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The unique electrochemical reactivity of small metal nanoparticles.

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THE UNIQUE ELECTROCHEMICAL REACTIVITY OF SMALL METAL
NANOPARTICLES

By

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B.S., Universidad Peruana Cayetano Heredia

A Dissertation

Submitted to the Faculty of the
College of Arts and Sciences of the University of Louisville
in Partial Fulfillment of the Requirements
for the Degree of

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Department of Chemistry

University of Louisville

Louisville, Kentucky

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A Dissertation Approved on

November 30, 2015

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*This Dissertation is dedicated to
my family and lovely wife, Karen*

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ABSTRACT

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This dissertation describes the factors controlling metal nanoparticle (NP) oxidation, using Au oxidation in Br^- and Ag oxidation in acid as model systems. We found that the oxidation potential depends on size, surface charge, and electrode material. Size has a dramatic effect, shifting about 200 mV from > 200 nm diameter down to 4 nm diameter. The shift is more dramatic below 4 nm. 2.3 nm average diameter Au NPs oxidized in the 300-500 mV range and 1.5 nm average diameter Au NPs displayed several sharp peaks from 200 mV to as low as -200 mV. These smallest Au NPs show catalytic activity for CO_2 reduction. The size-dependent oxidation results followed thermodynamic theory based on surface energy fairly well. A positive surface electrode charge also shifts the oxidation potential for Au and Ag NPs negative 100-200 mV, depending on the amount of charge, for NPs greater than about 10-15 nm. Ag NPs attached to different electrode materials show slightly different oxidation potentials, which is likely due to different electrode/linker work function relative to Ag. The negative shift in oxidation potential with decreasing NP size leads to size-dependent galvanic exchange. The level of galvanic replacement between PtCl_4^{2-} and citrate-coated Au NPs increases as the Au NP diameter decreases, another example of unique electrochemical reactivity of small NP sizes.

Throughout these studies, smaller particles often show low coverages and high size dispersity on the electrode. A new electrochemical precipitation approach based on the release of protons by H_2O_2 oxidation allowed for size-dependent deposition of electrodes without linkers from a solution containing different sized Au NPs. This work shows unique electrochemical oxidation, galvanic replacement, and electrocatalysis of metal NPs of 4 nm diameter and below. The developed electrochemical precipitation of small Au NPs could lead to high coverages of bare metal NPs for a variety of applications.

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CHAPTER I

INTRODUCTION

1.1. Main Goal/Summary

The main goal of this research was to study the unique electrochemical reactivity of small metal nanoparticles. Chapter I provides background information on the research findings in the area of synthesis of citrate-coated Au nanoparticles, size-dependent nanoparticle electro-oxidation, effect of surface charge and electrode material on the size dependent electro-oxidation, electrochemical precipitation of nanoparticles, and galvanic replace reaction of nanoparticles. Chapter II provides information about the experimental procedures and instrumentation used in this study. Chapter III focuses on the size-dependent oxidation of gold nanoparticles below 4 nm. Chapter IV describes the effect of surface charge and electrode material on the size-dependent oxidation of surface-attached Au and Ag nanoparticles. Chapter V describes a large negative potential shift and ultra sharp voltammetry of sub 2 nm diameter Au nanoparticle. Chapter VI size-dependent electrochemical precipitation of citrate-coated Au NPs. Chapter VII focuses on our research of a size-dependent galvanic replacement reaction. Finally, Chapter VIII summarizes the results of this research and provides future directions.

1.2. Motivation/Objective

The motivation behind this research was to better understand the unique electrochemical reactivity of small metal nanoparticles. Our findings provide useful information about the change in the E^0 value when we change the size of Au nanoparticles in the range of 1-4 nm and also provides useful information about the electrochemical reactivity of Au nanoparticles when we change the size (galvanic exchange, reactivity with halides, and electrochemical deposition).

An additional motivation for this study is to understand the influence of surface charge and electrode material on the oxidation potential of metal nanoparticles. In many studies of electrooxidation of nanoparticles, the metal nanoparticles are directly drop-cast deposited onto the electrode surface, causing two potential consequences. First, there is a direct interaction between the metal nanoparticle and the electrode surface that can influence the oxidation behavior. It is not clear if this is related to work function or some other interaction, including alloying. Second, the metal NPs are often aggregated on the electrode surface, which also likely alters the oxidation potential. Our findings demonstrate that surface charge can play a major role in the measured oxidation potential, while the electrode material can also have an affect even in the presence of an organic linker.

The synthesis of citrate coated Au NPs in the range of a few nanometers without strong ligands such as thiols would allow the study of the voltammetry of sub 2 nm diameter Au nanoparticles.

Another motivation for this study was the study of the mechanism of precipitation of Au nanoparticles during electrophoretic deposition. Previously, electrophoretic deposition (EPD) was used as an assembly method to deposit semiconducting,¹ insulating², and metallic^{3,4} NPs onto conductive substrates. Interestingly, no previous work studied the influence of Au NP size on the deposition of nanoparticle onto conductive substrates. Understanding the role of nanoparticle size on the deposition of citrate-coated Au NPs and the mechanism of deposition, would allow to separate nanoparticle based on size. In addition, the ability to assembly small Au NPs onto electrodes would allow the study of electrocatalysis with ultra-small citrate-coated Au NPs (1-2 nm).

The motivation for the galvanic exchange studies was based on the possibility to demonstrate the reactivity of small metal nanoparticles. We show that we are able to control the galvanic exchange between PtCl_4^{2-} and different sized Au NPs due to the decreased standard potential of Au with decreasing size, which is another example of the unique reactivity of small metal NPs. This also provides a new method to make alloys between noble metals.

1.3. Importance of metal nanoparticles research

A vast number of application have been explored for metal NPs; these include sensing,⁵ medical diagnostics,^{6,7} catalysis,⁸ medical therapies,⁹⁻¹¹ plasmonics,^{5,12-15} delivery of drugs,¹⁶ nanoelectronics,¹⁷ imaging¹⁸ and separations.¹⁹ Depending on the use, the NP size, composition, and environment of the metal will vary, and it is important for the metal in the NP to resist metal oxidation and remain stable. The surface chemistry of the NP will be changed by oxidation and could potentially dissolve the NPs, significantly

altering its properties and inhibiting NP function. Since tiny metal NPs display fluorescence and bright scattering, these are used in medical and biological applications and imaging. However, the stability of these small NPs play an important role in their application.²⁰ Considering that the metal oxidation is corrosion, new information gained could find new strategies for decreasing or stopping metallic corrosion.²¹ Finally, metal NP oxidation to the ionic form is often responsible for their toxicity (i.e. Ag).²² Studies on the factors that affect metal NP oxidation would allow us to better understand and predict how metal NPs behave under certain conditions; and therefore, improve their use in scientific and technological applications. The galvanic exchange reactions has recently been used for the synthesis of various metal alloy NPs. This technique allows scientists to make NPs with a composition and a structure which would be inaccessible by other techniques.²³ The data presented in this dissertation shows exciting results on the electrochemical reactivity of small Au NPs, allowing the potential development of novel materials with exclusive function, properties, and applications.

1.4. Electrochemical studies of metal nanoparticles

1.4.1. Synthesis of citrate-coated Au nanoparticles

Metal nanoparticles (NPs) display a fascinating range of chemical and physical properties not observed at the bulk level. Catalytic, plasmonics, and others properties are only observed for nanoscale size. These properties are size dependent. During the last decades great effort has been placed on synthetically controlling the size and shape of metal nanoparticles.²⁴⁻²⁶ From Faraday,²⁷ with his gold reduction, later with Turkevich,²⁸ and Frens,²⁹ with their synthetic methods for citrate coated Au nanoparticles, then followed by

Natan,³⁰ and Murphy,³¹ with their seeding growth approach and Brust³² and Crooks,³³ with the nanoparticles synthesis using alkanethiols and dendrimer respectively. Figure 1.1. shows the Turkevich method for the synthesis of citrate-coated Au nanoparticle. Additionally Figure 1.2. shows Murphy's method for the synthesis of citrate-coated Au nanoparticles.

In these days it is possible to synthesize metal nanoparticles with sizes from hundreds of nanometers to just only a few nanometers.^{34,35} In our group we were studying the effect of size dependence on the change of the E_p value.³⁶⁻³⁸ It is very well known that in many cases the reactivity of metal nanoparticles is directly correlated to the decrease in size. A decrease in size changes the coordination number of the atoms at the surface of the nanoparticle. This change in coordination often makes the surface atoms more reactive for catalysis and have different physical properties. Size and surface atoms are both important for catalysis.^{39,40} The synthesis of small size nanoparticles is possible with the help of organic ligands such as thiols,⁴¹ amines,⁴² and others. Au monolayer protected clusters (MPCs) are a good example of Au NPs coated with thiol ligands (e.g. Au₂₅).^{43,44} There is a covalent interaction between Au atoms and thiol groups from the ligand.⁴⁵ Figure 1.3. shows a representation of Au MPCs and the gold-sulfur interface at the nanoscale level. These methods allow the synthesis of sizes close to 1 nm but with the inconvenience of blocking surface atoms with thiols, making the nanoparticle less reactive due to the lack of accessibility to the surface atoms.^{43,44} A partial solution for this problem was developed by Crooks and co–

Figure 1.1. Turkevich method for the synthesis of citrate-coated Au nanoparticles. (a) overall reaction, and (b) half-reactions.

Figure 1.2. Murphy method for the synthesis of citrate-coated Au nanoparticles.

(a)

(b)

Figure 1.3. (a) Representation of Au MPCs and (b) gold-sulfur interaction at the nanoscale level.

workers with their dendrimer encapsulate NPs.³³ This versatile synthetic approach allows partial access to the metal core and make possible accessibility to surface atoms of small metal nanoparticles. Figure 1.4. shows a representation of dendrimer encapsulated Au NPs. Metal nanoparticles typically are prepared in solution by reducing the metal salt with a reducing reagent. The size and shape of the nanoparticle are controlled by the concentration of the metal source, the reducing agent and the ligand.^{34,46} The surface chemistry of the nanoparticle is intrinsically related to the type of ligand selected for the nanoparticle synthesis. The desired ligand could be added at the initial step of the synthesis or later (post-synthesis) by a ligand exchange approach.⁴⁷ The ligand shell has several roles in control of the nanoparticle solubility,⁴⁸ functionality (targeting biomolecules),⁴⁹ and electronic properties.⁵⁰ Table 1.1 shows common stabilizing ligands used in nanoparticle syntheses.

In chapter III we demonstrated that during the synthesis of citrate-coated Au nanoparticles of 4 nm, it is possible to collect small Au NPs sizes below 4 nm⁵¹ by simply using a 15 min reaction time instead of 2 h (regular time).

In chapter V we demonstrate for the first time the synthesis of citrate-coated Au NPs with size of 1.5 nm and SD of 0.7 nm and their correlation with TEM size analysis and Linear Sweep Voltammetry. The optimization of time, concentration, and pH made it possible to capture citrate-coated Au NPs with sizes close to these obtained with Au MPCs (few nanometers).⁵²

Figure 1.4. Representation of (a) the synthesis of dendrimer-encapsulated Au NPs and (b) chemical structure of poly(amidoamine) (PANAM)

Ligand	NPs Synthesized
<p>Cetyltrimethylammonium bromide</p>	Au, Ag, SiO ₂ , CuO
<p>Polyvinyl pyrrolidone</p>	Au, Cu, Ag
<p>Trioctylphosphine oxide</p>	CdSe, CdTe, ZnS
<p>Dodecanethiol</p>	Au, Ag, Cu, Pt, Pd
<p>Oleic acid</p>	TiO ₂ , ZnO, FeO _x , CdSe
<p>Oleylamine</p>	CdSe, Au, Pt,
<p>Trisodium citrate</p>	Au, Ag,

Table 1.1. Common ligand used in nanoparticle synthesis.

This result is important because it allows the study of the surface chemistry of nanoparticles on the order of only 1 to 2 nm, without the inconvenience of a blocking surface ligand that isolates the metallic nanoparticle from its intrinsic catalytic properties. Additionally, our results indicate that there is a strong correlation between E_p values from the electrooxidation of Au NPs and their size analysis from TEM images. This allows us to state that Linear Sweep Voltammetry technique (LSV) is a powerful technique in the correlation of nanoparticle size, going from sub nanometer scale (Few atoms) to particles on the order of hundreds of nanometer. This ability to correlate E_p values and size of nanoparticles in many ways mimics a mass spectral analysis. Additionally this new synthetic method make it possible to study citrate-coated Au NPs with diameters not previously studied for electrocatalysis applications.

1.4.2. Metal nanoparticle oxidation

In order to understand metal nanoparticle oxidation, it is necessary to discuss the Nernst equation. This equation relates the half cell potential to the standard potential and to the activities of the electro active species. For the redox couple $O + ne^- \rightleftharpoons R$, the Nernst equation is written as follows (equation 1.1) :

$$E = E^o + (0.059/n) \log (a^s / a^s_R) \quad (1.1)$$

Where n is the number of electrons transfered, E is the potential (V), E^o is the standard redox potential, and a^s is the activity of the electro active species at the electrode surface. Different redox active ions and molecules have

different standard reduction potentials. The list of elements with its standard reduction potential is called a table of standard reduction potentials. The standard reduction potential for metal/metal ion pair in tables based on bulk metals. The tables not consider the influence of the metal size. One way how to find the E^0 value for a redox couple is by applying stripping voltammetry using a potentiostat. The reduction or oxidation potential is registered as a peak in the plot of the potential vs current.

There is some theory and experimental data indicating that the standard redox potential of metal NPs decreases with decreasing size. According to Henglein's⁵³ and Plieth's⁵⁴ theories, a decreasing number of atoms in the metal negatively shifts the redox potential. Henglein *et al.*⁵⁵ in 1977 calculated the standard reduction potential for Ag particles with different amounts of atoms, showing a large change from -1.8 V to -1.0 V for 1 and 2 atoms of Ag, respectively, as compared to +0.799 V for bulk Ag (vs. NHE). Calculation based on sublimation energies. Additionally, Henglein found that small metals particles possess unusual catalytic properties in radiolysis that was explained qualitatively by a shift in the redox potential. The experiment of Henglein consist in the synthesis of Ag clusters under Y-ray irradiation by the reduction of Ag^+ by reactive species from the radiolysis of water, solvated electrons, e_{aq}^- , $\text{OH}^\cdot$, $\text{H}^\cdot$, or secondary radicals $\text{R}^\cdot$, followed by slow aggregation of isolated Ag atoms.

These clusters showed catalytic properties not observed with larger nanoparticles. Henglein explained this behavior by assigning a more negative standard potential to the smaller nanoparticles in comparison with larger ones.

Plieth⁵⁴ in 1982 explained the deviation in the electrochemical properties of clusters compared to bulk material to understand the activation and deactivation of electrodes found in Raman studies. Plieth started his study first with the equation for the shift of the reversible potential applied to clusters. He made an electrochemical cell consisting of two half cells. One with a large bulk metal containing x atoms, $\text{Me}_x^{\text{bulk}}$, where x would typically be greater than 10,000 atoms and the other one with metal clusters in a dispersed state, $n\text{Me}_{x/n}^{\text{nanoparticle}}$. The set of reactions below describe Plieth's cell.

The net equation is the transformation of one mol of metal bulk to one mole of metal as clusters. The potential of this cell can be calculated from the free energy, according to the next equations.

$$\Delta G_D = G_d - G_b \quad (1.7)$$

$$\Delta E_D = E_d - E_b = -\Delta G_D / zF \quad (1.8)$$

Where ΔE_D is defined as the difference in the oxidation potential between clusters (E_d) and bulk metal (E_b). Figure 1.5. shows the difference in the surface free energy between the atoms of bulk metal and the NPs with small size due to increased surface area.

n = # of nanoparticles

x/n = # of atoms per nanoparticle

The size of the nanoparticles decreases as n increases.

Total number of M atoms is X on both sides.

Figure 1.5. Change in Gibbs free energy when the size of the nanoparticle changes.

Plieth proposed that the change in free energy (ΔG_D) is associated with the change in surface area. The change of free energy with the change in surface is given by the next equation.

$$dG = YdA \quad (1.9)$$

Where Y is defined as surface tension and A is the change in surface area given as

$$dA = 8\pi r dr \quad (1.10)$$

$$dr = (V_M/4\pi r^2)dn \quad (1.11)$$

Where V_M is defined as molar volume and n is the number of moles turned in clusters. Doing the integration from $n=0$ to $n=1$, Plieth found an indirect correlation between change in free energy and the radius of the cluster. With this result and with the substitution in equation for the change in potential. Plieth develop his equation that is as follows.

$$\Delta E_D = -2YV_M/zFr \quad (1.12)$$

Where ΔE_D is $E_{p, AuNP} - E_{b, bulk Au}$, Y is the surface tension, V_M is the molar volume, z is the number of electrons, F is the Faraday's constant, and r is the radius. Figure 1.6. shows the plot of the shift in the standard reduction potential of Au NPs as a function of their radius.

Figure 1.6. Theoretical shift in potential for Au NPs based on Plieth's equation.

Compton described the electrochemical oxidation (stripping) of different-sized Ag NPs, which were attached to a basal plane pyrolytic graphite electrode in 0.1 M NaClO₄.⁵⁶ The diameter of the NPs varied from 25 to 100 nm. There was no dependence of oxidation on the size of the NPs in this range.

In this study, the stripping of silver nanoparticle is assumed to progress by the simple one electron transfer as follow.

