Nanoparticle alloys of platinum (Pt) and another metal are desirable for catalytic applications to decrease the loading of the precious metal and alter the physiochemical structure of these materials to enhance their catalytic properties. This study explores the potential of producing gold and platinum nanoparticle alloys using a microplasma reduction technique. In this process, metal salt precursors (chlorauric acid and chloroplatinic acid) and poly-vinyl-alcohol (PVA) are dissolved in distilled water and exposed to an atmospheric argon microplasma. The as-grown particles are characterized by XRD and UV-Vis to confirm the formation an alloy.
1. Introduction

Platinum (Pt) is a material that finds wide use due to its strong catalytic properties. Applications of platinum include CO oxidation in fuel cells and catalytic converters, electrochemistry (platinized electrodes), and chemical synthesis.

Generally, platinum is used as a heterogeneous catalyst in these applications. This means that the phase of platinum (bulk solid) is different from that of the reactants (gas, liquid, aqueous ions, etc.) of the catalyzed reaction/process. Because of this, the catalytic properties of platinum are strongly dependent on surface area. For example, platinum catalyzes the reaction $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ (CO oxidation) by allowing two molecules of CO and one molecule of O$_2$ to adsorb onto its surface\(^1\). A larger surface area means that more molecules of both gases can adsorb and react.

Nanoparticles are attractive because the catalytic action of platinum depends on surface area. The surface area of nanoparticles is on the order of thousands of times larger than that of an equivalent mass of bulk material. For instance, a sample of 100 nm (spherical) particles of platinum totaling to 1 kg has a surface area of approximately 1400 m$^2$ whereas a 1 kg cube of platinum has a 0.07 m$^2$ surface area, a factor of 20,000 times less. See figure 1.

However, platinum remains a rare and expensive metal. An alloy of platinum and another metal may preserve the catalytic action but it will reduce the loading of platinum. Furthermore, if the composition of the nanoalloy can be controlled then perhaps certain properties of the material can be fine-tuned to optimize a given application.

This study explores the alloying of platinum and gold (Au) as nanoparticle alloys. Although gold is not much cheaper than platinum, there exists plenty of literature on the topic of Pt-Au nanoalloys\(^3,5,6\). Furthermore, the prior works of Sankaran\(^2\) have shown that the technique discussed in this paper can easily produce gold nanoparticles (monometallic). Therefore, the successful alloying of Pt and Au using this technique without significant alteration will give confidence to the possibility of alloying Pt with other, more economic metals, such as Palladium (Pd) and Ruthenium (Ru).

![Figure 1: The total surface area of 1 kg worth of spherical particles as a function of particle radius.](image1)

![Figure 2: All reactions must overcome some energy barrier to occur, even if the final state of reactants is a lower energy state. A catalyst reduces the energy barrier.](image2)
2. Background

2.1 Monometallic nanoparticles

Metallic nanoparticles are generally produced by first dissolving a metal containing compound in water (though other solvents may be used) and then reducing the aqueous metal ions with an appropriate reducing agent (ex. citrate, borohydride). The end result is a colloidal dispersion of particles in solution. The aforementioned compound can dissolve into metal ions (e.g. silver nitrate: \( \text{AgNO}_3 \rightarrow \text{Ag}^+ + [\text{NO}_3^-] \)) or into metal ion complexes (e.g. chloroplatinic acid: \( \text{H}_2\text{PtCl}_6 \rightarrow [\text{PtCl}_6]^{2-} \)). Either way, the metal has a positive charge and will readily reduce (i.e. accept electrons) to metal atoms. Note that the total charge of an ion complex need not be positive; only the charge on the metal in the ion complex needs to be positive.

Once reduced, the metal atoms will agglomerate into particles. However, unless the process is inhibited the particles will continue to agglomerate into bulk material and precipitate out of the solution they were dissolved and reduced in. The particles are stabilized by an additional chemical thrown into the solution. Many stabilization agents have been used over the years; examples include thiol containing compounds, phosphines (particularly \( \text{PPh}_3 \)), sugars, and polymers such as poly-vinyl-alcohol (PVA) and poly-vinyl-pyrrolidone (PVP).

The stabilization agent can bind to the metal either before or after reduction of the ion. If the stabilization agent binds to the metal after reduction, then the reduction parameters (reduction rate, particle size dispersion, etc.) are dependent on the reduction conditions. If the stabilization agent binds to the metal before reduction, then the reduction parameters depend on the interaction of the stabilization agent and the metal. Naturally, some reduction schemes are designed around the interaction with a metal ion and a carefully chosen binder. Furthermore, an interaction that precedes reduction is favored as particle size and uniformity are better controlled.

