact with each other and how other shape-determining factors affect the growth process.

For the ruthenium/iridium-gold particles, the system responded best to changes in bromine concentration. When synthesized in CTAC, the particles lost all shape definition. By slowly adding in small amounts of Br, shape-control was recovered for the IrAu particles. While the RuAu system did not respond in the same manner, it is very likely that had the concentration of Br been increased further, shape definition would have been recovered. This can be assumed due to the fact that when grown in CTAB, RuAu particles do indeed have some facets. Increasing the temperature also proved effective in promoting shaped morphologies for these bimetallic alloys. Unfortunately, these particles did not appear to incorporate significant amounts of Ru or Ir. It is possible that the percentage was too low for the EDS to detect, therefore it could be beneficial to analyze these particles with ICP-MS,
which is a much more precise. If there is Ru or Ir incorporated, the next step would be to determine the catalytic capabilities of these alloys.

In the AuAg synthesis with Pt, there were determined to be a couple possible reasons for CC formation. As temperature increased, so did CC formation. This suggests that the increased rate of reduction favors the formation of these facets over THH facets. The results from the seed dilution experiments also suggest a correlation to shape-control. At lower dilutions, more cubic particles were formed. This could be due to the residual Pt in solution from the seeds, or possibly from the smaller size of the particles. It is also possible that the Pt in solution could be incorporating into the particles to cause this change; there is evidence to suggest that Pt incorporates more into AuAg containing particles at lower seed dilutions. Lastly, the acidic environment in the synthesis of AuAg particles from Pt seeds was determined to be absolutely necessary for shape-control to be observed. The low pH must affect the reduction rate in such a way for growth to proceed in an organized manner. Future exploration should focus on determining if it is the seed dilution or the residual platinum that is causing the cubic particles to form. It could be suggested to attempt a synthesis of AuAg particles from more diluted seeds and adding in small amounts of platinum. If there is platinum in these particles despite their size, than this would support Pt being the shape-causing factor.

Lastly, it was determined that Cu can underpotentially deposit on the Au surfaces. While this was an important step in the original intention to create core-shell AuCu particles, this does not definitively prove that Cu is depositing uniformly on the surface. In order to visualize the deposition of Cu on the Au particles, XPS analysis
should be used to create an elemental map. After confirmation of the composition of these particles, their catalytic capabilities merit being explored due to the past successes of AuCu catalysts in energy-efficiency related reactions.

As discussed previously, the implications of this type of research are infinite. The energy crisis will not be solved solely by catalysis, however it could prove a powerful tool. Catalysts such as metallic nanoparticles have the ability to enhance the efficiency of many energy-intensive reactions. They can also be tuned to balance their reactivity and selectivity to create an ideal catalyst. This thesis has explored many pathways of cause and effect in gold alloyed syntheses, which hold promise for applications in the realm of catalysis and industry.
References

26. EIA Biomass Explained. eia.gov/energyexplained/?page=biomass_home.