Compton adapted the equation for the electrochemically reversible limit from the work of Brainina and co-workers.^{57,58}

$$E_p = E^0_f + (RT/nF) \ln(2c^0r_s/[A]^*) (\sqrt{nF/RTD}) + (RT/2NF) \ln v \quad (1.14)$$

Where E_p is the peak potential; E^0_f is the formal potential; R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹); T is the temperature (298 K); n is electrons; F is the Faraday's constant (96485 C mol⁻¹); c^0 is the average concentration of metal on the electrode surface; r_s is the radius of the particle; $[A]^* = 1 \times 10^{-3}$ mol cm⁻³ as a standard concentration; D is the diffusion coefficient; N is the number of particles and v is the scan rate. This equation predicts that the peak potential, E_p , will be dependent of the initial average concentration of the metal on the electrode surface, c^0 . Finally the c^0r_s value is linked to the stripping charge, Q , by the equation.

$$2c^0r_s = Q/nFN\pi r_0^2 = Q/nFA_{\text{elec}} \quad (1.15)$$

$$N = A_{\text{elec}} / \pi r_0^2 \quad (1.16)$$

Where Q is the total stripping charge, N is the number of particles, and A_{elec} is the total electrode area. According to this E_p should depend on $(RT/F)\ln(Q)$ and be independent of the size of the nanoparticle at reversible limit.

Additionally, Compton *et al.* described the oxidation of hemispherical deposits of bismuth attached to a single crystal Au (111) electrode under electrochemically irreversible conditions.⁵⁹ Their conclusions established that the difference in the voltammetry occurs mainly due to the morphology/orientation of deposits, leading to differences in the kinetics and thermodynamics of the process of stripping.

Ivanova and Zamborini showed for the first time by voltammetry the size-dependent oxidation of chemically-synthesized Ag NPs and electrodeposited Au NPs.³⁶

Ag can be oxidized by the following reaction:

And Au can be oxidized in the presence of halides by the following reaction.⁵¹

These NPs were synthesized with negatively-charged citrate stabilizer and electrostatically attached to an amino-functionalized glass/ITO working electrode³⁶ or electrochemically-deposited directly on bare glass/ITO electrodes.³⁷

The amount of metal was kept constant in both cases. The size of Ag NPs varied from 8 to 50 nm and the oxidation potential shifted negatively from 391 to 278 mV with decreasing NPs size. The same general behavior occurred for electrochemically-deposited Au NPs, which agreed better with the predicted shift in redox potential based on Plieth's theory. This is explained by the change in free energy associated with the difference in surface energy as a function of the particle size. Plieth predicted a shift that has an inverse dependence on radius (r), where the shift is proportional to $1/r$.

Brainina *et al.* described the theoretical study of metal NP oxidation.⁶⁰ Their preliminary experiments demonstrated the appearance of metal nanoparticles electrooxidation peak on voltammogram at less-positive potential, then bulk metal electrooxidation peak. Brainina *et al.* took into account the Gibbs energy and the size of the particle for their calculation.

Brainina *et al.* described three different energetic states of the metal, M_I ($\Delta G^0 < 0$), M_{II} ($\Delta G^0 = 0$), and M_{III} ($\Delta G^0 > 0$). M_I , M_{II} and M_{III} denotes metals in the first, second and third energy state respectively and ΔG^0 is Gibbs energy. In M_I the metal is strongly bonded to the electrode surface in comparison with bulk crystal lattice that is M_{II} and M_{III} is for a metal-electrode system where the surface energy must be taken in consideration.

Brainina's model for electrooxidation of nanoparticle is based on the next set of assumptions. The surface layer is estimated base on the specific surface per unit volume (S/V), the electrooxidation of the metal is described by the next equation:

The kinetics of the process is determined by the rate of the electron transfer and the diffusion removal of metals ions from the surface. The surface of the electrode S_e is considered as an infinite plane. The sample taken in consideration for this mathematical calculations is a mixture of spherical nanoparticles with $r_{o\text{ II}}$ and $r_{o\text{ III}}$, larger and smaller than a certain critical radius r_{cr} . The change in potential E from the initial value E_{in} with scan rate v , lead to the electrooxidation of particles with current equal to $i=i_{\text{II}} + i_{\text{III}}$, the total charge from the electrooxidation of the sample is $Q_0 = Q_{0\text{ II}} + Q_{0\text{ III}}$, there is plenty electrolyte available to suppress migration effects.

The simulation of the electrooxidation of nanoparticle and the construction of the corresponding voltammograms allowed Brainina *et al.* to show that there is a strong dependence of the Gibbs surface energy and the nanoparticle radius. Her results agrees with the dependence of the decrease on the melting point on metal nanoparticles once there is a reduction in size.

Au NPs and Au nanoclusters (NCs) are widely studied due to their unique properties. Some of these properties led to a variety of applications in catalysis,⁶¹ plasmonics,⁶² sensing^{63,64} and biomedicine.⁶⁵ The chemical and physical properties of Au nanomaterials depends on their size, their shape, their combination with other metals, and functionalization with organic linkers. In

each of these cases, these interactions affect the properties of Au nanomaterials.

It is known that the chemical and physical properties of Au NPs are size-dependent and the dramatic change in these properties occurs at ranges below 4 nm. Brainina^{60,66} and our group,^{36,37} reported experimentally a negative shift in the oxidation potential of Au and Ag NPs. Sieradzki⁶⁷ demonstrated the instability of Pt nanoparticles of 1 to 3 nm in diameter at different potential. All of these studies agree with the described Plieth's theory.⁵⁴ In our study, we are showing a dramatic negative shift for the oxidation potential of Au NPs < 4 nm attached to indium tin oxide-coated glass electrode (glass/ITO) in Br⁻ and Cl⁻ solution.

1.4.3. Effect of surface charge and electrode material

Smith and White described a theory of the interfacial potential distribution and reversible voltammetric response of electrodes coated with electroactive molecular film.⁶⁸ They found that the driving force for a reversible electron transfer between the metal and electroactive adsorbate is calculated from the interfacial potential distribution and is used to predict the current-voltage wave shape in cyclic voltammetric experiments. Their model accounts for changes in interfacial potential distribution due to charges on a monolayer. The Smith-White model predicts shifts of 200-400 mV or higher from the true E^o .⁶⁸ Figure 1.7. shows the scheme described by Smith and White to understand the drop of the interfacial potential between the metal electrode (ϕ_M) and the plane of electron transfer (PET), on this plane are located the electroactive O/R centers (open circles), these centers are separated from the metal electrode surface by a dielectric film (zig-zag lines). The physical interpretation of the nonideal

Figure 1.7. Drop in the interfacial potential between the metal electrode (ϕ_M) and the plane of electron transfer (PET). On this plane are located the electroactive O/R centers (open circles). These centers are separated from the metal electrode surface by a dielectric film (zig-zag lines).

voltammetric shapes is coming from the change of potential distribution across the electroactive film as a function of the applied potential. Figure 1.8. shows a representation of the voltammetric behavior for an electroactive film which undergo the reaction,

at different levels of surface coverage of the electroactive O/R centers. As the charge increases, the maximum current decreases, the wave shifts toward more positive potentials, and the peak broadens becomes more asymmetric.

Brainina *et al.* determined the influence of substrate on the oxidation potential change of Au NPs with sizes from 10-150 nm.⁶⁹ The results showed that the shift of the oxidation potential of the NPs was more negative for small sizes if the substrate was inert to the particle. The shift was more positive if the metal nanoparticle interacted with the substrate, which provided stability. This occurred when the work function of the substrate was larger than the NP. For Au NPs, the oxidation potential followed the order of Pt>Au>glassy carbon.

In the substrate study of Brainina *et al.*, two opposite effects were reported to shift the E_p of metal NPs from the bulk value.⁶⁹ One of them is the (-) shift of E_p by decreasing the radius due to a thermodynamic shift in the standard potential, according to Plieth theory. The second one of them is a (+) shift of E_p that arises from interactions of the electrode surface with the NP. The magnitude of this positive shift will vary depending on the NP size and the difference in work function of the metal NP with the electrode. If the work function of the electrode is significantly larger than the metal NP, the NP will be stabilized by it, changing the oxidation potential in a more positive direction.

Figure 1.8. Representation of the voltammetric behavior for an electroactive film which undergoes the reaction $O^+ + e^- \rightleftharpoons R$, at different levels of surface coverage of the electroactive O/R centers. 1, 10 and 100 are ratios of concentration for the electroactive film. The scan started on the right side and stopped on the left side.

According to previous work by Brainina and co-workers a positive shift will be displayed in the oxidation of Au NPs with 10 nm diameter on Pt when compared to glassy carbon; however, there was no significant shift for Au NPs with 150 nm diameter on the two substrates.⁶⁹ Their overall conclusion was that the electrode has a greater influence on smaller Au NPs due to an increased number of interaction points relative to larger NPs.

Brainina described the negative or positive shift of E_P value, as a result of the magnitude on the Gibbs free energy of the interaction metal-substrate (substrate influence) and the surface Gibbs free energy of the nanoparticle itself (size dependence in the oxidation of the metal nanoparticle). So the total change of ΔG^0 of the system is divided in two parts as follow:

$$\Delta G^0 = \sum (\Delta G_1^0 + \Delta G_2^0) \quad (1.23)$$

Where ΔG_1^0 is surface Gibbs free energy of metal-electrode interaction ($\Delta G_1^0 \leq 0$), and ΔG_2^0 is surface Gibbs free energy of the nanoparticle due to surface area ($\Delta G_2^0 \geq 0$).

The ΔG_1^0 is directly proportional to the electron work function of metal electrode ($\Delta\Phi$), the next set of equations show the relation between work function and Gibbs free energy:

$$\Delta E = \alpha \Delta\Phi \quad (1.24)$$

Where $\alpha = 0.5 \text{ V/eV}$ and $E^0 = \Delta G^0 / zF$, giving the resulting equation:

$$\Delta G_1^0 = \alpha F \Delta \Phi \quad (1.25)$$

The ΔG_2^0 is directly proportional to the surface tension of nanoparticle metal, as already described:

$$\Delta G_2^0 = \sigma \times S \quad (1.26)$$

Where σ is surface tension of the metal nanoparticle, and S is the mole surface of nanoparticles. The predominance of one of the terms determines the E_p value for the electrooxidation of the metal nanoparticle shift to a more positive or negative value of the E_p bulk metal value.

In our study, we show that the size-dependent oxidation of Au NPs electrodeposited or drop-coated directly on glass/ITO electrodes is different compared to those chemically synthesized and electrostatically or drop-cast deposited onto aminopropyltriethoxysilane (APTES)-modified glass/ITO electrodes. This is caused by different surface charge. Additionally, we demonstrate that the E_p of 9 nm diameter citrate-capped Ag NPs attached to Au, Pt, glassy carbon (GC), and glass/ITO electrodes follows the order of work function of the electrode substrate.

1.4.4. Electrophoretic Deposition

The assembly of metallic or semiconductor nanostructures on solid surfaces is of tremendous interest in many areas of science and technology

due to the important applications of nanostructures in sensing, optical, electronic, photovoltaic, biomedical, and catalytic devices. Many assembly methods exist, including drop-cast deposition, chemical assembly, and electrophoretic deposition.^{38,70-72}

In the case of negatively-charged, citrate-coated Au nanoparticles (NPs), most methods employ chemical attachment to thiol (SH)-functionalized surfaces or electrostatic attachment to positively charged amines ($-\text{NH}_3^+$). In this type of approach the particle transport is governed solely by Brownian motion, resulting in completely random particle-particle and particle-substrate collisions.

Electrophoretic deposition (EPD) is an alternative assembly method previously employed to deposit metallic,^{3,4} semiconducting,¹ and insulating² nanoparticles on conductive substrates. Several studies involve EPD of Au NPs. For example, Giersig and Mulvaney prepared highly ordered 2D films of Au NPs from aqueous and organic media onto TEM grids by EPD.^{4,73} Hupp *et al.* prepared patterned thin films of colloidal gold by EPD.³ Kamat *et al.* made an assemble of gold nanoparticles as a nanostructured film.⁷⁴ They described the application of an electric field to drive the movement of the colloidal Au NPs from the solution to the surface of the substrate.³ In order to perform electrophoretic deposition they applied a directional force that moves the colloidal nanoparticles to the surface of the substrate. This force must overcome the natural forces of gravitation, buoyancy, and friction. The equation of the force that a colloid experience in the presence of an electric field is defined as :

$$F_E = QE E \quad (1.27)$$

where Q_E is the surface charge and E is the applied voltage. This force must be greater than the natural forces on the particle defined by the following next equation, in order to manipulate the colloid with an electric field.

$$F_N = v3\pi\eta d \quad (1.28)$$

where v is the velocity of the colloid, η is the viscosity of the medium, and d is the diameter of the colloid.

The surface charge of the colloid is an important parameter in EPD and is defined by :

$$Q_E = u_E 3\pi\eta d \quad (1.29)$$

Where u_E is the electrophoretic mobility of the colloid which can be defined as the coefficient of proportionality between the electric field strength, E and the particle velocity, v .

$$V = u_E E \quad (1.30)$$

The electrophoretic mobility can be estimated from the zeta potential of the colloid, ξ . The relation between electrophoretic mobility and zeta potential is defined by the Huckel equation:

$$\xi = 3/2\eta u_E / \epsilon_r \epsilon_0 \quad (1.31)$$

Where ϵ_0 is the permittivity of the free space and ϵ_r is the relative permittivity of the medium.

Poelsema *et al.* studied the potential dependence on the EPD of nanocolloidal Au particles by spectroscopic ellipsometry. At low voltage, the deposition of 8.6 nm octadecylamine coated Au NPs did not occur, while at higher voltage, a strong increase in the deposition rate occurred.⁷⁵ David *et al.* studied EPD of colloidal Au NPs on a silicon wafer by scanning electron microscopy. They found a dense and uniform distribution of NPs with no aggregation over the surface.⁷⁶

The deposition of citrate coated nanoparticles is the result of the adsorption of the negative charges particles at the positively charged electrode under the influence of an applied electric field. This process is call anodic electrodeposition. The applied electrophoretic force overcome repulsive particle-particle electrostatic interaction. According to Besra *et al.*⁷⁷ there are two groups of parameters that determine the characteristic of this process related to the suspension and the process.

The parameters related to the suspension are particle size, dielectric constant of liquid, conductivity of suspension, viscosity of suspension, zeta potential and stability of suspension. The parameters related to the process are effect of deposition time, applied potential, concentration of solid in suspension and conductivity of the substrate. Other mechanisms involved in the motion of fluid and particles are electroosmotic⁷⁸ and electrohydrodynamic⁷⁹ transport processes.

Although the movement of the colloidal nanoparticle in a fluid under an electric field is understood, the electrophoretic deposition mechanism is not fully

understood and still under debate. There are several theories. In 1940, Hamaker and Verwey⁸⁰ suggested that EPD is the result of the accumulation of the charged particles on the electrode under the influence of an electric field.

In 1992, Grillon *et al.*⁸¹ suggested that EPD occurs by particle charge neutralization between the electrode and the particle, the result of the neutralization is the precipitation of the particle. In 1999, De and Nicholson⁸² proposed the theory of coagulation. Electrochemical reactions happens at the surface of the electrode. These reactions increase the ionic strength close to the electrode surface in comparison to bulk. The result is a change in the reduction of the repulsive forces between particles in the proximity to the electrode, which lowers the zeta potential and result in precipitation. The last theory comes from Sakar and Nicholson,⁸³ who suggested that EPD comes from the distortion and thinning of the double layer, followed by the coagulation of the particles on the surface of the electrode.

Despite the broad application of the EPD technique and the existence of several theories about the deposition of colloidal particles on a charged electrode surface with an opposite charge of the particle, few experiments have been performed in order to understand the process of deposition. Hanaor *et al.* described the effect of carboxylic acids on the electrophoretic deposition of ZrO_2 .⁸⁴ Grzybowski *et al.* showed the ionic-like behavior of oppositely charged nanoparticles of different sizes and charge ratios that precipitate at the point of overall neutrality.⁸⁵ Besra *et al.* measured a larger shift in pH near the electrode surface in EPD by continuous direct current electrophoresis. The pH localization at the electrode surface was assigned as the mechanism of particle consolidation during continuous and pulse direct current techniques.⁸⁶

In our study, our goal was to controllably assemble citrate-coated Au nanoparticles of different size on electrode surfaces. In our attempt to use EPD for deposition, we found that the deposition mechanism is an electrochemical process that happens at the electrode surface and is dependent on the voltage and time of EPD. The applied electric field served as a low pass filter for the size-controlled deposition of Au NPs onto glass/ITO.

1.4.5. Metal nanoparticle galvanic replacement reaction

The most common method of forming monometal or alloy nanoparticles with controlled size and shape is by reduction of metal ion or metal complex in the presence of some stabilizer. This can be performed in one step with one or more metal precursors or in multiple steps for form core/shell type alloy nanoparticles. Three less common strategies that allow both morphological and chemical change to preformed metal nanoparticles by chemical reactions⁸⁷ are the Kirkendall effect,⁸⁸⁻⁹⁰ anion exchange,⁹¹ and galvanic replacement (or exchange) reactions.^{92,93} These versatile reactions allow the formation of complex morphologies and variable composition of metal nanoparticles. Figure 1.9. shows a scheme with the three different types of strategies.

Chemical transformation on the surface of the nanomaterial can produce core-shell nanoparticles or core-sheath nanowires. Promoting the dissolution of the unreacted core generates hollow nanostructures. Total chemical transformation may keep the original shape, break the original structure into small fragments, or turn into hollow structures.

(a) Kirkendall effect for metal nanoparticles

(b) Anion exchange with the Kirkendall effect

(c) Galvanic exchange with pinhole dissolution

Figure 1.9. Three less common strategies that allow both morphological and chemical change to preformed metal nanoparticles by chemical reactions are (a) the Kirkendall effect, (b) anion exchange, and (c) galvanic replacement (or exchange) reactions.

In the last decade, the galvanic replacement reaction has been heavily explored on metallic nanostructures. It has led to interesting structures not possible to directly synthesize, such as nanotubes,⁹⁴ nanorattles,⁹⁴ nanocages,⁹⁵ shells,⁹⁶ and others. It has also been used to reduce the amount of Pt in catalytic materials to lower the cost without sacrificing performance.