Stabilization agents prevent agglomeration by adsorbing onto the surface of the particles. Binders with physically large functional groups (such as the three phenols in \( \text{PPh}_3 \)) or polymers are effective stabilizers by virtue of steric effects. Stabilizers can also prevent agglomeration through electrostatic repulsion; an example is citrate, which was used by Faraday to both reduce aqueous \( \text{Au}^{3+} \) and stabilize the resulting gold atoms.

![Figure 3: The interaction of a polymer with a metal ion complex. [3]](image)
Certain stabilizers, such as PVP and PVA, interact to form polymer-ion complexes with the metal ion complexes. The polymer-ion complexes can then be reduced to form polymer-atom complexes. These complexes will aggregate and form particles with the polymer already bound to the surface. See figure 3.

2.2 Bimetallic Alloys

The techniques used to produce monometallic particles can be extended to producing bimetallic (or multi-metallic) alloys in two distinct ways: co-reduction or serial reduction. In co-reduction, compounds containing the metals of interest are dissolved in solution simultaneously before adding the reducing agent. In serial reduction, one metal is dissolved and reduced first, then the second metal is added and reduced.

These methods attempt to control the structure of the alloy. That is, whether or not the particles are a mixture or whether the particles have a specific structure such as a core of one metal and a shell of the other. These structures will be discussed in more detail later.

2.3 Microplasma reduction

In the preceding section, preparation of nanoparticles was described by the conventional wet chemical method. That is the metal of interest is a component of a compound that is dissolved in solution into the constituent ionic species. Reduction of the metal is done by an appropriate chemical via a typical redox reaction. The resulting nanoparticles are stabilized and held in colloidal dispersion.

Figure 4: Schematic of setup. Note that this method has an advantage over conventional particle synthesis methods and that is that synthesis occurs at exactly one site – the plasma-solution interface. Also, the plasma electrode is negatively biased so that the current is reversed (but due to convention this means electrons flow the opposite direction of current).
In this study, the redox reagent responsible for the role of reduction is replaced by an argon microplasma. Furthermore, this change also moves the process into the realm of electrochemistry. Metal particles are still reduced from dissolved metal containing compounds. Additionally, metal ions can be obtained by dissolving a bulk metal electrode, although this method is not employed in this study. The plasma is sustained by continuous argon flow through a hollow electrode positioned above the solution. The hollow electrode is connected to a power supply that provides the current necessary to sustain and charge the plasma. Electrons from the argon ions in the plasma reduce the metal ions through a collision interchange occurring at where the plasma hits the solution surface. The solution is grounded via a ground electrode placed into the solution. Particles formed in this fashion still require a stabilization agent to prevent precipitation.

2.4 Characterization of nanoparticles

There are a number of methods used to characterize nanoparticles. Among them is direct visual measurement via Transmission Electron Microscopy (TEM). TEM allows the particles to be viewed at the nanometer scale. This allows the particle size and shape to be directly evaluated, as well as the dispersion in size and shape.

![Figure 5: A TEM image of shape-controlled platinum nanoparticles. Notice the high degree of uniformity in size and shape.](image)

Certain metals can be characterized by UV-Vis absorption spectroscopy. A UV-Vis measurement shines light through a sample of interest. The sample is generally a solution containing a chemical of interest. For the case of this study, the solution is a colloidal dispersion of the nanoparticles. The light is a set intensity of monochromatic and is modulated from near infrared to near ultraviolet. The resulting spectrum shows what wavelength of light is absorbed (and how much is absorbed) by measuring the intensity of the light that passes through the sample. For example, a colloidal dispersion of gold nanoparticles absorbs light from about 600
nm to UV, with a strong peak at 540 nm, resulting in the characteristic red color of the solution. Absorption is due to electronic excitation by the photons. UV-Vis spectroscopy can be used to verify the formation of nanoparticles but reveals nothing about the physical structure of the particles.

Furthermore, UV-Vis can be used to measure particle concentration through the Beer-Lambert law which relates the transmittance of light to the absorptivity, path length through the sample, and density of absorbers. However, UV-Vis will only be used to verify the formation of particles in this study.

X-ray methods are invaluable in the characterization of nanoparticles. Among them, X-ray diffraction (XRD) is the most pertinent to this study as it is employed. For a given sample of interest, XRD measures properties of the sample’s crystal structure. It does so by measuring at what angle a beam of x-rays reflects off the surface of the sample. The angle is related to the spacing of atoms in the crystal lattice of the sample and is described by Bragg’s law (which will not be discussed here). Crystalline structures have a well-defined peak at the angle for which they reflect x-rays and thus can be used as an identification technique. X-rays are used because their wavelength is comparable to the spacing between adjacent crystal planes in most materials.