Figure 1.10. shows a scheme with four different types of structures, core/shell nanotubes, nanorattles, nanocages and shells made by galvanic replacement reaction.

The synthesis of core/shell nanostructures can be achieved by galvanic replacement. This strategy allows the formation of a shell of the noble metal (e.g Pt), which will replace a layer of a less noble metal (e.g. Cu or Ag).^{33,96,97} The core is usually made of a non-catalytic, less-expensive material that decreases the cost of the catalytic nanostructure. This strategy displays similar or better catalytic activity as if the NP is a pure catalytic metal. In others cases the core is made of materials that increase the stability and catalytic activity of the core shell nanostructures. Recently, Geng *et.al.*⁹⁸ showed the synthesis of a Au/Pt yolk/shell structure with a high catalytic activity for methanol oxidation. Podlovchenko showed the deposition of Pd over Mo by galvanic displacement, which had a high electrocatalytic activity to the oxidation of methanol and formic acid.⁹⁹

The galvanic replacement reaction is a reaction between solid metal and metal ion. This reaction is the result of the difference in standard potential of the two metals. This reaction leads to the deposition of a more stable metal and dissolution of a less stable metal.

Figure 1.10. Scheme with four different types of structures, including core/shell nanotubes, nanorattles, nanocages and shells, made by galvanic replacement reactions.

The following reaction is a galvanic displacement reaction, which is a simple oxidation/reduction reaction involving two metals

This reaction occurs between ionic metal and metallic metal when

$$E_{eq}(M_2^{z+} / M_2^0) \gg E_{eq}(M_1^{n+} / M_1^0) \quad (1.33)$$

The following is a typical example of galvanic displacement between two metals:

The standard reduction potential of $AuCl_4^-/Au$ (0.99 V vs. SHE) is higher than that of Ag^+/Ag (0.8 V vs. SHE). The difference in reduction potential has made this reaction possible.

In our studies, we demonstrate that the reduction of nanoparticle size on metallic noble nanoparticle made possible galvanic displacement that is not possible at the bulk level between noble metals. This study of galvanic displacement is based on the change of size of metal nanoparticles. The reaction is possible based on the negative shift in the reduction potential when the nanoparticle size decreased. We demonstrate for exchange between Au NPs and $PtCl_4^{2-}$ as a function of Au NPs size. This study represent a new strategy in the synthesis of metallic nanostructures.

1.5. Summary and Accomplishments

In the main part of this dissertation (Chapter III to Chapter VII) I will present the unique electrochemical reactivity of small metal nanoparticle.

In Chapter III, we report a significant negative thermodynamic shift in the oxidation potential for Au NPs with <4 nm diameter when compared to the

oxidation potential of the value for bulk Au. Based on Plieth equation, we obtained Au NPs with 1–2 nm diameter according to the lowest oxidation potentials observed. We also observed that, in the presence of Br^- and Cl^- , the oxidation of the smallest Au NPs exhibits less dependence on the halide used; also making a huge difference from bulk Au behavior. This part of the study shows a significant difference in the reactivity and a huge instability of small metallic NPs.

In Chapter IV, we showed two effects of electrodes that significantly alters the oxidation potential of metal NPs. One of the effects is the presence of the positively charged (3-aminopropyl)triethoxysilane (APTES) on glass/ITO/APTES electrodes. At acidic pH the oxidation potential for Au and >10 nm Ag NPs greatly decreased compared to the more neutral glass/ITO, glass/ITO/3-mercaptopropyl-trimethoxysilane (MPTMS), and glass/ITO/APTES (at neutral pH) electrodes. For smaller 4–6 nm Au NPs and 9 nm Ag NPs, the E_p value did not change significantly with different surface charge. We also observed that the method of Au NP synthesis does not change the stability or the E_p value on glass/ITO of Au NPs for both electrodeposited Au NPs and chemically synthesized, drop-cast deposited Au NPs while electrostatic effects do play an important role in modifying the E_p value. The second important finding from this work is that the underlying electrode material has an effect on the oxidation potential of metal NPs even when there is a linker present. For Ag NPs of 9 nm average diameter attached to various electrodes electrostatically through similar amine-terminated linkers, the oxidation order followed as $\text{Au} \sim \text{Pt} > \text{GC} > \text{glass/ITO}$. This follows the order of work function, except that the Au and Pt are reversed.

In Chapter V, we describe the oxidation of 1.5 nm diameter Au nanoparticles (NPs) attached to indium tin oxide-coated glass electrodes in Br⁻ solution. Borohydride reduction of AuCl₄⁻ in the presence of potassium hydroxide and trisodium citrate (1 min) led to Au NPs 1.5 nm in diameter. The oxidation potential of citrate-coated Au NPs is in the 295 to -85 mV range vs (3 M KCl), which is between 555 to 935 mV negative of the bulk Au oxidation peak. The large negative shift in potential agrees with theory for NPs in the 1-2 nm diameter range. The formation of ultra-sharp peaks during the stripping of Au NPs 1.5 nm diameter predominate over the symmetrical wave shape of nanoparticle bigger than 2.3 nm, showing higher negative shift on E^0 as the nanoparticles decrease on size.

In Chapter VI, we reported a size selection of citrate-coated Au NPs by electrochemical precipitation on Glass/ITO. We used an electric field cut-off ~2.0 V/cm for the deposition of both citrate-coated Au NPs with ≤ 33 nm, and ≤ 4 nm diameter, and ~1.5 V/cm for the deposition of ≤ 4 nm diameter. If the applied electric field is absent, we did not observed any measurable deposition of any 4-33 nm diameter Au NPs on glass/ITO. The lowest deposition potential tested in this study 0.4 V is applied to obtain the electrochemical precipitation of Au NPs sizes < 4 nm.

In Chapter VII, we describe a strong size dependence on a galvanic replacement reaction, using exchange of citrate-coated Au NPs with PtCl₄²⁻ as a model system, since it is not generally favored. Citrate-coated Au NPs 4 nm in diameter are more prone to the galvanic replacement reaction as compared to 15 nm, 50 nm, and 128 nm diameter Au NPs. We believe the driving force

for this reaction is the decrease in Au oxidation potential with decreasing NP size and the ability of small metal NPs to catalyze metal deposition.

Chapter VIII summarizes and provides future directions of this research. The work presented in this dissertation may inspire future fundamental and applied studies in the area of electrochemistry of nanomaterials, especially citrate-coated nanometals below 4 nm diameter in size.

CHAPTER II

EXPERIMENTAL

This chapter describes the experimental procedures followed in this study. Figure 2.1 shows the general scheme for the procedures used in this research.

2.1. Substrates

2.1.1. Indium Tin Oxide (ITO) coated glass slides

Indium tin oxide (ITO or tin-doped indium oxide) is made of indium (III) oxide (In_2O_3) and tin (IV) oxide (SnO_2), usually 90% In_2O_3 , 10% weight of SnO_2 . Due to its electrical conductivity and optical transparency, it is widely used as an electrode for spectroelectrochemistry and solar cell applications. We used unpolished float (soda - lime) glass coated ITO slides (Delta Technologies, LTD, Part No. CG-50IN-CUV) in experiments as an electrode material for electrochemical experiments and also for UV -Vis measurements. These electrodes have a resistance of 8-12 ohms. We cut the slide to a final size of 25 x 6 mm using a diamond pen, and cleaned them by 20-min sonication in acetone, ethanol and 2-propanol. Finally, we dried the slides under a N_2 stream before use.

2.1.2. Gold, Platinum and Glassy carbon disk electrodes

A gold disk electrode (0.0314 cm^2), platinum disk electrode (0.0314 cm^2) and glassy carbon (0.0707 cm^2) were purchased from CH Instruments (Austin, TX). Gold and Platinum disk electrodes were cleaned by polishing with alumina powder of 1.0, 0.3, and 0.03 micron size for 20 s each in that order, rinsing with

Figure 2.1. General scheme of procedures used in this study.

nanopure water, sonicating for 5 min in 20 mL of nanopure water, and drying under N₂. Next, the gold and platinum electrodes were cleaned electrochemically in a solution of 0.1 M H₂SO₄ by cycling the potential from 0 to 1.5 V versus a Ag/AgCl (3 M KCl) reference electrode until the metal surface oxidation and reduction peaks were stable and well defined. After removal from the electrochemical cleaning cell, the electrodes were rinsed with nanopure water. Glassy carbon (GC) disk electrodes were polished and cleaned as described above for the gold and platinum disk electrodes.

2.2. Chemicals

HAuCl₄·3H₂O was synthesized from metallic Au according to a literature procedure,¹⁰⁰ AgNO₃ (Sigma-Aldrich ≥99.0% ACS reagent), potassium bromide (EMD, GR ACS), potassium tetrachloroplatinate (II) (Sigma Aldrich, 99.99%), potassium chloride (Aldrich, ACS reagent), potassium iodide (Aldrich, 99%), perchloric acid (Merck, 60%), potassium perchlorate (Sigma-Aldrich ≥ 99.0% ACS reagent), potassium bicarbonate (Sigma Aldrich ≥ 99.7%), sulfuric acid (VWR, 95–98%), potassium sulfate (Sigma-Aldrich ≥99.0% ReagentPlus), tetraoctylammonium bromide (Alfa Aesar, 98%), 2-propanol (Sigma Aldrich, ACS reagent), ethyl alcohol (Pharmco-AAPER, ACS/USP grade), acetone (Pharmco-AAPER, ACS/USP grade), toluene (Pharmco-AAPER, reagent grade ACS), acetonitrile (Honeywell Burdick and Jackson ,HPLC grade), potassium hydroxide (Sigma Aldrich 85+% ACS reagent), 1-hexanethiol (Aldrich, 95%), 3-mercaptopropyl-trimethoxysilane (Aldrich, 95%), sodium borohydride (Sigma Aldrich, ≥ 98.5 reagent grade), citric acid, trisodium salt (Bio-Rad laboratories). hydrogen peroxide solution (Sigma-Aldrich 30 wt %), (3-aminopropyl)triethoxysilane (Sigma-Aldrich ≥98.0%), (2-aminoethanethiol

(Sigma-Aldrich $\geq 98.0\%$), and ethylenediamine (Sigma-Aldrich $\geq 99.0\%$) were used as received. NANOpure ultrapure water (Barnstead, resistivity of 18.2 M Ω -cm) was used for all aqueous solutions. Indium-tin-oxide (ITO)-coated glass (Glass/ITO) electrode CG-50IN-CUV were purchased from Delta Technologies Limited (Stillwater, MN). Carbon dioxide and Nitrogen gases were purchased from Welders Supply, (Louisville, KY). TEM grids of silicon oxide coated 400 mesh Au were purchased from SPI supplies.

2.3. Procedures

2.3.1. Nanoparticle synthesis

2.3.1.1. Chemical Synthesis of 1.5 nm Diameter Citrate-Coated Au nanoparticles (NPs)

These nanoparticles were synthesized according to the following procedure. 0.5 mL of 0.01 M citric acid, trisodium salt (TRIS) was added to 19.4 mL of nanopure water with 5 μ L of 1 M KOH under intense stirring. Then, 0.1 mL of 0.01 M HAuCl₄ solution was added. Finally, 0.6 mL of ice cold 0.1 M sodium borohydride was added all at once. The solution was allowed to stir for 1 min before attachment to the electrode for 1 min. This synthesis led to 1.5 ± 0.7 nm diameter Au NPs according to the TEM images. Figure 2.2. shows the scheme for the synthesis of 1.5 nm diameter citrate-coated Au NPs and the conformation of citrate anions adsorbed on Au NPs.¹⁰¹

2.3.1.2. Chemical Synthesis of 4 nm Diameter Citrate-Coated Au NPs

Our protocol for the chemical synthesis of Au NPs with 4 nm average diameter is based on that described by Murphy¹⁰² and co-workers. We mixed 20 mL of 0.25 mM HAuCl₄ solution with 0.25 mL of 0.01 M trisodium citrate.

Figure 2.2. Procedure for the synthesis of 1.5 nm diameter citrate-coated Au NPs. (a) Formation of $\text{AuCl}(\text{OH})_3^-$ and $\text{Au}(\text{OH})_4^-$ after the addition of KOH to pH 9.8, (b) redox reaction during the formation of 1.5 nm diameter citrate-coated Au NPs, and (c) citrate absorption on the surface of Au NPs at different pH values.

Then, 0.6 mL of ice cold 10 mM NaBH₄ was added into the solution with rapid stirring and stirred for 2h. The solution turned red after the addition of NaBH₄; this indicated Au NP formation. NaBH₄ works as a reducing agent, while citrate is the capping agent that stabilize the particles by electrostatic repulsion, preventing aggregation. We obtained an average particle size of 4 nm according to literature and confirmed by scanning electron microscopy imaging.¹⁰³ Later, we attached this NP to the surface of an electrode that served for the study of the oxidation properties of metal nanoparticles with different size. Figure 2.3. shows schematic of Au NPs synthesis according to Murphy's method.

2.3.1.3. Chemical Synthesis of <4 nm Diameter Citrate-Coated Au NPs

The procedure is identical to the synthesis of 4 nm average diameter citrate-stabilized Au NPs, except that the solution was allowed to stir for only 15 min before attachment to the electrode. The average diameter of these Au NPs was 2.3 ± 0.5 nm based on TEM images.

2.3.1.4. Chemical Synthesis of 12 nm Diameter Citrate-Coated Au NPs

0.5 mL of 0.01 M HAuCl₄ and 0.5 mL of 0.01 M citric acid, trisodium salt (TRIS) were added to 19 mL of nanopure water in that order. The solution was stirred while heating to 80–90 °C for 25 min before cooling ~10 min and attaching to the electrode as described later. The average diameter was ~ 12 nm based on scanning electron microscopy images. Figure 2.4. shows the procedure to synthesize 12 nm diameter by citrate reduction.

2.3.1.5. Chemical Synthesis of 15 nm Diameter Citrate-Coated Au NPs

We used the procedure described by Natan and co-workers to chemically synthesize Au NPs of 15 nm average diameter.³⁰ Briefly, a 50 mL aqueous

Figure 2.3. Procedure for the synthesis of 4 nm diameter citrate-coated Au NPs.

Figure 2.4. Procedure for synthesis of 12 nm and 15 nm diameter Au NPs by the citrate reduction method.

solution of 0.001 M HAuCl₄ was brought to boiling at 160 °C while stirring. Immediately after boiling, 5 mL of 38.8 mM trisodium citrate was added and stirred for 10 min. Finally, the resulting solution was stirred for 15 min more at room temperature. This procedure is a variation of the synthesis of 12 nm diameter citrate reduction.

2.3.1.6. Synthesis of 17 nm Diameter Citrate-Coated Au NPs by Chemical Seed-Mediated Growth

The chemical synthesis of 17 nm average diameter Au NPs is based on the procedure described by Pyatenko.¹⁰⁴ We added 2 mL of 1% trisodium citrate solution (by weight) and 4 mL of the Au NPs seed solution (4 ± 2 nm average diameter) to a boiling solution of 1 mL of 0.01 M HAuCl₄ and 99 mL of water and stirred constantly for 1 h. Then, the solution was cooled to room temperature. Figure 2.5. shows the procedure for the seeded growth synthesis of citrate-coated Au NPs.

2.3.1.7. Synthesis of 33 nm Diameter Citrate-Coated Au NPs by Chemical Seed-Mediated Growth

The chemical synthesis of 33 nm average diameter Au NPs is similar to the chemical synthesis of 17 nm diameter citrate-coated Au NPs with the addition of 6 mL of 0.01 M HAuCl₄ and 94 mL of water instead.

2.3.1.8. Synthesis of 38 to 156 nm Diameter Citrate-Coated Au NPs by Chemical Seed-Mediated Growth

We used the procedure described by Wang and coworkers to chemically synthesize monodisperse, quasispherical, citrate-stabilized Au NPs that were 38, 54, and 156 nm in diameter via H₂O₂ reduction of HAuCl₄.¹⁰⁵ According to Wang *et al.*,¹⁰⁵ H₂O₂ reduces HAuCl₄ to Au⁰ catalyzed by Au NPs, thus leading

Figure 2.5. Procedure for the synthesis of 17 nm diameter citrate-coated Au NPs by seed-mediated growth.

to NP enlargement. Au NPs obtained by this method are uniform in comparison with fairly nonuniform Au NPs obtained by H₂O₂ reduction without Au NP seeds.

The difference is thought to be due to fast deposition of Au⁰ on the Au NPs seed that minimize the formation of new Au NPs. The proposed reaction for the reduction of AuCl₄⁻ by H₂O₂ is as follows.

Briefly, 5 mL of 30 wt % H₂O₂ was added to an aqueous solution containing 4.90 mL of nanopure water, a variable amount of 1 wt % HAuCl₄·3H₂O, and 25 µL of 1 wt % citrate under stirring, immediately followed by the injection of a variable amount of 12 nm diameter Au NPs (seeds) while stirring. After the addition of the 12 nm diameter Au NPs, the color of the solution changed within 1 min from colorless or slightly yellow to a pink-red color, suggesting the formation of Au NPs. 12 nm diameter Au NPs act as a seed and were controllably grown to large sizes. Figure 2.6. illustrates the synthesis of citrate-coated Au NPs by H₂O₂ reduction.

By assuming that all the HAuCl₄ injected is consumed during the reaction, particles are spherical in shape, and reduction and growth take place without further nucleation, the size of the grown particles can be estimated by the following equation.³⁴

$$r_{\text{AuNP}}^3 = r_{\text{seed}}^3 + \frac{3}{4} \frac{m_{\text{Au}}}{\pi \rho_{\text{Au}} n_{\text{seed}}} \quad (2.2)$$

Figure 2.6. Schematic for seed-mediated growth of citrate-coated Au NPs by H_2O_2 reduction.