![Figure 6: The UV-Vis spectra of colloidal gold nanoparticles. Notice that the signal becomes more shallow towards the UV with decreasing Au concentration. [2]](image)

XRD allows identification of particles by virtue of the diffraction spectra. However, nanoparticles introduce some artifacts into the observed pattern. See figure 7. Most noticeable is a broadening of the characteristic peaks from the bulk material, which is due to a number of effects. The fact that the particles are independent of one another means they are randomly oriented and not necessarily right-side up. Particle size also plays a role in the broadening. Scherrer’s equation relates particle size to the FWHM (full width at half maximum) of a diffraction peak.
Of the three mentioned, only UV-Vis and XRD are employed in this study. Other methods exist to characterize nanoparticles, but they will be discussed later.

2.5 Characterization of bimetallic nanoparticles

The same techniques used to characterize monometallic nanoparticles can be used to characterize bimetallic nanoparticles. There are effects unique to each measuring scheme that bimetallic particles introduce. Most of these are composition-dependent.

The UV-Vis spectrum of a bimetallic nanoparticle is linearly related to the composition of the particles. See figure 8. This means that the spectrum of a particle will linearly transform from the pure metal spectrum of the first metal to the pure metal spectrum of the other metal. Furthermore, if both metals (such as gold and silver) have a well-defined peak in their respective spectrum, then the presence of an alloy is verified by only one peak somewhere in between the two pure species peaks. In contrast, a mixture of pure gold particles and pure silver particles will produce a UV-Vis spectrum that shows both their peaks.

XRD shows a similar trend where the diffraction pattern changes (approximately) linearly from one pure metal to the other. Furthermore, the presence of one peak in the pattern of a suspected alloy confirms that the structure is an alloy and not a physical mixture of two pure metal particles.

3 Method

The production of platinum-gold nanoalloys was done by microplasma reduction of aqueous metal ion complexes as described in section 2.3.
The metal precursors are H$_2$PtCl$_6$ (chloroplatinic acid) and HAuCl$_4$ (chlorauric acid). A stock solution of dissolved PVA with a concentration of 1 g/mL was prepared with distilled water. Prior to preparing a sample for plasma reduction, the PVA solution was stirred continuously for two days, interspersed with rigorous shaking and sonication to ensure complete dissolution of the PVA. Samples of 1 mM total metal concentration in 10 mL distilled water were prepared with 0.1 g PVA and then sonicated for 15 minutes prior to plasma reduction. Solutions with gold to platinum ratios 1:0, 4:1, 3:2, and 2:3 were prepared. The resulting solutions were clear with a faint yellow hue.

The plasma setup consisted of thin stainless steel tube which served as the plasma electrode. This electrode was connected to an argon supply line through an electronic mass flow controller. The argon flow was set to 25 sccm for all plasma runs. The electrode was also in electrical contact with a high voltage power supply. A ballast resistor in series served to limit current to the mA range.

The end of the argon electrode was filed down to a short point so as to stabilize the plasma so that it also formed from inside the tube. Otherwise, the plasma had a tendency to jump from the outside edge of one side of the electrode to the other.

Figure 8: The UV-Vis spectra of different compositions of Ag-Au nanoalloys. Notice the linear relationship between peak location and nanoalloy composition. [11]
A platinum foil electrode in electrical contact with ground was placed into the sample solution. Prior to each run, the platinum electrode was washed with acetone and rinsed thoroughly with distilled water.

The sample was open to the atmosphere during the plasma run and hence the experiment was conducted in a fume hood in order to prevent contaminants from falling into the sample solution.

3.2 Plasma control

The surface of the solution was brought in close proximity with the end of the argon electrode prior to striking the plasma. The electrode would be lowered to about 1 mm distance from the solution surface via a micrometer. The power supply output was ramped to approximately -1.4 kV to ignite the plasma. The plasma distance and voltage were then fine-tuned to control the plasma current to 4 mA, which was measured by measuring the voltage across a small resistor in series with the ballast resistor.

It should be noted that the current would slowly drift to larger values. This was due to two main reasons. Firstly, as particles form the conductivity of the solution changes and hence the current through the plasma will change. Secondly, the plasma slowly evaporates some of the solution (this is slow but the effects become noticeable over 10 minutes) and increases the distance between the electrode and solution surface. This slightly changes the breakdown voltage of an argon atmosphere and thus affects the plasma current. Throughout the experiment, the current was manually controlled to 4 mA by either tuning the voltage on the power supply or tuning the distance of the plasma electrode and solution surface.

At first, plasma runs were to be 30 minutes, but the rapid color change of the pure gold sample from faint yellow to dark red in a matter of minutes changed the intended 30 minutes to 10 minutes. Furthermore, the current drift described above significantly slows after about 5 minutes, which signifies stagnation in particle formation. This rapid color change was observed in all subsequent samples, though the final color would change from dark red to a purplish red with the increased loading of platinum.

3.3 Particle characterization

UV-Vis measurements were conducted immediately following the 10 minutes of plasma treatments. XRD preparation required about two weeks’ time as 5 mL of the samples were dried on a glass substrate by dropping 0.7 mL of a given sample per day (excluding weekends).

UV-Vis measurements measured absorbance from 800 nm to 400 nm. XRD scanned through the angles in the vicinity of the first two peaks of gold. That is, from 37° to 41° and 42° to 47°. The first peak (corresponding to the [111] crystal plane) occurs at 38.4° and the second ([200] plane) occurs at 44°. The first two platinum peaks are no further than 2° higher than the first two gold peaks. Note that the first two samples (1:0 and 4:1 gold: platinum) had a near-full scan from 36° to 70° in order to locate the pertinent peaks.

4 Results and discussion

4.1 Expected trends
The expected UV-Vis trend for Pt-Au alloys should start with a strong peak at 540 nm corresponding to pure gold. The peak should flatten to a decreasing slope with increasing platinum concentration. While this trend gives indication of the formation of gold and platinum, it does not reveal whether or not an alloy is formed. Unlike silver, platinum does not have a well-defined absorbance peak in the UV-Vis range. Platinum does have a peak further into the UV range, but such a measurement would push the limits of the machine. Therefore, if UV-Vis shows the formation of gold and platinum then XRD will show whether or not a nanoalloy is formed.

There are a couple things to look for in the XRD spectrum. First is that the indication of nanoalloy formation is shown by looking closely at where the 2nd peak for gold and platinum should be. If an alloy is formed, then there should only be one peak. If both pure gold and pure platinum are formed, then there will two peaks where the 2nd peak should be. Note that this is the case for the first peak as well, but this effect will be hard to observe when taking into account the peak broadening phenomena discussed in section 2.4. Second is that there is not a significant peak shift until high platinum concentrations. This means that the XRD pattern should look similar to pure gold’s with only minor peak shifts from sample to sample.

4.2 UV-Vis and XRD results

The results from UV-Vis measurements (figure 9) show the expected trend of the flattening gold peak. This gives confidence that both gold and platinum are produced. If only gold was produced then this particular trend wouldn’t occur as the high sloping towards the UV range is indicative of either a high gold concentration or the response from platinum. A lower gold concentration without platinum would have a shallower approach towards the near UV.

![Figure 9: UV-Vis results. Notice the flattening of the peak. This indicates that less gold is being formed. However, the fact that the slope of the spectra on towards the UV region doesn’t change indicates that platinum is being formed as well.](image)

XRD shows mixed results however (figure 10). The peaks occur where they are expected to occur. This, along with UV-Vis, gives confidence that both gold and platinum are reduced. However, the 4:1 Au:Pt sample shows two peaks in the 44°-47° range. This is evidence that both
metals are reduced but that they also tend to form separate pure metal particles. Note that this does not mean that alloying did not occur. The second peak in this range disappears with the increase of platinum concentration, which seems to suggest that a physical mixture is only significantly produced at low Pt concentrations.

![Graph showing XRD results](image_url)

Figure 10: XRD results. Notice the two peaks that appear in the 44°-46° in the red trace on the upper right picture. This indicates that a physical mixture has been formed and not an alloy. However, those two peaks coalesce into one as the concentration of platinum increases. This signifies that an alloy has been formed at even compositions of gold and platinum.

### 4.3 Discussion

The results of this experiment are consistent for the most part with results for Pt-Au bimetallic alloys from other methods of synthesis. This gives confidence that the microplasma technique is capable of producing bimetallic nanoparticle alloys via co-reduction. The inconsistency in one sample suggests that low concentrations of platinum tend to reduce to pure platinum particles.
However, at more even concentrations of the two metals, the data suggest that alloys are primarily formed.

5 Future work

A few things were never finished in this study, namely the 1:4 Au: Pt sample. The XRD on this sample may have showed that a physical mixture is produced again but at low concentrations of gold this time. Furthermore, TEM measurements of the samples would have allowed measurements to the geometric properties of the particles such as size, shape, and their distributions. This would have allowed the uniformity (or quality) of the particles to be evaluated.