Where m_{Au} , n_{seed} , and ρ_{Au} are the Au mass added, the number of seed particles, and the gold density, respectively. The variable amount of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was 20, 33 and 100 μL , and the variable amount of 12 nm diameter Au NPs was 100, 50, and 5 μL for the synthesis of Au NPs of 38, 54, and 156 nm in diameter, respectively.

2.3.1.9. Chemical Synthesis of 9 nm Diameter Citrate-Coated Ag NPs

We used the procedure described by Murphy and co-workers to prepare 9 nm diameter Ag NPs. A 20 mL aqueous solution of 0.25 mM silver nitrate and 0.25 mM trisodium citrate was prepared. Ice-cold 10 mM NaBH_4 (0.6 mL) was injected at once into the solution with stirring for 2 hr. The solution went from colorless to yellow after the addition of NaBH_4 . The synthesis of Ag NPs is similar to the 4 nm diameter citrate-coated Au NPs.

2.3.1.10. Chemical Synthesis of hexanethiolate (C6S) Au monolayer-protected cluster (MPCs)

2.5 nm diameter hexanethiolate-(C6S) coated gold monolayer-protected cluster (Au MPCs) were synthesized according to the Brust reaction.³² 1.2 g of HAuCl_4 was dissolved in 10 mL of water and 2.6 g of tetraoctylammonium bromide (TOABr) was dissolved in 40 mL of toluene. The two solutions were combined and stirred until all of the AuCl_4^- transferred into the toluene phase. The toluene phase was separated and 1.34 mL of hexanethiol, corresponding to a 3:1 thiol: Au ratio, was added to the toluene and stirred until the solution became colorless. The solution was cooled to $\sim 0^\circ\text{C}$ using an ice bath and a 10-fold excess of NaBH_4 (1.2 g in 10 mL of water) was added to the toluene solution with stirring. The solution turned black within a few seconds, indicating the formation of metallic Au MPCs. The solution was stirred overnight. The

toluene layer was separated and removed by rotatory evaporation. The remaining black product was suspended in 125 mL of acetonitrile and collected by filtration on a glass fritted Büchner funnel. The black solid product was washed thoroughly with ethanol and acetonitrile and dried before collecting. Below are the set of reactions for the Au MPCs synthesis.

Figure 2.7. shows a schematic representation of metal monolayer protected cluster (MPCs) obtained as a product of synthesis.

2.3.1.11. Electrochemical growth of metal nanostructures directly on the electrode surface

Electrodeposition of Au NPs was performed directly on Glass/ITO electrodes. We monitored the deposition by chronocoulometry (CC) using Ag/AgCl (3 M KCl) as a reference electrode and Pt wire as a counter electrode to complete the cell. The potential was stepped negative from 1.0 V to a final deposition potential which ranged between -0.6 and 0.7 V until 1.02 to 1.45×10^{-4} Coulombs (C) of charge passed during deposition from a solution of 5×10^{-5} M AuCl_4^- in 0.5 M H_2SO_4 , similar to the procedure previously described by our group.³⁷ Once we achieved the desired charge, we removed the

Figure 2.7. Schematic representation of Au monolayer protected cluster (MPCs) obtained as a product of synthesis.

glass/ITO/Au NPs electrode from the cell. Then, we gently rinsed the electrodes with water and dried under a stream of N₂. This led to glass/ITO coated with Au NPs with an average diameter ranging from 6 to 232 nm, as the deposition potential increased, that had similar coverages in terms of total Au atoms on the surface per area. Figure 2.8 shows a typical CC plot of the electrochemical deposition of Au NPs from a solution of 0.5 M H₂SO₄ plus 5×10⁻⁵ M HAuCl₄ during a step from 1.0 V to 0.2 V with the passed charge of 2.5×10⁻⁴ C. The final total charge and the potential of deposition selected are important to control the final size and coverage of the nanoparticles. More charge and more positive potential leads to the deposition of large Au NPs.

2.3.1.12. Galvanic replacement of Au NPs with PtCl₄²⁻

Citrate-coated Au NPs from 4 to 155 nm were synthesized by chemical methods. Then, the glass/ITO/(3-aminopropyl)triethoxysilane /Au NPs samples were placed in 10 mL of 1×10⁻⁵ M and 1×10⁻⁴ M PtCl₄²⁻ solution. After 3 min, the electrode was thoroughly rinsed with nanopure water before drying under N₂. Galvanic replacement is a simple oxidation-reduction reaction that occurs when the oxidized form of one metal reacts with the reduced form of another metal. The reaction is spontaneous if the metal in the oxidized form has a more positive standard reduction potential than that of the metal in the reduced form. Since it is more energetically favorable in the reduced form compared to the other metal, the two metals will spontaneously exchange with one another. During this replacement reaction, the oxidation and reduction of the two metals involves the intermediate steps of alloy formation and dealloying as follows (assuming the same number of electrons in the oxidation and reduction):

Figure 2.8. Chronocoulometry (CC) plot showing the charge as a function of time during the electrochemical deposition of Au NPs from a solution of 0.5 M H₂SO₄ plus 5×10⁻⁵ M HAuCl₄ during a step from 1.0 V to 0.2 V. Plot is shown after the step to 0.2 V.

Figure 2.9. shows a schematic representation of the galvanic replacement reaction. Table 2.1. shows a full summary of the synthesis of metal nanoparticles performed in this dissertation.

2.3.2. Nanoparticle functionalization and attachment

2.3.2.1. Functionalization of Glass/ITO with organic silane linker and attachment of nanoparticles

Most of the studies involve attachment of citrate-coated metal nanoparticles to the electrodes before measuring the electrochemical properties. We functionalized the substrates with aminopropyltriethoxysilane (APTES) or mercaptopropyltrimethoxysilane (MPTMS). We heat the electrode (65-70 °C) for 30 min in a solution with 10 mL of 2-propanol, 100 µL of APTES or MPTMS and about 5 drops of nanopure water. This step allows the hydroxyl groups (-OH) present on the surface of the glass to covalently react with ethoxy (-O-CH₂-CH₃) group of APTES or the methoxy (-O-CH₃) groups of MPTMS forming a thin single layer. Then the surface of the substrate will be modified with MPTMS producing a surface covered with thiol (-SH) groups. For APTES treated substrates, the surface of it will be covered with amine groups. The schematic structures of APTES and MPTMS molecules and the substrate functionalization of Glass/ITO is shown in Figure 2.10.

All Au or Ag NPs and Au MPCs were attached to the functionalized Glass/ITO by the immersion of the electrode in a colloidal solution of NPs as

Figure 2.9. Schematic representation of a galvanic replacement reaction between Au NPs and PtCl_4^{2-} .

Table 2.1. Summary of the synthesis of the metal nanoparticles performed in this dissertation					
Metal salt	Stabilizer	Reducing agent	Solvent	Average particle diameter	Metal NPs
HAuCl ₄	citrate	NaBH ₄	water	1.5 nm *	Au
HAuCl ₄	citrate	NaBH ₄	water	≤ 4.0 nm	Au
HAuCl ₄	citrate	citrate	water	12, 15, 17 and 33 nm	Au
HAuCl ₄	citrate	H ₂ O ₂	water	38, 54 and 156 nm	Au
AgNO ₃	citrate	NaBH ₄	water	9.0 nm	Ag
HAuCl ₄	Hexanethiol (C6)	NaBH ₄	toluene	2.5 nm	Au
HAuCl ₄	---	potential	water	6 to 232 nm	Au
K ₂ PtCl ₄	---	Galvanic replacement**	water	4 to 155 nm	AuPt

*Chemical synthesis of citrate-coated Au NPs at pH 9.8.

**Galvanic replacement reaction between citrate-coated Au NPs and PtCl₄²⁻.

Figure 2.10. Functionalization of Glass/ITO electrode with mercaptopropyltrimethoxysilane (MPTMS) or aminopropyltriethoxysilane (APTES).

shown in Figure 2.11. Through a covalent type bond, Au and Ag NPs strongly bind to the -SH group of MPTMS as metal-S-. On the other hand, both metal NPs attach to the surface functionalized with APTES through electrostatic interactions between positively-charged amines of the APTES and the negatively-charged particles. By following this procedure, it is possible to control the coverage of NPs on the surface by modifying the soaking time within the colloidal NPs solution.

The glass/ITO/APTES electrodes were soaked in as-prepared solutions of the different-sized Au NPs for 10–60 min, rinsed thoroughly with nanopure water, and dried under N₂ prior to electrochemical analysis. The soaking time was chosen to obtain a similar Au coverage in terms of total Au for the different Au NP sizes.

The Glass/ITO/MPTMS electrode was directly immersed into a 5 mg/mL toluene solution of the Au MPCs for 2-5 days, leading to adsorption of the Au MPCs to the electrode either through Au thiolate or non-polar interactions.

2.3.2.2. Functionalization of Gold or Platinum Disk Electrodes with aminoethanethiol (AET) and attachment of Ag nanoparticle

The electrodes were polish and electrochemically clean then rinsed with nanopure water and then immersed into a 20 mM aqueous solution of aminoethanethiol (AET) overnight. The next day the electrodes were thoroughly rinsed with nanopure water before drying under N₂. These electrodes are referred to as Pt/AET and Au/AET throughout the dissertation.

All Ag NPs were attached to the functionalized Au/AET, and Pt/AET electrodes by the immersion of the electrode in a colloidal solution of Ag NPs. Figure 2.12.(a) shows functionalization of Au and Pt electrodes and Figure

Figure 2.11. Attachment of metal NPs to the surface of MPTMS- or APTES-functionalized Glass/ITO electrode.

Figure 2.12. Functionalization of (a) Au and Pt disk electrode with 2-aminoethanethiol and (b) Glassy carbon disk electrode with ethylenediamine.

2.13.(a) shows attachment of Ag NPs to the functionalized electrode. Au/AET, and Pt/AET electrodes were soaked in a solution of the 9 nm diameter Ag NPs (adjusted to a pH of 5.5 by adding 0.1 M HCl) for 5–180 min, rinsed thoroughly with nanopure water, and dried under N₂ prior to electrochemical analysis. The soaking time was chosen to obtain a similar Ag NP coverage on the different electrodes.

2.3.2.3. Functionalization of a Glassy Carbon Disk Electrode with ethylenediamine (ED) and attachment of nanoparticles

The GC disk electrode was functionalized with ethylene diamine (ED) following the procedure described by Downard and co-workers.¹⁰⁶ Briefly, the potential of the GC electrode was scanned from 0.0 to 1.2 V at 0.1 V/s using cyclic voltammetry in a solution containing 6 μ L ED and 658 mg [Bu₄N]BF₄ in 20 mL of acetonitrile using a silver wire pseudoreference and platinum wire counter electrode. The functionalized GC electrode was rinsed thoroughly with nanopure water before drying under N₂. This electrode is referred to as GC/ED throughout the dissertation. Figure 2.12.(b) illustrate the functionalization of GC electrodes.

All Ag NPs were attached to the functionalized GC/ED electrodes by immersion of the electrode in a colloidal solution of NPs as was described in the previous section. Figure 2.13.(b) illustrate attachment of Ag NPs to the ED-functionalized GC electrode.

Figure 2.13. Attachment of Ag NPs to the surface of (a) Au disk electrode and Pt disk electrode and (b) Glassy carbon disk electrode.

2.3.2.4. Attachment of Au and Ag NPs to Electrodes by drop cast deposition

Drop-cast deposition of 27 nm radius Au NPs directly onto glass/ITO/APTES, glass/ITO/MPTMS, and glass/ITO was performed by the addition of 150 μ L of the Au NP solution on the surface of the substrate followed by drying at room temperature

2.3.2.5. Electrochemical Assembly of Au NPs

Au NPs were deposited onto a clean glass/ITO working electrode using a potentiostat 660E in chronocoulometry mode with a gold foil counter electrode two electrode cell. First, the glass/ITO working electrode and gold foil electrode were immersed in a citrate-coated Au NPs suspension approximately 1 ± 0.2 cm apart from one another. Second, a fixed positive potential was applied to the glass/ITO working electrode. The applied potential developed an electric field between the two electrodes that could drive the negative nanoparticles to the positive electrode electrophoretically or lead to an electrochemical deposition process. Figure 2.14. shows electrophoretic assembly of Au NPs on the glass/ITO electrode.

2.3.3. Linear Sweep Voltammetry (LSV), electrochemical SET-UP

The electrochemical cell consisted of the metal NPs attached to a functionalized electrode or metal NPs attached to a bare electrode working electrode, a Pt wire counter electrode, and an Ag/AgCl (3 M KCl) reference electrode. All electrochemical measurements were performed with a potentiostat in 0.1 M HClO₄ plus 0.01 M KBr or 0.01 M KCl electrolyte solution

Figure 2.14. Set-up for the assembly of citrate-coated Au NPs on glass/ITO electrode by electrochemical or electrophoretical deposition.

for citrate-coated Au NP electrodes using LSV mode. The LSV scan was started at -0.2 V with the reference and counter electrodes in the electrolyte solution and the working electrode out of solution. The potential was scanned positive at 0.001 V/s or 0.01 V/s and paused when it reached -0.1 V, at which time the working electrode was immersed into the electrolyte solution. The scan was then “unpaused” and the potential scanned up to 1.6 V at a continued rate of 0.001 V/s or 0.01 V/s.

The surface area of citrate-coated Au NPs was measured electrochemically by oxidation and reduction of the Au NPs surface. Briefly, the electrochemical cell consisted of the glass/ITO/APTES/Au NP electrode, a Pt wire counter electrode, and an Ag/AgCl (3 M KCl) reference electrode. Cyclic voltammetry was performed with a potentiostat in 0.5 M H₂SO₄ electrolyte using cyclic voltammetry mode at a scan rate of 0.5 V/s.

2.4. Characterization and Instrumentation

2.4.1. Electrochemical Methods

Electrochemical techniques are a branch of analytical chemistry that measure electrical and chemical changes, such as, potential, current, or charge, in order to determine a concentration, characteristic or electrochemical reactivity of an analyte. The analyte is part of an oxidation–reduction reaction. This reaction occurs in a solution at the interface of an electrolyte and an electrode, where the transfer of electrons occurs between them or other species in the solution. This section will describe the electrochemical set-up and techniques that were used in this study. Figure 2.15. shows the basic electrochemical set-up used in this study. The electrochemical set up includes

Figure 2.15. Electrochemical set up.

the working electrode, counter electrode, reference electrode, a beaker with electrolyte, a potentiostat, and a computer for data analysis.

Electrochemical cell. Here, we used a three-electrode system: a working electrode, a reference electrode, and counter electrode.

The **working electrode** is where the electrochemical reaction occurs. Here in this study, we used Glass/ITO, Glass/ITO/NPs, Glass/ITO/APTES, Glass/ITO/APTES/NPs, Pt/AET/NPs, Au/AET/NPs and GC/ED/NPs served as a working electrode.

The **reference electrode** was used to determine and control the potential of the working electrode. This electrode does not pass any electric current and has a fiber wick to contact the external solution. In our studies we used an Ag/AgCl reference electrode. Ag/AgCl reference electrode consists of a silver wire electrode coated with solid AgCl and immersed in a solution of 3 M potassium chloride. Additionally, we used an alkaline/mercury oxide reference electrode in the study of removal of 1-hexanethiol SAM from C6S Au MPCs. The electrode consisted of Hg/HgO/1M NaOH.

The **counter electrode**, or auxiliary electrode, was used to connect the electrolyte closing the circuit and balance the current detected at the working electrode. Here, we used a Pt wire that worked as the counter electrode that carried the current and completed the cell circuit.

The electrolytic solution used in a particular experiment will be stated in each experiment in the following chapters.

Potentiostat. A potentiostat is an electronic instrument that is capable to control the voltage difference between the reference electrode and the working

electrode and measure the current flow between the working and counter electrode. The potentiostat sets the potential and the reaction produces a current that is then measured. In this study we used a potentiostat CH Instruments (Austin, TX) 620, 660A and 660E electrochemical workstation for all electrochemical experiments.

2.4.1.1. Linear Sweep Voltammetry (LSV)

Linear Sweep Voltammetry (LSV) is a method where the current at the working electrode is measured while the potential is swept linearly with time between the working electrode and a reference electrode. In LSV, the voltage was scanned from a lower limit to an upper limit or from an upper limit to a lower limit. The species becomes oxidized or reduced, and this will be recorded as a peak in the current signal at the specific potential at which the species in the cell will be oxidized or reduced. The LSV shape depends on several factors: (a) The rate of electron transfer, (b) The reactivity of the electroactive species and (c) the voltage scan rate. The LSV plot shows the current response as a function of voltage. This technique can identify the electroactive species from the potential in some cases, provide the concentration of the electroactive species in a solution or on the surface, and provide information about the rate of electron transfer. The slope of the excitation wave will be:

$$Slope = \frac{\Delta E}{\Delta time} \text{ [Volts/time]} \quad (2.9)$$

The scan rate (slope) is the ratio of change in potential and time. The integration of a peak produced by the current from an oxidation or reduction reaction involving the electroactive species gives the total charge (Q) in Coulombs passed during the reaction. This total charge follow Faraday's 1st

law, which states that the quantity of an electroactive species oxidized/reduced at the surface of an electrode during the electrochemical reaction is directly proportional to the amount of electricity transferred at that working electrode.

This law is as follow:

$$mol = \frac{Q}{nF} \quad (2.10)$$

Where Q (Coulombs) is the total charge passed through the working electrode during the electrochemical reaction, n is the number of the electrons for the electrochemical reaction, and F is Faraday's constant ($F = 96,485 \text{ C}\cdot\text{mol}^{-1}$). The quantity of charge per second is the current in Amperes (A).

LSV was used for studying the shift in the oxidation potential (E_p value) for different sizes of citrate-coated Au NPs, Ag NPs and Pt/Au NPs. Figure 2.16. shows a typical linear sweep voltammogram of glass/ITO/Au NPs (~4 nm) at a scan rate of 1 mV/s in a solution of 0.01 M KBr plus 0.1 M HClO₄.