There are a few things that can be done to continue this work but these are separate endeavors in their own right. The primary focus of future work would be the attempt to alloy other metals with Pt as that is the natural progression and overall objective of this study.

5.1 Determining crystal structure

While UV-Vis and XRD can show whether or not particles are formed and whether or not alloys are formed they do not reveal anything about the structure of the alloys. That is, the alloys can have one of three structures: mixed or random, separated, and core-shell. The mixed (or random) structure is a structure where there is no particular arrangement tendency of the metals. In other words, any given atom of a particle could be either metal. The separated structure has distinct regions of the constituent metals. For example, one half might be entirely gold and the other half might be entirely platinum. The core-shell structure could be viewed as a special case of the separated structure, but nonetheless deserves attention.

The core-shell structure has one metal making up the core of a particle and the other metal making up a shell around it. Of the three structures listed, this one would be the most ideal for the desired applications of platinum nanoparticles, if the platinum forms the shell. This could mean that nanoparticles could be controlled such that nearly every platinum atom contributes to the total surface area.

There are two x-ray related spectroscopy techniques that can give details about the structure of the measured sample. The first is extended x-ray absorption fine structure (EXAFS) which is similar to UV-Vis except with x-rays. The x-rays can be energy-controlled to match electron binding energies of a chosen element. EXAFS can give data about a particular metal atom in a sample such as identity, number of atoms surrounding the metal, and the interatomic distances between adjacent metals. The crystal structure of an alloy can be inferred from this data. Furthermore, EXAFS is a strong spectroscopic technique even for low concentration samples (such as colloidal dispersions of nanoparticles). Unfortunately, EXAFS spectroscopy requires synchrotrons to produce the keV to MeV x-rays. The second x-ray related technique is energy disperse x-ray microanalysis (EDX), which measures emitted x-rays from electron irradiated samples. EDX can be used in conjunction with TEM to focus the electron beam onto specific particles and measure the emitted x-ray spectra of that particle. The spectra will give information about the composition of the particle, from which the structure can be inferred. Furthermore, for sufficiently large particles, compositional data of the surface of the particle can be obtained.
5.2 Controlling the crystal structure of particles

Wet chemical techniques with Pt and Au co-reduction as polymer-ion complexes with PVP have shown that Au tends to reduce first and agglomerate while the platinum reduces second and forms a shell around the gold particle. This can be explained from the basis of the reduction potentials of gold and platinum. More specifically, the reduction potentials of [AuCl₄]⁻, [PtCl₆]²⁻, and [PtCl₄]²⁻ which are (with respect to the standard hydrogen electrode) 1.00 V, 0.68 V, and 0.73 V, respectively. Note that the tetrachloroaurate reduces to pure gold whereas the hexachloroplatinate first reduces to tetrachloroplatinate then reduces to pure platinum. The values indicate that the gold ion complex is more readily reduced to pure gold than the other two. Furthermore, the platinum ion-complex must undergo two reduction steps. See figure 11 for a schematic of a potential mechanism.

It is unsure whether reduction potential plays any significant part in the plasma reduction method due to the fact that the plasma electrons are such high energy that the difference in reduction potential of the two metal complexes can be considered insignificant. However, the fact that the hexachloroplatinate requires two steps to reduce to pure platinum suggests that the gold would form more rapidly. Furthermore, the PVA used in this experiment could have a similar effect to the PVP in forming the gold core – platinum shell structure described in the above paragraph.

5.3 Using metals other than gold

As mentioned in the beginning, the primary motivation is to reduce the loading of precious metal in the particles. Gold was initially selected because there has been success with the plasma method reducing gold ions and because plenty of literature data exists for gold-platinum nanoalloys. The results of this study have given confidence to the capability of the plasma
technique forming nanoalloys and therefore other, more economic metals should be explored. Candidates include palladium (Pd), ruthenium (Ru), and nickel (Ni). There are also data in the literature for all three of these proposed Pt-based alloys.

6 Conclusion

Platinum remains a valued catalyst in a number of industries, particularly fuel cells. The catalytic action of platinum can be improved by employing platinum nanoparticles in these applications. Unfortunately, platinum remains a rare and expensive metal, inhibiting commercialization of fuel cells. This study explores the possibility of alloying platinum with gold as a proof of concept with a plasma reduction technique. The results give confidence to the plasma technique’s capability of producing alloys of platinum and other metals. Ruthenium and nickel are attractive candidate metals as they are significantly less expensive than platinum (though ruthenium is still relatively expensive) and conventional methods of nanoparticle synthesis has already produced data for these alloys.

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8 Citations