The starting potential was -0.2 V and the ending potential 1.2 V (the range of 0.35 to 0.85 V is shown in the figure). The peak at ~ 650 mV results from an increase in current that corresponds to the oxidation of Au by Br⁻ by one or both of the two possible reactions as follows:

Figure 2.16. Typical linear sweep voltammogram of glass/ITO/Au NPs (~4 nm) at a scan rate of 1 mV/s in a solution of 0.01 M KBr plus 0.1 M HClO₄.

Figure 2.17. shows a scheme of the process of electrochemical oxidation of Au NPs. Integration of the oxidation peak obtained from the LSV provides the amount of Au present on the surface of the working electrode

2.4.1.2. Cyclic voltammetry (CV).

CV is an electrochemical method and similar to LSV. This method is equivalent to two LSVs the first LSV goes forward and the second LSV goes backwards completing a full cycle. Because this technique is a cycle it is possible to record the oxidation and reduction of an electroactive species present at the surface of the working electrode. In this technique the potential applied to the working electrode is swept at a specific rate and the resulting current measured as a function of potential. In cyclic voltammetry, the experiment begins at a potential where there is no electrodechemical reaction and moves to potentials where there is reduction or oxidation of the electroactive species.

A typical cyclic voltammogram is shown in Figure 2.18. where $i_{p,c}$ is the cathodic peak current, $i_{p,a}$ is anodic peak current, $E_{p,c}$ is potential of the cathodic peak and $E_{p,a}$ is potential of the anodic peak. Figure 2.19. shows the excitation wave of a CV.

2.4.1.3. Chronocoulometry (CC).

In a chronocoulometry experiment, we measure the total charge (Q) vs time after applying a potential step. We are able to obtain Q by integrating the current, i with time following the potential step. The CC experiment begins at the starting potential where there is no electrolysis. Then the potential step was applied, which led to oxidation or reduction of the electroactive species in the

Oxidation

Figure 2.17. Schematic representation of Au oxidation by Br⁻.

Figure 2.18. Typical cyclic voltammogram for a solution that is 0.004 M $K_3Fe(CN)_6$ in 1.0 M KNO_3 .

Figure 2.19. The excitation waveform in a CV experiment.

electrolyte. The potential was held according to the parameters of the experiment. CC was used with a single potential step for the electrochemical deposition of Au nanoparticles with different size and also for the electrophoretic/electrochemical deposition of citrate-coated Au NPs.

2.4.2. Ultraviolet-Visible Spectroscopy (UV-vis)

UV-vis spectroscopy is the result of the measurement of the transmittance T that is converted to absorbance by the Beer's law. See equation 2.13. Our UV-VIS measurements were obtained using a Varian Cary 50 Bio UV-visible Spectrophotometer. The sample was placed inside a cuvette and the absorbance measured from 900 nm to 300 nm. The transmittance of the sample is the ratio of the intensity of the light after passing through the sample (I) and the light intensity after passing through the black medium (solvent) (I_0). The ratio I/I_0 is called transmittance, T .

$$A = -\log (T) \quad (2.13)$$

2.4.3. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a powerful tool for analyzing size, shape and morphology of nanomaterials. Image formation in the SEM is dependent on the acquisition of signals produced from the interaction between the electron beam and the sample. Fig 2.20 (a) shows the interaction between the electron beam and the sample and (b) a typical SEM image. The major components in a SEM are the electron gun, electromagnetic lenses, apertures, a high-vacuum environment, a specimen stage, electron beam scanning coils, signal detection and a processing system that provide real time observation and image recording. Electron microscopy has been developed by replacing the light

source with a high energy electron beam. The interaction of the electron beam with the sample produces a set of signals, which is usually the measurement of secondary electrons. Another valuable method of producing an image in SEM is by detection of backscattered electrons, which provides both composition and topographic information in the SEM. Another class of signals produced by the interaction of the primary electron beam with the specimen is characteristic X-rays. The analysis of characteristic x-rays provides chemical information. In addition to the previous signals there are also Auger electrons.

In this work, SEM images of Au NPs, Ag NPs and PtAu NPs attached to the substrate (glass/ITO or glass/ITO/APTES) were collected by a Carl Zeiss STM AG Supra 35VP field emission scanning electron microscope (FESEM) operating at an acceleration voltage of 20 kV and using an in-lens ion annular secondary electron detector.

2.4.4. Transmission Electron Microscope (TEM)

The transmission electron microscope (TEM) has become one of the main tools for nanomaterials characterization. The major components in a TEM are electron gun, acceleration tube, a vacuum system, condenser, specimen holder, objective aperture, objective lens, intermediate lens, projector lens, fluorescent screen, camera chamber, binocular and viewing port. The microscope may be fully enclosed to reduce interference from environmental sources, and operated remotely. Figure 2.21 (a) shows the interaction of the electron beam and the sample in a TEM instrument.

Figure 2.20. (a) Scheme of electron beam and sample interactions. (b) Typical SEM image of Ag NPs attached to the surface of a glass/ITO electrode.

The optics of electron microscopes can be used to make images of the electron intensity transmitting through the sample. A TEM includes elements analogous to those of an optical microscope. The light source of the optical microscope is replaced by an electron gun. The glass lenses are replaced by electromagnetic lenses. Unlike glass lenses, the power (focal length) of magnetic lenses can be changed by changing the current through the lens coil. The eyepiece or ocular is replaced by a fluorescent screen and/or a digital camera. The electron beam emerges from the electron gun, and passes through a thin sample, transmitting electrons which are collected, focused, and projected onto the viewing device at the bottom of the column. The entire electron path from gun to camera must be under vacuum.

TEM images were obtained using two different instruments (a) FEI Tecnai F20 transmission electron microscope. A field emission gun (FEG) was used for the electron source and the studies were performed with an accelerating voltage of 360 keV. Figure 2.21 (b) shows a representative TEM image of 4 nm diameter Au NPs (University of Louisville). (b) 300 keV JEOL JEM 3200FS equipped with an in-column energy filter, a Gatan UltraScan 4000 CCD camera, a JEOL STEM system (scanning coils with bright field and high angle annular dark field detectors), and an Oxford INCA EDX system (Indiana University).

2.4.5. Measurement of electrophoretic mobility and zeta potential

The Zeta potential measurement and mobility were acquired using a Brookhaven Instruments NanoBrook Zeta PALS Zeta Potential Analyzer (Holtsville, NY).

Figure 2.21. (a) Scheme of electron beam and sample interactions in TEM.

(b) Typical TEM image of 4 nm average diameter Au NPs.

ÓΠΕΙΝΟΥΑΙΑ

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ΨΥΝΩΠΩΣΑ

3.1. Introduction

Here we describe the oxidation of <4 nm diameter Au nanoparticles (NPs) attached to indium-tin-oxide (ITO) – coated glass electrodes in Br⁻ and Cl⁻ solution. Borohydride reduction of AuCl₄⁻ in the presence of hexanethiol or trisodium citrate (15 min) led to Au NPs <4 nm diameter. After electrochemical and ozone removal of the hexanthiolate ligands from the thiol-coated Au NPs, Au oxidation peaks appeared in the 0 – 400 mV range versus Ag/AgCl (1 M KCl), which is 850 – 450 mV negative of the bulk Au oxidation peak near 850 mV. The oxidation potential of citrate-coated Au NPs is in the 300 – 500 mV range and those of 4 nm and 12 nm diameter Au NPs in the 660-780 mV range. The large negative shift in potential agrees with theory for NPs in the 1 – 2 nm diameter range. The oxidation potential of Au in Cl⁻ solution is positive of that in Br⁻ solution, but the difference decreases dramatically as the NP size decreases, showing less dependence on the halide for smaller NPs.

Metal nanoparticles (NPs) exhibit fascinating size-dependent properties that are useful for a wide range of applications. Smaller sized NPs are often the most effective for certain applications, especially in catalysis, sensing, and nanoelectronics, due to the high surface area and dramatic change in their electronic structure. Small NPs of Au and Ag have exhibited fluorescence¹⁰⁷ and there has been a recent heightened awareness about the toxicity of metallic NPs, which is often attributed to the liberation of metal ions.¹⁰⁸ Thus, the stability of metal NPs against oxidation is a crucial issue.

Previously, on the basis of sublimation energies, Henglein predicted a large negative shift in the oxidation potential of small Ag clusters of a few atoms and showed that such clusters behave as strong reducing agents.⁵³ On the basis of the increase in the surface area, Plieth predicted a $1/r$ -dependent negative shift in the oxidation potential relative to the bulk metal for metal NPs with radius r .⁵⁴ Recently, Sieradzki and co-workers showed that <4 nm diameter Pt NPs dissolve at potentials well below the bulk value and by a different mechanism.¹⁰⁹ They developed size-dependent potential-pH diagrams and imaged dissolving Pt NPs by scanning tunneling microscopy (STM).¹¹⁰ Del Popolo *et al.* reported that small Pd NPs dissolve at more negative oxidation potentials relative to the bulk,¹¹¹ while Kolb¹¹² and Penner¹¹³ showed an enhanced stability for Cu and Ag NPs on Au and highly ordered pyrolytic graphite, respectively, by STM. Compton and co-workers observed no change in the oxidation potential for Ag NPs over the range of 25-100 nm in diameter range.¹¹⁴ Brus and co-workers described an electrochemical Ostwald ripening process for Ag on conductive substrates that was due to the more negative

oxidation potential for smaller NPs.¹¹⁵ Recently, Brainina and co-workers described the size-dependent oxidation of metal NPs theoretically⁶⁰ and later compared theory to experimental data for the oxidation of Au in chloride solution.⁶⁶

Our group was the first to quantify the negative shift in the oxidation potential of Ag (8 to 50 nm diameter)¹¹⁶ and Au (4 to 250 nm diameter)³⁷ NPs as a function of size directly by voltammetry and compare the results to the theory developed by Plieth.⁵⁴ The agreement was better for Au, which showed an ~200 mV negative shift in potential between bulk Au (≥ 60 nm) and 4 nm diameter NPs. On the basis of the expected $1/r$ dependence, the negative shift should increase dramatically for sizes below 4 nm, which is the focus of this work.

3.2. Experimental

3.2.1. Steps in the Determination of the Oxidation Potential of C6S Au MPCs on glass/indium tin oxide (Glass/ITO) Substrates

The determination of the oxidation potential of C6S Au MPCs free of 1-hexanethiols was performed by 5 steps. Step 1 involved the synthesis of C6S Au MPCs. Step 2 was the functionalization of an indium tin oxide (ITO) - coated glass electrode (Glass/ITO) with 3-mercaptopropyltrimethoxysilane (MPTMS). This is referred to as Glass/ITO/MPTMS. Step 3 was soaking the Glass/ITO/MPTMS in a toluene solution of C6S Au MPCs for 2-5 days. Step 4 was the electrochemical removal of the monolayer of 1-hexanethiolates from the Au by electrochemical desorption and ozone. Step 5 was obtaining a LSV

of the Glass/ITO/MPTMS/Au MPCs to directly measure the peak potential (E_P) for Au oxidation. The 3 first steps are described in Chapter 2.

3.2.1.1. Removal of the 1-hexanethiol Self Assembly Monolayer (SAM) from C6S Au MPCs

The 1-hexanethiol SAM was removed from C6S Au MPCs on Glass/ITO/MPTMS by scanning from 0 to negative values (-0.5 to -1.0 V) and holding the potential for various amounts of time in a 9:1 (0.1 M KOH:ethanol) solution. This is known to cause reductive desorption of the alkanethiols from Au surfaces.¹¹⁷ The removal of the thiols was assessed by observing the oxygen reduction peak on the next scan. As shown in Figure 3.1. The first scan shows a peak near -0.9 V, which we attribute to oxygen reduction at the Au nanoparticle surfaces. The peak appears at a large overpotential due to the presence of the hexanethiolate monolayer covering the Au. With more scans and holding the potential negative, the peak for oxygen reduction eventually shifted to between -0.4 and -0.5 V, which is where it occurs on a bare Au nanoparticle surface. This indicates that the Au nanoparticles were mostly free of hexanethiols after the 15 scans (or steps) and various hold times. The hold times were 2 min for steps 1 to 5, 10 min for steps 6 to 11, and 1 h for step 12. After each potential scan and hold, the Glass/ITO/MPTMS/Au MPC electrode was cleaned gently with nanopure water and 2-propanol. To be sure the hexanethiolates were completely removed we then placed the electrode in a Jelight Company, Inc. model N42 UVO ozone cleaner (Irvine, CA) for 2 min before each step from steps 13 to 15. After the final step, the electrode resembles a bare Au nanoparticle electrode.

Figure 3.1. Linear sweep voltammograms obtained in 9:1 (0.1 M KOH:ethanol) solution of Glass/ITO/MPTMS/C6S Au MPCs after various steps in the hexanethiolate removal procedure.

3.2.1.2. Linear sweep voltammetry of the thiol-free Glass/ITO/3-mercaptopropyl-trimethoxysilane (MPTMS)/Au MPC Electrode

All electrochemical measurements were performed at a scan rate of 0.01 V/s in linear sweep voltammetry (LSV) mode. The electrolytic solution was 0.1 M HClO₄ + 0.01 M KBr or 0.1 M HClO₄ + 0.01 M KCl as indicated in the results section and the scan range was from -0.1 to 1.0 V.

3.2.2. Steps in the Determination of the Oxidation Potential of Citrate-Coated Au Nanoparticles on Glass/ITO Substrates

The determination of the oxidation potential of citrate-coated Au nanoparticles was performed by 4 steps. Step 1 involved the synthesis of citrate-stabilized Au nanoparticles. Step 2 was the functionalization of an indium tin oxide (ITO) - coated glass electrode (Glass/ITO) with 3-aminopropyltriethoxysilane (APTES). This is referred to as Glass/ITO/APTES. Step 3 was soaking the Glass/ITO/APTES in an aqueous solution of the citrate Au nanoparticles (NPs). The Glass/ITO/APTES substrate was directly immersed into 10-fold diluted solution of the appropriate citrate-stabilized Au NPs for approximately 5 min. Step 4 was obtaining a LSV of the Glass/ITO/APTES/Au NPs to directly measure the peak potential (E_P) for Au oxidation. The same procedure was used as that described for Au MPCs above. Steps 1 and 2 are described in Chapter 2.

3.3. Results and Discussion

Figure 3.2A shows the results of the oxidation of 2.5 ± 0.7 nm average diameter C6S Au MPCs (blue plot) on a thiol-functionalized glass/ITO electrode. The size was based on TEM images, which showed NP diameters

ranging from 1 to 5 nm, with ~79% of the NPs below 3 nm and 21% above 3 nm (Figure 3.3). After attachment to the electrode, we removed the C6S ligands electrochemically and with ozone (Figure 3.1). The LSV showed a large oxidation peak near 720 mV along with four smaller oxidation peaks in the 0–400 mV range. Au can be oxidized in the presence of halides by the following reactions:¹¹⁸

The three-electron (3e) oxidation is thermodynamically favorable, but our group previously reported an average oxidation of 1.5 electrons, while others reported 1.9 electrons.¹¹⁸ This could be due to a combination of the direct 3e and one-electron (1e) oxidations or the third chemical step shown above. While the situation is quite complex, we previously observed one main peak for the oxidation of Au NPs from 4 to 250 nm in diameter.³⁷ Accordingly, we attribute the distinct peaks in the LSV in Figure 3.2 to different Au NP sizes as opposed to the different reactions above. The red and black dashed plots, respectively, show the oxidation of well characterized 12 and 4 nm average diameter citrate-coated Au NPs attached to amine-functionalized glass/ITO for comparison. Figure 3.2 B shows an expanded view of the LSV from -100 to 500 mV. The peaks are somewhat symmetrical and consistent with surface oxidative

Figure 3.2. A) LSVs for Au NPs with diameter of 2.5 nm (blue solid plot), 4.0 nm (black dashed plot), and 12 nm (red dashed plot) in 0.1 M HClO₄ + 0.01 M KBr from -0.1 to 1.0 V. B) Expanded view of the region from -0.1 to 0.5 V, marked by the dotted box in (A). (C) LSV of 2.5 nm diameter Au MPCs from -0.10 to 0.45 V (first scan) and -0.1 to 1.0 V (second scan).

Figure 3.3. TEM image and particle-size histogram for C6S Au MPCs synthesized and used in the experiments. The particle-size histogram is based on 462 randomly selected particles.

stripping. No peaks exist in the low potential range for the larger 12 nm diameter Au NPs and two broad, weakly defined peaks exist for the 4 nm diameter sample. On the basis of the three plots, we attribute the peak at 720 mV for the Au MPC sample to the oxidation of Au NPs near 4.0 nm in diameter and those from 0 to 400 mV to the oxidation of < 4.0 nm diameter Au NPs. Figure 3.2 C shows an experiment where we attached the 2.5 nm average diameter Au NPs onto the electrode and performed the first scan from -0.1 to 0.45 V and a second scan from -0.1 to 1.0 V. The first scan shows a noticeable oxidation peak near 100 mV, which we attribute to the oxidation of <4.0 nm diameter Au NPs. In the second scan, this peak was absent, and we observed only an oxidation peak near 740 mV. The absence of a peak in the 0 to 400 mV range in the second scan is consistent with removal of the Au NPs by oxidative dissolution, whereby the Au dissolved and diffused away from the electrode. The peak at 740 mV correlates with the oxidation of 4nm diameter Au NPs that did not oxidize in the first scan because the potential was not positive enough.

Figure 3.4 shows the LSV of 2.5 nm average diameter Au MPCs on thiol-functionalized glass/ITO in 0.1 M HClO₄ + 0.01 M Cl⁻ solution (red curve) compared with 0.01 M Br⁻ (blue curve). The peak at 720 mV in Br⁻ shifted to ~940 mV in Cl⁻, and the four lower oxidation peaks shifted in the positive direction to the 110 to 550 mV range. The oxidation of Au in Cl⁻ solution occurs by the reactions shown above with Br⁻ replaced by Cl⁻, at potentials ~140 mV and 19 mV more positive than the values for Br⁻ for the 3e and 1 e oxidations, respectively, since Cl⁻ coordinates more weakly with Au than Br⁻ does. We

Figure 3.4. A) LSVs of 2.5 nm average diameter Au MPCs in 0.1 M HClO_4 plus 0.01 M KBr (blue plot) or 0.01 M KCl (red plot). B) Expanded view of the region from -0.1 to 0.7 V (dotted box in A).

observed the same peaks in both LSVs, but the peaks were shifted in the positive direction in Cl^- , consistent with Au metal oxidation by the halides. The shift in the oxidation of the 4 nm diameter NPs (~ 220 mV) is larger than expected for the $3e^-$ process and much larger than expected for the $1e^-$ process. The shift in the oxidation of the smaller < 4 nm diameter Au NPs (~ 110 - 180 mV) decreased with decreasing oxidation potential (or smaller Au NP size). For the smallest Au NPs, the shift was smaller than expected for $3e^-$ process but larger than expected for a $1e^-$ oxidation. While the shifts are not exactly as expected on the basis of the reported E^0 values, the fact that a shift occurs strongly suggests that the peaks are due to oxidation of Au in the presence of halides, which was an important conclusion in order to confirm the dramatic negative shift in oxidation potential with decreasing NP size. If we assume that the different-sized NPs oxidize by the same process, then the difference in oxidation of Au in the presence of Br^- and Cl^- depends on the size of the Au, since the shifts in the potential are very different with decreasing Au NP size. This unexpected result is the first report of size-dependent reactivity between Au and halides.

While Figures 3.2 and 3.4 show convincing evidence of a dramatic negative shift in oxidation potential for small < 4 nm diameter Au NPs in the presence of halides, the peaks in the low potential region were relatively small. To increase the peak current (or charge) associated with smaller NPs, we synthesized Au NPs by borohydride reduction of AuCl_4^- in the presence of citrate, stopping the reaction after 15 min instead of the normal 2 h, with the hope of capturing smaller Au NPs at an earlier stage of the nucleation and

growth process. Figure 3.5A (blue plot) shows the LSV in 0.01 M KBr + 0.1 M HClO₄ for the Au NPs synthesized for 15 min and attached to amine-functionalized glass/ITO. The LSV exhibits two oxidation peaks in the low potential region (300-500 mV) with a much larger intensity relative to the higher-potential oxidation peak near 670 mV. In comparison, the LSV for 4 nm average diameter Au NPs prepared by reduction for 2 h (green plot) shows only one very small oxidation peak in the low-potential region and a relatively larger peak near 675 mV. The LSV for the larger 12 nm average diameter Au NPs (grey plot) exhibits one main peak near 780 mV with no discernable peaks at the lower potential, consistent with the larger size. Figure 3.5.A also shows LSVs for the amine-functionalized glass/ITO electrode with no Au NPs (black plot) in KBr + HClO₄ and for amine-functionalized glass/ITO coated with 15 min Au NPs in HClO₄ only (red plot), which demonstrate that these peaks are not present in the background or for Au NPs without Br⁻ present. On the basis of the absence of these peaks for larger Au NPs and the control experiments, we attribute the peaks at lower potentials to the oxidation of < 4 nm diameter Au NPs, confirming that reduction for 15 min successfully allowed the isolation and measurement of a larger population of < 4 nm diameter Au NPs.

Figure 3.5.B compares the LSVs of amine-functionalized glass/ITO electrodes coated with the 15 min-synthesized Au NPs in solutions containing Cl⁻ and Br⁻. The results for three different samples (Figures 3.6 and 3.7) showed that the peak potentials were highly reproducible while the peak current (or charge) varied because of differences in NP coverage on the electrode. The same three peaks appeared in both sets of LSVs but were again shifted in the

Figure 3.5. A) LSVs of citrate-coated Au NPs of 12 nm, 4 nm, and <4 nm in 0.1 M HClO₄ plus 0.01 M KBr. The sample of glass/ITO only and 4 nm diameter citrate-coated Au in HClO₄ only is shown for comparison. B) LSVs of citrate-coated <4 nm diameter Au NPs in Br⁻ solution (blue plot) and Cl⁻ solution (red plot).

	Peak III	Peak II	Peak I
Average	662 mV	487 mV	345 mV
SD	4 mV	11 mV	1 mV

Figure 3.6. Linear sweep voltammograms obtained in 10 mM KBr plus 0.1 M HClO₄ from 0 to 1.0 V versus Ag/AgCl at a scan rate of 0.01 V/s. The blue, brown, and green plots correspond to three different Glass/ITO/APTES/Au NP (<4 nm) electrodes and the black and grey plots correspond to Glass/ITO/APTES electrodes. All plots were obtained after bubbling the solution with N₂ for 5 min. The intensity of the Au peaks vary due to different coverages of Au NPs on the electrode, but the peak potentials were highly reproducible.

	Peak III	Peak II	Peak I
Average	852 mV	648 mV	311 mV
SD	5 mV	6 mV	9 mV

Figure 3.7. Linear sweep voltammograms obtained in 10 mM KCl plus 0.1 M HClO₄ from 0 to 1.0 V versus Ag/AgCl at a scan rate of 0.01 V/s. The blue, brown, and green plots correspond to three different Glass/ITO/APTES/Au NP (<4 nm) electrodes and the black and grey plots correspond to Glass/ITO/APTES electrodes. All plots were obtained after bubbling the solution with N₂ for 5 min. The intensity of the Au peaks vary due to different coverages of Au NPs on the electrode, but the peak potentials are highly reproducible. Peaks II and III are shifted positive relative to those in KBr, while peak I is similar.

positive direction for Cl^- relative to Br^- . The shifts decreased with decreasing oxidation potential, with values of 190 and 160 mV for peaks III and II, respectively, while the lowest oxidation peak (peak I) near 300 mV was actually ~ 30 mV more negative for Cl^- than for Br^- . The halide-dependent oxidation potentials strongly suggest that the peaks are due to halide-assisted Au oxidation, and the LSVs clearly show a dramatic negative shift for <4 nm diameter Au NPs. The oxidation potential of the very smallest population of Au NPs again appeared to be less sensitive to the halide present. Further experiments are needed to better understand this interesting phenomenon.

Figure 3.8. shows UV-vis absorption spectra of Au NPs reduced for 15 and 120 min. The localized surface plasmon band for Au near 530 nm was more pronounced for the Au NPs reduced for 120 min, which is consistent with the larger average diameter of 4.1 ± 0.7 nm for the 120 min sample relative to the value of 2.3 ± 0.5 nm for the 15 min sample, as measured by TEM in Figure 3.9. Figure 3.10. shows a plot of the peak oxidation potential for the Au NPs (E_{particle}) as function of the diameter from 0 to 6 nm, based on the Plieth equation:⁵⁴

$$E_{\text{particle}} = (-2\gamma V_m / ZF) * (2/d) + E_{\text{bulk}} \quad (3.1)$$

where E_{bulk} is the oxidation potential of the bulk metal (taken as 850 mV on the basis of the oxidation of ~ 50 nm diameter Au NPs under our condition), γ is the surface tension (1880 erg cm^{-2}),⁵⁴ V_m is the molar volume ($10.21 \text{ cm}^3 \times \text{mol}^{-1}$)⁵⁴, Z is the number of electrons, F is Faraday's constant, and d is the NP diameter. It should be noted that surface stress, instead of surface tension, is

Figure 3.8 UV-visible spectra of citrate-coated Au NPs reduced for 15 and 120 min as indicated. The more intense plasmon band at 530 nm is indicative of larger Au NPs after 120 min of reduction compared to the sample reduced for 15 min, which is consistent with the smaller average diameter determined by TEM (Figure 3.9.) and the more negative oxidation potential in the linear sweep voltammograms.

Figure 3.9. TEM image and histogram of citrate-coated Au NPs after 15 min and 120 min of reaction time. For 15 min of reaction time, the number of counts for the histogram was 88, the average size 2.3 nm and SD 0.5 nm. In the counting of the histogram, Au NPs that appeared aggregated were omitted in order to avoid overestimation of size. For the 120 min reaction time, the number of counts for the histogram was 97, the average size 4.1 nm and SD 0.7 nm.

Figure 3.10. Theoretical shift in the oxidation potential as a function of size from 0 to 3 nm radius. The green dashed lines represent the potential observed in Au MPCs (2.5 nm) average diameter.

more appropriate for the calculation, so the use of τ could be a potential source of error.¹⁰⁹ Three plots are shown with different values of Z , since we previously showed that the oxidation on average involves 1.5 electrons.³⁷ Others determined an average of 1.9 electrons¹¹⁸ or used one electron⁶⁶ in the analysis of Au NP oxidation in the presence of halides. The dashed lines in the plot show the potential ranges where we observed oxidation peaks in Figure 3.2, 3.4 and 3.5. The low potential region (0-500 mV), corresponding to 1.0 to ~ 2.3 nm diameter Au NPs according to eq 3.1, is highlighted in green. The higher-potential region (600-700 mV), corresponding to ~3-5 nm diameter Au NPs, is highlighted in violet. The ranges would be slightly different yet still reasonable for $Z= 1.5$, but the plot for $Z=3$ would not fit our data. Given the uncertainty in the surface stress, we believe the data fit reasonably well for $1e^-$ or $1.5e^-$ process.

It is important to make a rough comparison of the TEM data and the electrochemical data in these studies. For example, the charge under the high-potential oxidation peak for Au MPCs is 50 times larger than the cumulative charge of the low-potential oxidation peaks. Taking into account the fact that a 4 nm diameter Au NP contains ~2400 atoms, as compared with ~300 atoms for a 2 nm diameter Au NP,⁵² that would correspond to ~86% of the 4.0 nm Au NPs versus 14% of the 2.0 nm Au NPs on the electrode surface. If we roughly consider ≥ 3.0 nm Au NPs as 4.0 nm NPs and ≤ 2.9 nm Au NPs as 2.0 nm NPs, the TEM based percentages for these populations would be 29% and 71%, respectively. The electrochemical and TEM data are therefore not in good agreement. For the same analysis with the 15 min citrate-coated Au NPs, the

LSV determined values are 24% and 76%, compared with the TEM based values of 14% and 86% for ≥ 3.0 nm and ≤ 2.9 nm Au NPs, respectively. This is much better agreement. For the Au MPCs, we believe the larger value for the LSV data relative to the TEM data is due to a greater propensity for large Au MPCs to adsorb to the electrode surface because of their lower solubility in the toluene solution and the longer time period used for adsorption (≥ 2 days). Aggregation or the electrochemical desorption and ozone treatment could also have resulted in larger NPs on the electrode surface than expected. In the case of the citrate-coated Au NPs, we believe the agreement is better because the attachment is electrostatic and relatively fast (5 min) and there was no other treatment.

The oxidation peak for larger-sized Au NPs appears as one broad peak in Figures 3.2, 3.4 and 3.5, whereas the population of smaller Au NPs appears as multiple distinct peaks. This is due to the much larger oxidation potential difference for a small change in diameter for Au NPs in the 1–2 nm range. For example, the expected difference in the oxidation potential between 3.0 and 4.0 nm diameter NPs is 66 mV. The difference between 2.0 and 2.4 nm diameter Au NPs is also predicted to be 66 mV and the difference between 1.4 and 2.0 nm diameter NPs is 170 mV. These large differences in oxidation potential with a small difference in Au NP size render them more resolvable by LSV, leading to multiple peaks. In general, it is difficult to make an exact comparison between the TEM and electrochemistry results because of the uncertainties in the TEM-measured diameters at these very small sizes and in the size of the Au NPs actually adsorbed on the electrode surface.

3.4. Conclusions

In summary, we have reported a dramatic negative thermodynamic shift in the oxidation potential for <4 nm diameter Au NPs. The oxidation was as large as 850 mV negative of the value for bulk Au for the smallest NPs synthesized. The lowest oxidation potentials observed are consistent with 1–2 nm diameter Au NPs on the basis of the Plieth equation. While the details of the oxidation reactions involved ($3e^-$, $1e^-$, and chemical) are not well understood, the data fit best with the Plieth equation for a process involving one or an average of 1.5 electrons. Interestingly, the oxidation of the smallest Au NPs in the presence of Br^- and Cl^- exhibits less dependence on the halide used, which is very different from bulk Au behavior. While more details must be worked out, this study clearly shows the remarkable difference in reactivity and large decrease in stability for small metallic nanostructures.

linkers depends on the electrode material, following the order (vs Ag/AgCl) of Au (384 ± 7 mV) $\approx$ Pt (373 ± 12 mV) > GC (351 ± 2 mV) > glass/ITO (339 ± 1 mV). The underlying electrode material affects the Ag NP *Ep* even though the NPs are not directly interacting with it. In addition to size, the electrode material and its surface charge have a strong influence on the oxidation potential of surface-confined metallic nanostructures.

Metal nanoparticles (NPs) have interesting optical, electronic, chemical, magnetic, and electrochemical properties, which are useful for a wide variety of applications, e.g. catalysis,¹¹⁹ sensing,¹²⁰ nanoelectronics,¹²¹ imaging,¹²² therapeutics,¹²³ and plasmonics.¹²⁴ The size of the metal nanostructure is a critical factor for most applications and smaller-sized NPs with increased surface area and altered reactivity are sometimes the most effective, especially in catalysis and sensing applications. However, based on early predictions of Henglein¹²⁵ and later by Plieth,¹²⁶ smaller metal NPs are also more prone to oxidation, which could greatly limit their practical applications. Since these early theoretical studies, there have been several experimental studies exploring the main factors affecting metal NP oxidation, for which size is usually the main consideration. Early electrochemical scanning tunneling microscopy studies (ECSTM) by Kolb¹¹² and Penner¹²⁷ showed an enhanced stability for Cu clusters on Au and Ag nanoclusters on highly-oriented pyrolytic graphite (HOPG), respectively, in disagreement with the early predictions. This was attributed to possible quantum size effects in small clusters providing stability, but the effect of the substrate and possible electrode-cluster alloying was not ruled out. Later, Del Popolo attributed the stability of Cu and Pd clusters on Au

surfaces to alloying as studied theoretically and by ECSTM.^{111,128-131} These early studies raised awareness about the potential effect of the electrode material on the oxidation potential of small metal NPs, especially in cases where alloying can occur.

Using scanning electron microscopy (SEM), Brus and co-workers described an electrochemical Ostwald ripening process for films of Ag NPs formed by thermal evaporation on a conductive substrate.¹¹⁵ Large Ag NPs grew at the expense of smaller Ag NPs in a reforming process that is due to the more positive standard potential for the larger NPs,¹¹⁵ in agreement with the theory of Henglein¹²⁵ and Plieth.¹²⁶

A few years later, Compton and co-workers described theoretically the voltammetry for the oxidation of an array of Ag NPs of varied size attached to an electrode surface.¹¹⁴ They ignored the predicted size dependent shift in the standard reduction potential for the Ag/Ag⁺ couple and focused on shifts in the peak oxidation potential (E_p) in the voltammetry based on diffusional and kinetic effects. Experimentally, they showed no shift in E_p for Ag NPs of 25 to 100 nm in diameter drop-coated onto basal plane pyrolytic graphite under conditions of planar diffusion, fast electron transfer kinetics, and equal Ag loading, consistent with their theory.¹¹⁴ Our group soon after showed by voltammetry a clear negative shift in E_p for Ag NPs attached electrostatically to indium-tin-oxide coated glass (glass/ITO) electrodes through aminopropyltriethoxysilane (APTES).¹¹⁶ This was the first demonstration of a voltammetric shift in E_p with size due to a shift in the standard potential, which was approximately 110 mV negative going from about 50 nm to 8 nm in diameter, but the data did not fit

very well the $1/\text{radius}$ dependence predicted by Plieth.¹²⁶ Around the same time, Sieradzki and co-workers showed with ECSTM that <4 nm diameter Pt NPs dissolved at potentials well negative of the bulk value and by a different mechanism.^{109,132} They developed size-dependent potential-pH diagrams.¹³²

Ivanova and Zamborini later described an approximately 100 mV negative shift in E_p for Au NPs electrodeposited on glass/ITO that decreased in size from 250 to 8 nm in diameter, which is similar to the shift for Ag NPs in this size range and also due to a thermodynamic shift in the standard potential with size.¹³³ An additional 80 mV negative shift (total of 180 mV) in E_p occurred for 4 nm diameter citrate-coated Au NPs that were chemically-synthesized and attached electrostatically to glass/ITO/APTES and the entire range of sizes fit the expected $1/\text{radius}$ dependence fairly well.¹³³ Brainina *et al.*¹³⁴ and Compton and co-workers¹³⁵ refined Compton's original theory by including a size-dependent standard reduction potential for the M/M^{n+} redox couple¹³⁶ and compared experiment and theory for the oxidation of Au and Ag NPs drop-coated onto electrodes. In 2012, Masitas and Zamborini described an ~ 850 mV negative shift in the E_p of citrate-coated Au NPs electrostatically-attached to glass/ITO/APTES that are in the 1 to 2 nm diameter range, which is the largest shift in E_p observed to date and correlates well with the $1/\text{radius}$ dependence.¹³⁷ This also demonstrated the dramatic instability towards oxidation for very small metal NPs < 4 nm diameter.

Brainina and co-workers recently described the effect of polydispersity¹³⁸ and substrate¹³⁹ on the electrochemical oxidation of metal nanoparticles. In the substrate study, they described two opposite effects that can shift the E_p of

metal NPs from the bulk value.¹³⁹ The first is the negative shift in E_p with decreasing radius due to a thermodynamic shift in the standard potential, which is thought to have a $1/\text{radius}$ dependence as already described. The second is a positive shift in E_p that arises from interactions between the NP and the electrode surface. The magnitude of this positive shift depends on the size of the metal NP and the difference in work function between the metal NP and electrode. When the electrode work function is larger than the NP, it will serve to stabilize it, shifting the oxidation potential in a positive direction. Accordingly, Brainina and co-workers demonstrated a positive shift in the oxidation of 10 nm diameter Au NPs on Pt compared to glassy carbon, but no significant shift for 150 nm diameter Au NPs on the two substrates.¹³⁹ They conclude that the electrode has a larger influence on smaller Au NPs due to more points of interaction. This work is relevant to the early findings where small metal clusters showed a positive shift in oxidation potential^{112,127} instead of the predicted negative shift and is similar to the phenomenon of underpotential deposition.¹⁴⁰

More recently, Kuo and Hwang showed by voltammetry that the oxidation potential of Ag NPs depends on the shape and follows the order of cubes > spheres > decahedrons > triangular plates.¹⁴¹ Giovanni *et al.* studied the size-dependent oxidation of Ag NPs of 10 to 107 nm in diameter¹⁴² while Buttry and co-workers showed a negative shift in the oxidation potential of Pd NPs with decreasing size by voltammetry.¹⁴³ There has also been an enormous effort to study the electrochemical behavior of individual nanoparticles.¹⁴⁴ These studies involve electrocatalysis at the single particle level¹⁴⁵ and

electrochemical oxidation of individual nanoparticles,¹⁴⁵⁻¹⁴⁸ either attached to a small nanoelectrode^{145,146} or diffusing to microelectrodes in solution.^{147,148}

In many of the previous studies, including Compton and co-workers and Brainina and co-workers, the metal NPs were directly drop-cast deposited onto the electrode surface. There are two potential consequences of doing that. First, there is a direct interaction between the metal NPs and the electrode surface that can influence the oxidation behavior as recently described by Brainina and co-workers.¹³⁹ It is not clear if this is related to work function or some other interaction, including alloying. Second, the metal NPs are often aggregated on the electrode surface, which also likely alters the oxidation potential.¹³⁵ In our previous work we controllably attached Au NPs of 8-250 nm diameter on glass/ITO by direct electrodeposition¹³³ and Ag NPs of 8-50 nm diameter¹¹⁶ or Au NPs of 1-4 nm diameter¹³⁷ on glass/ITO by chemical synthesis (citrate-coated) and electrostatic attachment through an amine-terminated silane linker. In both cases the metal NPs were well-separated on the electrode, avoiding any possibility of aggregation, but it was not clear if the linker affects the oxidation potential or if the electrode material affects the oxidation potential when a linker is or is not present. In our previous work, the oxidation of Au NPs of varied size directly deposited on glass/ITO¹³³ seemed to fit the $1/\text{radius}$ dependence suggested by Plieth¹²⁶ better than Ag NPs attached to glass/ITO through a linker,¹¹⁶ suggesting that the linker may play a role in the oxidation behavior.

Here we report the oxidation of chemically synthesized, citrate-coated Au NPs from 4-150 nm in diameter attached to glass/ITO electrostatically through an

amine-terminated silane linker in comparison to Au NPs of similar size electrodeposited directly on glass/ITO in order to better understand the effect of the linker. In addition, we report on the oxidation of chemically-synthesized, citrate-coated 9 nm diameter Ag NPs electrostatically-attached to amine-terminated linkers on various electrodes, including glass/ITO, glassy carbon (GC), Au, and Pt in order to better understand the effect of the electrode under the linker. Our results show a significant effect of both electrode and linker that are clearly important in metal NP oxidation. These issues are crucial to understand as small metal NPs are often attached to solid supports directly or through linking chemistry for a variety of applications, such as sensing or catalysis. The mode of attachment is clearly important in their stability against oxidation.

4.2. Experimental

4.2.1. Attachment of Au and Ag Nanoparticles to Electrodes

The glass/ITO/APTES electrodes were soaked in as-prepared solutions of the different-sized Au NPs for 10 to 60 minutes, rinsed thoroughly with nanopure water, and dried under N₂ prior to electrochemical analysis. The soaking time was chosen to obtain a similar Au coverage in terms of total Au for the different Au NP sizes. Glass/ITO/APTES, GC/ethylenediamine (ED), Pt/2-aminoethanethiol (AET), and Au/AET electrodes were soaked in a solution of the 9 nm diameter Ag NPs (adjusted to a pH of 5.5 by adding 0.1 M HCl) for 5 to 180 minutes, rinsed thoroughly with nanopure water, and dried under N₂ prior to electrochemical analysis. The soaking time was chosen to obtain similar Ag NP coverage on the different electrodes. The drop-coat deposition

of 27 nm radius Au NPs directly onto Glass/ITO/APTES, Glass/ITO/MPTMS and Glass/ITO was performed by the addition of 150 μ L of the Au NP solution on the surface of the substrate followed by drying at room temperature.

4.2.2. Linear Sweep Voltammetry of the Electrodes Functionalized with Au and Ag Nanoparticles.

The electrochemical cell consisted of the metal NP functionalized working electrode, a Pt wire counter electrode, and an Ag/AgCl (3 M KCl) reference electrode. All electrochemical measurements were performed with a CH Instruments model 660A electrochemical analyzer in 0.1 M HClO₄ plus 0.01 M KBr (pH 1.65), 0.1 M HClO₄/KClO₄ plus 0.01 M KBr (pH 3.50), and 0.1 M KClO₄ plus 0.01 M KBr (pH 7.12) electrolyte solution for Au NP-coated electrodes and 0.1 M H₂SO₄ (pH 1.50), 0.1 M H₂SO₄/K₂SO₄ (pH 3.50), and 0.1 M K₂SO₄ (pH 5.38) electrolyte for the Ag NP-coated electrodes using linear sweep voltammetry (LSV) mode. The LSV scan was started at -0.2 V with the reference and counter electrodes in the electrolyte solution and the working electrode out of solution. The potential was scanned positive at 0.001 V/s and paused when it reached -0.1 V, at which time the working electrode was immersed into the electrolyte solution. The scan was then “unpaused” and the potential scanned up to 1.6 V at a continued rate of 0.001 V/s. The data for the electrodes with Ag NPs are plotted as current density versus potential due to the different electrode areas.

4.3. Results and Discussion

Electrochemical Synthesis and Chemical Synthesis of Au Nanoparticle. As described in the experimental section, we attached arrays of

Au NPs onto glass/ITO and glass/ITO/APTES electrodes by electrodeposition and by chemical synthesis and electrostatic attachment, respectively, as illustrated in Figure 4.1. These two strategies allowed us to study the effect of the linker and electrode on the Au NP oxidation potential while preventing Au NP aggregation.

The electrodeposition of Au NPs by chronocoulometry allowed the controlled synthesis of Au NPs of different sizes that were well-separated on the electrode surface. The average size of the Au NPs decreased with decreasing deposition potential as demonstrated previously by our group.¹³³ Figure 4.2. shows scanning electron microscopy (SEM) images of glass/ITO electrodes after electrodeposition of Au NPs at potentials of -0.6, -0.2, 0.2, 0.4, and 0.7 V in Frames A-E, respectively, where the total amount of deposited Au was constant by controlling the time of deposition. The average diameter of the Au NPs ranged from 6 nm in diameter at -0.6 V up to 232 nm at 0.7 V, similar to our previous work.¹³³ Additional images of electrochemically-synthesized Au NPs are shown at different magnifications in Figure 4.3.

Au NP Chemical Synthesis and Electrostatic Attachment. Figure 4.4. shows SEM images of glass/ITO/APTES electrodes after chemical synthesis and electrostatic attachment of 4, 38, 54, and 156 nm average diameter Au NPs. We synthesized the 4 nm diameter Au NPs by the method of Murphy and co-workers¹⁴⁹ and the larger sizes by the seeded growth method of Wang and co-workers.¹⁰⁵ The average radii are similar to the electrodeposited Au NPs. Additional images of chemically-synthesized Au NPs are shown with different magnifications in Figure 4.5.

Figure 4.1. Procedure for attachment of Au NPs to glass/ITO by electrodeposition (left) and by chemical synthesis followed by electrostatic attachment (right).

Figure 4.2. Scanning electron microscopy (SEM) images of glass/ITO electrodes after electrodeposition of Au NPs at (A) -0.6 V, (B) -0.2 V, (C) 0.2 V, (D) 0.4 V and (E) 0.7 V. The average radius for these Au NPs is (A) 3 nm, (B) 19 nm, (C) 24 nm, (D) 29 nm, and (E) 116 nm. The scale bar in part E applies to all images.

Figure 4.3. Scanning electron microscopy (SEM) images of glass/ITO electrodes coated with Au NPs of (A1-A2) 3 nm, (B1-B2) 19 nm, (C1-C2) 24 nm, (D1-D2) 29 nm, and (E1-E2) 116 nm radius.

Figure 4.4. Scanning electron microscopy (SEM) images of glass/ITO/APTES electrodes coated with Au NPs of (A) 2 nm, (B) 19 nm, (C) 27 nm, and (D) 78 nm radius. The scale bar in D applies to all images.

Figure 4.5. SEM images of glass/ITO/APTES electrodes coated with Au NPs of (A1-A2) 2 nm, (B1-B2) 19 nm, (C1-C2) 27 nm, and (D1-D2) 78 nm radius.

Figure 4.6. shows linear sweep voltammograms (LSVs) of electrodeposited Au NPs (Frame A) and chemically-synthesized/electrostatically-attached Au NPs (Frame B) obtained in 0.1 M HClO₄ plus 0.01 M KBr solutions at a scan rate of 0.001 V/s. The one main peak observed in the range of 0.7 V to 0.9 V is due to the one or three electron oxidation of the Au NPs by Br⁻ to form AuBr₂⁻ and AuBr₄⁻, respectively, as discussed previously.^{133,137} The anodic current at potentials above 1.0 V is due to the glass/ITO or glass/ITO/APTES electrode, and its magnitude is variable from electrode to electrode with no correlation to the amount or size of the Au NPs and it does not affect the Au oxidation potential. In the case of the electrodeposited Au NPs with radii from 3 to 116 nm, (Figure 4.6. A), we observed a negative shift in the peak oxidation potential (E_p) from about 900 mV to 700 mV with decreasing Au NP size, similar to that observed by our group previously.¹³³ In the case of chemically-synthesized and electrostatically attached Au NPs (Figure 4.6. B), E_p also shifts negative with decreasing size but over a much narrower range of potentials ranging from 726 to 700 mV over a similar range of Au NP sizes.

Table 4.1. shows the Au NP radius, method of preparation and attachment, and E_p values and Figure 4.7 shows a plot of the E_p value as a function of the Au NP radius for the two methods. While the E_p of the 3 nm radius electrodeposited and 2 nm radius chemically synthesized/electrostatically attached Au NPs are very similar (~700 mV), the E_p of the larger sizes are dramatically different for the two different types. For example, the 29 nm radius electrodeposited Au NPs have an E_p value of 881 mV, while the 27 nm diameter

Figure 4.6. LSVs in 0.1 M HClO₄ + 0.01 M KBr at a scan rate of 0.001 V/s of (A) glass/ITO electrodes coated with Au NPs of 3, 19, 24, 29, and 116 nm radius by electrodeposition and (B) glass/ITO/APTES electrodes coated with chemically synthesized Au NPs of 2, 19, 27, and 78 nm radius by electrostatic attachment.

Electrochemical synthesis of Au NPs		
Radius [nm]	Average Charge [Coulombs] $\times 10^{-4}$	Potential [mV]
3 (± 1)	1.22 (± 0.15)	693 (± 2)
19 (± 6)	1.07 (± 0.14)	788 (± 13)
24 (± 7)	1.02 (± 0.22)	851 (± 9)
29 (± 11)	1.13 (± 0.44)	881 (± 9)
116 (± 23)	1.45 (± 0.28)	882 (± 10)
Chemical synthesis of Au NPs		
2 (± 1)	1.21(± 0.11)	700 (± 5)
19 (± 2)	1.62 (± 0.52)	717 (± 5)
27 (± 4)	2.03 (± 0.15)	726 (± 1)
78 (± 7)	1.23 (± 0.04)	726 (± 1)

Table 4.1. Average charge and peak potential of Au NPs attached to glass/ITO by electrodeposition or chemical synthesis and electrostatic attachment

Figure 4.7. E_p of electrochemically synthesized vs chemically synthesized Au NPs as a function of radius. Error bars represent standard deviation in size and E_p .

chemically synthesized/electrostatically attached Au NPs have an E_p of 726 mV, a difference of 155 mV. There is clearly a large difference in stability against oxidation for these two types of Au NPs. The negative shift in E_p as size decreases for both preparation methods is due to the shift in the standard potential as the surface energy increases with decreasing size, which was described by Plieth theoretically¹²⁶ and our group^{116,133,137} and others^{109,132,134,136,143} experimentally. We believe the difference in the E_p values on glass/ITO and glass/ITO/APTES is due to a variation in the interfacial potential distribution caused by the positively charged NH_3^+ groups of APTES.

Smith and White previously described the variation in interfacial potential distribution that results in nonideal voltammetric behavior for charged electroactive surface confined species.¹⁵⁰ Electrostatic potentials can lead to large variations in the observed peak potentials, which we believe accounts for the large negative shift in the oxidation potential of Au NPs attached electrostatically to the APTES linker. Interestingly, we only observe this electrostatic effect for relatively large Au NPs.

The difference in E_p is as large as 155 mV for 27 nm radius NPs and larger, but only 7 mV for the 2-3 nm radius NPs, which is negligible considering the standard deviation of the E_p value. We are not sure at this time why the electrostatic effect only occurs for larger Au NPs.

To confirm this surface charge effect, we compared the behavior of Au NPs prepared the same way, since those discussed in Figures 4.6-4.7 were prepared differently (electrochemical vs. chemical) and attached in a different environment (direct vs. electrostatic). We therefore compared the oxidation of

27 nm diameter chemically synthesized Au NPs drop-cast deposited directly on glass/ITO to those drop-cast deposited on glass/ITO/APTES. In this way, both of the Au NPs were chemically synthesized and the same size, but just attached to surfaces with different charge. The glass/ITO should be mostly neutral with surface OH groups at low pH, and the glass/ITO/APTES should be highly positively charged due to the protonated amines (NH_3^+ groups). Figure 4.8 shows the LSVs for these two electrodes obtained using the same electrochemical setup as described in Figure 4.6. The results clearly show a more positive E_p value of about 120 mV for the oxidation of the chemically-synthesized Au NPs on glass/ITO as compared to their oxidation on glass/ITO/APTES. Although the difference in E_p is not exactly the same as that in Figures 4.6 and 4.7 (see Table 4.1), the general trend confirms that the method of synthesis (chemical vs. electrochemical) does not lead to the difference in E_p ; it is likely due to an electrostatic effect. This is not conclusive, since direct attachment to glass/ITO could lead to higher stability due to alloying or some other direct interaction.

In order to confirm conclusively that there is an influence of the interfacial potential distribution on the change in the E_p values and that this only occurs for larger Au NPs, we chemically synthesized 2 nm radius and 27 nm radius Au NPs and attached them electrostatically to glass/ITO/APTES electrodes. We then obtained LSVs of the 2 nm radius Au NPs in a solution of 10 mM KBr with 0.1 M HClO_4 (pH 1.65) as before and a solution of 10 mM KBr with 0.1 M KClO_4 (pH 7.12). Similarly, we obtained LSVs of the 27 nm radius Au NPs in KBr solutions of pH 1.65, pH 3.5, and pH 7.12 by varying the amounts of HClO_4 and

Figure 4.8. LSVs in 0.1 M HClO_4 + 0.01 M KBr at a scan rate of 0.001 V/s of glass/ITO and glass/ITO/APTES electrodes coated with and without chemically synthesized Au NPs of 27 nm radius by drop-cast deposition.

KClO₄ in the electrolyte. By varying the pH, we should also vary the level of protonation of the amine groups from highly positively-charged at low pH to mostly neutral at pH 7 (See Figure 4.9.). The LSVs in Figure 4.10. show that the E_p value of the 2 nm radius Au NPs is independent of the pH, or change in surface charge. The E_p value is 674 mV at pH 1.65 and 671 mV at pH 7.12. This is consistent with the data for small Au NPs attached electrochemically on glass/ITO and electrostatically on glass/ITO/APTES as discussed in Figures 4.6-4.7 and Table 4.1. On the contrary, the LSVs of the 27 nm radius Au NPs in Figure 4.10. shows that the E_p value shifts from 705 mV at pH 1.65 to 714 mV at pH 3.5 and more dramatically to 820 mV at pH 7.12. This 115 mV shift from pH 1.65 to pH 7.12 is very similar to the 120 mV shift observed for 27 nm radius Au NPs drop-cast deposited on glass/ITO and glass/ITO/APTES and oxidized at pH 1.65. These results conclusively show that the shift in E_p is due to an electrostatic effect on the interfacial potential distribution since both of these samples have the same nanoparticles and same APTES linker, but a different charge controlled by pH. This eliminates any possible alloying or other substrate effect from direct interaction with glass/ITO.

As another test of the electrostatic effect on Au NP oxidation, we obtained an LSV of 27 nm radius chemically synthesized Au NPs drop-cast deposited onto glass/ITO/MPTMS and compared it to those drop-cast deposited on glass/ITO and glass/ITO/APTES (Figure 4.11). MPTMS is a similar three carbon chain silane linker like APTES, but with a thiol group instead of an amine group on the end. This means it will not be charged at low pH. The E_p value in this case was 791 mV, which is very similar to the same Au NPs drop-cast

Figure 4.9. Glass/ITO/APTES/Au NPs electrodes at pH 1.65 and pH 7.12.

Figure 4.10. Linear sweep voltammograms (LSVs) from 0.5 to 1.0 V versus Ag/AgCl (3 M KCl) at a scan rate of 0.001 V/s. The blue plots correspond to Glass/ITO/APTES/Au NPs (4 nm) electrodes obtained in pH 1.65 10 mM KBr plus 0.1 M HClO₄ (—) and pH 7.2 10 mM KBr plus 0.1 M KClO₄ (---). The brown plots correspond to Glass/ITO/APTES/Au NPs (54 nm) electrodes obtained in pH 1.65 10 mM KBr plus 0.1 M HClO₄ (- · - · -), pH 3.50 10 mM KBr plus 0.1 M HClO₄ and KClO₄ (—) and pH 7.12 10 mM KBr plus 0.1 M KClO₄ (---).

Figure 4.11. LSVs obtained in 10 mM KBr and 0.1 M HClO₄ from 0.6 to 0.9 V versus Ag/AgCl (3 M KCl) at a scan rate of 0.001 V/s of 54 nm diameter Au NPs drop-cast deposited onto Glass/ITO/APTES (black plot), Glass/ITO (blue plot), and Glass/ITO/MPTMS (maroon plot) electrodes

deposited onto glass/ITO ($E_p = 782$ mV), with is another more neutral surface. Both of those E_p values are significantly more positive compared to the E_p on glass/ITO/APTES ($E_p = 715$ mV). The positive shift is not quite as dramatic as in Figure 4.8. in this experiment, but the general trend is the same, again showing that Au NPs oxidize at E_p values 70-120 mV higher on neutral versus positively charged surfaces. Figure 4.12. shows a bar chart summarizing the E_p values for the different size Au NPs as a function of electrode functionalization and pH.

When Au oxidizes in bromide solutions it forms negatively-charged AuBr_2^- and AuBr_4^- complexes. When Ag NPs oxidize, the result is positively-charged Ag^+ ions. We explored the same electrostatic effects on the E_p of Ag NPs to determine if a different metal and different charged oxidation product have any effect on the general trend.

We synthesized citrate-coated Ag NPs, attached them to glass/ITO/APTES as with Au NPs, and obtained LSVs at pH 1.5 and 5.38 for 4.5 nm radius Ag NPs and pH 1.5, 3.5, and 5.38 for 17 nm radius Ag NPs (Figure 4.13. and 4.14.). We used pure H_2SO_4 , pure K_2SO_4 , or mixtures of the two to control the pH with a total molarity of ~ 0.1 M. Similar to 2 nm radius Au NPs, the E_p value of 4.5 nm radius Ag NPs was independent of pH. Similar to 27 nm radius Au NPs, 17 nm radius Ag NPs showed a negative shift in E_p at lower pH due to the electrostatic effect (+ charge) on the interfacial potential distribution. The total shift was about 15 mV from pH 1.5 to pH 5.38. This is a smaller, but similar trend as that for 27 nm radius Au NPs. The smaller total shift is due to the lower pH value and smaller Ag NP size.

Figure 4.12. A bar chart showing the influence of pH on the oxidation potential (E_p) of Glass/ITO/APTES/AuNPs (4 nm) (A) and Glass/ITO/APTES/AuNPs (54 nm) (B). (C) shows a bar chart of the different oxidation potentials for 54 nm diameter drop-cast deposited Au NPs on the various charged (APTES) and more neutral (ITO and MPTMS) surfaces. For large NPs, the oxidation potential is significantly more positive on neutral surfaces. For small NPs, the oxidation potential is independent of surface charge.

Figure 4.13. LSVs from 0.15 to 0.4 V versus Ag/AgCl (3 M KCl) at scan rate of 0.001 V/s. The blue plots correspond to Glass/ITO/APTES/Ag NPs (9 nm) electrodes obtained in pH 1.50 0.1 M H_2SO_4 (—) and pH 5.38 0.1 M K_2SO_4 (---). The brown plots correspond to Glass/ITO/APTES/Ag NPs (34 nm) electrodes obtained in pH 1.50 0.1 M H_2SO_4 (—), pH 3.50 0.1 M H_2SO_4 and K_2SO_4 (— · —) and pH 5.38 0.1 M K_2SO_4 (---).

Figure 4.14. Bar chart and line plot showing the peak oxidation potential (E_p) of 9 nm and 34 nm average diameter Ag NPs attached to Glass/ITO/APTES as a function of the pH of the stripping solution. E_p is referenced to an Ag/AgCl (3 M KCl) reference electrode.

Overall, the large negative shift in E_p values at low pH for Au and Ag NPs attached electrostatically to glass/ITO/APTES electrodes relative to glass/ITO and glass/ITO/MPTMS at low pH and glass/ITO/APTES at high pH confirms that the protonated amine groups of APTES alter the interfacial potential distribution, leading to a negative shift in E_p for metal NP oxidation. This effect is only present for NPs larger than about 10 nm in diameter. The role of metal NP size is not fully understood at this time.

In order to evaluate the influence of the underlying electrode material on the oxidation of metal NPs when a linker is also present, we synthesized 9 nm average diameter citrate-stabilized Ag NPs and electrostatically attached them to similar amine-terminated linkers assembled on glass/ITO, glassy carbon (GC), Au, and Pt electrodes, as shown in Figure 4.15. The linkers were APTES, ethylene diamine (ED), 2-aminoethanethiol (AET), and 2-aminoethanethiol (AET) for the 4 electrode materials, respectively.

These electrodes are referred to as glass/ITO/APTES, GC/ED, Au/AET, and Pt/AET, accordingly. Figure 4.16. shows an SEM image of the Ag NPs attached to glass/ITO, where size analysis showed them to be 9 ± 1 nm in diameter ($N = 58$ Ag NPs).

Figure 4.17 shows LSVs of the different electrodes obtained in 0.1 M H_2SO_4 solution. The one main peak corresponds to the one electron oxidation of Ag^0 in the Ag NPs to the Ag^+ ion, which then dissolves away from the electrode surface. It is clear that the E_p value depends on the electrode material, following the order of $\text{Au} \sim \text{Pt} > \text{GC} > \text{Glass/ITO}$. The average of Au is larger than Pt, but the standard deviation in the average does not allow us to

Figure 4.15. Attachment of Ag NPs to the four different electrode materials through amine-terminated linkers.

Figure 4.16. Scanning Electron Microscopy (SEM) image of 9 ± 1 nm diameter Ag NPs attached to glass/ITO/APTES.

Figure 4.17. LSVs in 0.1 M H_2SO_4 at a scan rate of 0.001 V/s of glass/ITO/APTES, GC/ED, Pt/AET, and Au/AET electrodes coated with 9 nm average diameter Ag NPs. The oxidation peak potential (E_p) follows the order of Au/AET > Pt/AET > GC/ED > Glass/ITO/APTES.

distinguish between them with certainty. Table 4.2 shows the data for the oxidation of Ag NPs on the different electrodes, including the E_p value, Ag coverage, and peak current.

According to the work of Brainina, if the work function of the electrode is more positive than the work function of the oxidizing metal NP, then it should provide added stability and shift the E_p to more positive values, similar to the process of underpotential deposition (UPD) of one metal on another metal.^{139,140} The work function of Ag is 4.3-4.8,¹⁵¹ depending on the literature reference, and does not strongly deviate from the bulk value for a 9 nm diameter Ag NP.¹⁵² The work function of the electrodes have different values in the literature, but follow the general order of Pt (5.4-5.6)¹⁵³ > Au (4.8-5.2)^{151,154,155} > GC (4.6-4.9)¹⁵⁵ > glass/ITO (4.2-4.8).¹⁵³ It is also important to note that the linker affects the work function of the electrodes. Electron donating groups lower the work function while electron withdrawing groups increase the work function of the electrodes.¹⁵⁶ Accordingly, APTES has been shown to lower the work function of glass/ITO due to the amine group.¹⁵⁷ AET would similarly lower the work function of Au and Pt because of the amine group, but also due to the thiol-metal bond.^{154,156,158} ED would serve to lower the work function of GC due to the terminal amine group. The change in work function of the electrode is also sensitive to the coverage of the linker molecule and the influence of the water and ions on the different electrodes. It is therefore difficult to conclusively predict the net result of these different variables on the overall electrode work function.

Electrode	Peak Oxidation Potential, E_p (mV)	Ave. Charge ($\times 10^{-4}$ C)	Ave. Peak Current ($\times 10^{-5}$ A)
ITO/APTES	339 (± 1)	8.123	1.998
GC/ED	351 (± 2)	8.605	2.640
Pt/AET	373 (± 12)	8.839	2.070
Au/AET	384 (± 7)	8.557	1.863

Table 4.2. E_p , charge, and peak current for the oxidation of 9 nm diameter Ag NPs attached to the various electrodes through short amine-terminated linkers.

Despite the different possible effects on work function, we observe E_p values that generally follow the work function order of the electrodes obtained in vacuum. The only surprise is that oxidation of Ag on Au is equal to or larger than oxidation on Pt, even though Pt has a larger work function. Consistent with this, Kolb and coworkers reported a larger difference in work function between Pt and Ag compared to Au and Ag, but a larger difference between the oxidation of Ag UPD and bulk Ag on Au compared to Pt.¹⁴⁰ There may be some other stabilizing factor for Ag on Au compared to Ag on Pt other than work function, but it is difficult to determine in this work because of the uncertainty in the E_p values. The most important conclusion is that there is an electrode effect on the Ag NP oxidation even in the presence of very similar linkers. The Ag NP can communicate through the linker and sense the electrode properties. This is consistent with the work of Fermin and co-workers, who showed that multilayers of Ag NPs assembled on an Au surface electrostatically through polyelectrolytes equilibrate with the Au and exhibit an increased work function around 5.2 to 5.3 eV.¹⁵¹ This shows strong communication between the Ag NPs and Au surface, consistent with our results.

It is important to point out that Brainina and co-workers previously found that the electrode material in contact with Au NPs can provide stabilization against electrooxidation, which they believe is related to electrode work function.¹³⁹ Another possibility for stabilization in their work is the formation of an interalloy between the metal NPs and electrode material.^{128,139} A third possibility is a different level of metal NP aggregation on the various electrodes.¹³⁵ In our experiment, we observed an electrode effect with a linker

molecule, which rules out the possibility of interalloy formation, showing that the electrode work function or some other property can still play a role in metal NP oxidation even when the NP is not in direct contact. Another advantage of our approach is that the metal NPs are well dispersed and separated on the electrode surface in a 2D arrangement, avoiding NP aggregation or 3D assemblies that could modify the final E_p value for oxidation. Finally, it is important to note that the results in Figure 4.17. cannot be explained by differences in electrostatic positive charge on the different amine-terminated monolayers since the E_p of the small 9 nm diameter Ag NPs is independent of electrostatic effects (Figure 4.13. and 4.14.).

4.4. Conclusions

In summary, this study shows two very different and important electrode effects that can significantly alter the oxidation potential of metal NPs. First, the presence of the positively-charged APTES linker on glass/ITO/APTES electrodes at low pH (1-3) greatly decreased the peak oxidation potential for Au (as much as 155 mV) and Ag NPs that were greater than about 10 nm in diameter relative to the more neutral glass/ITO, glass/ITO/MPTMS, and glass/ITO/APTES (pH 7) electrodes. For smaller Au NPs of 4-6 nm in diameter and Ag NPs of 9 nm diameter, the E_p value was independent of surface charge. The increased stability for Au NPs directly on glass/ITO occurred similarly for both electrodeposited Au NPs and chemically-synthesized, drop-cast deposited Au NPs, confirming that the method of Au NP synthesis does not play a role in the E_p value; electrostatic effects dominate. The second important finding from this work is that the underlying electrode material has an effect on the oxidation

potential of metal NPs even when there is a linker present. For Ag NPs of 9 nm average diameter attached to various electrodes electrostatically through similar amine-terminated linkers, the oxidation order follows as Au~Pt>GC>glass/ITO. This follows the order of work function, except that the Au and Pt are reversed. Electrostatic effects were ruled out in this case since the E_p of 9 nm diameter Ag NPs is independent of surface charge. Inter Alloying and aggregation were also ruled out due to the presence of the linker and well-dispersed, separated NPs on the surface.

The results of this work are extremely important to the practical use of solid-supported metal NPs in catalysis and sensing as well as solution-based electrochemical studies of impacting nanoparticles and many other potential applications of metal nanostructures. There is a significant effect of metal NP size and method of attachment to solid supports on the stability of metal NPs against oxidation, which is important to understand for practical use. On the basis of our results, the direct attachment to substrates without charged linkers generally leads to more stable metal NPs against oxidation for sizes above ~10 nm in diameter. For those below 10 nm, the oxidation potential is dominated by their particular size, while the electrode material also plays a small role, even with an organic linker present.

5.1. Introduction

Here we describe the oxidation in Br^- solution of 1.5 nm average diameter citrate-coated Au nanoparticles (NPs) attached to indium tin oxide-coated glass electrodes. Borohydride reduction of AuCl_4^- in the presence of potassium hydroxide and trisodium citrate for 1 min led to Au NPs 1.5 nm in average diameter. The oxidation potential of citrate-coated Au NPs is generally range -85 to 295 mV versus an Ag/AgCl (3 M KCl) reference electrode. This is 555 to 935 mV negative of the bulk (> 50 nm diameter) Au oxidation peak. The large negative shift in potential agrees fairly well with predictions of Plieth for NPs in the 1-2 nm diameter range, which are based on thermodynamics considerations governed by different surface area with different sized particles.

Ultra-sharp stripping peaks appearing during the stripping of 1.5 nm average diameter Au NPs for reasons that are not perfectly clear.

Metal nanoparticles (NPs) display a fascinating range of chemical and physical properties not observed at the bulk level. Catalysis, plasmonics, and others properties are often only observed for nanoscale sizes and they are size dependent. Great effort has been placed during the last decade to control the

size and shape of metal nanoparticles during synthesis and understand their size and shape dependent properties.²⁴⁻²⁶ Now it is possible to control size from hundreds of nanometers to only a few nanometers.^{34,35}

Our group have been studying the effect of metal NP size on the standard potential, E^0 .³⁶⁻³⁸ We were the first to show a negative shift of ~ 850 mV for citrate-coated Au NPs < 4 nm and were also the first to demonstrate the unusual change in reactivity for 1-2 nm diameter citrate-coated Au NPs oxidizing in Cl⁻ and Br⁻ solutions.⁵¹ It is well-known that in many cases the reactivity of metal NPs is directly correlated to the size. Henglein found that small metal particles possess unusual catalytic properties in radiolysis, which was explained qualitatively by a shift in the redox potential.⁵⁵ On the basis of the increase in surface area, Plieth predicted a 1/r dependent negative shift in the oxidation potential relative to the bulk metal for metal NPs with radius r.⁵⁴ Sieradzki and co-workers reported a more negative oxidation potential to < 4 nm diameter Pt NPs well below the bulk value.¹¹⁰ Other groups have also observed size-dependent metal NP oxidation. For example, Giovanni *et al.* studied the size-dependent oxidation of Ag NPs of 10-107 nm in diameter,¹⁵⁹ while Buttry and co-workers showed a negative shift in the oxidation potential of Pd NPs with decreasing size by voltammetry.¹⁶⁰ Our group was the first to quantify the negative shift in the oxidation potential of Ag (8-50 nm diameter)³⁶ and Au (4 to 250 nm diameter)³⁷ as a function of size directly by voltammetry and compared the results to the theory develop by Plieth.⁵⁴ In 2012, Masitas and Zamborini described and approximately 850 mV negative shift in the peak oxidation potential (E_p) of citrate-coated Au NPs electrostatically attached to

glass/ITO/APTES that were in the 1-2 nm diameter range, which was the largest shift observed to date and correlated well with the 1/radius dependence.⁵¹ We also recently described the effect of electrode surface charge and the electrode material on the oxidation of surface-attached Au and Ag NPs.³⁸ The NP diameter is found to be the most important factor, but the surface charge can also lead to a significant shift for larger NPs. The electrode material has a relatively smaller effect.

In this study we demonstrate for the first time the oxidation in Br⁻ of 1.5 nm average diameter Au nanoparticles (NPs) attached to indium tin oxide-coated glass electrodes. TEM size analysis and Linear Sweep Voltammetry show a good correlation between *E_p* values from the electrooxidation of Au NPs and their size analysis from TEM images. This demonstrates the use of Linear Sweep Voltammetry for determining NP size, going from sub 2 nm to bulk size (~ 50 nm). The correlation of *E_p* with NP size, especially those below 4 nm, mimics a mass spectra analysis in some ways. Instead *m/z* values, we obtain *E_p* values that correlate with NP size and charge that relates to the total number of particles.

We synthesized citrate-coated Au NPs 1.5 nm in average diameter. The synthesis of these NPs results from of 3 factors. The pH, the time and the concentration of AuCl₄⁻ in the solution.

Previously, Henglein and Giersig showed that the reduction of PtCl₄²⁻ occurs more slowly in the presence of citrate and NaOH.¹²⁷ It is well-known that pH plays a role in the synthesis of citrate-coated metal NPs. Peng and co-workers described the influence of pH on the size/shape distribution and the

size/shape evolution of Au NPs. They found that when pH increased, the reduction of Au(III) ions decreased substantially.²⁶ This slows down the reaction. Similarly Bruylants and co-workers reported the key role of pH on the reaction rate and on the size and size distribution of Au NPs. In order to get Au NPs with a narrow size distribution, citrate should be polydeprotonated, but Au(III) should not be polyhydroxylated.¹⁶¹ For our synthetic method, higher pH helped slow down the reduction of AuCl_4^- , by forming hydroxides, and it fully deprotonated, providing greater NP stabilization. Diluted Au(III) precursor also helped decrease the final NP size. In this study also we describe the enhancement of CO_2 reduction on 1.5 nm diameter citrate-coated Au nanoparticles (NPs).

5.2. Experimental

Chemical synthesis of citrate coated Au NPs of 1.5 nm average diameter is described in chapter 2.

5.3. Results and Discussion

We synthesized 1.5 nm, 2.3 nm and 4.2 nm average diameter citrate -protected Au NPs in solution, chemically attached them to functionalized glass/indium tin oxide (ITO) electrodes, and studied the electrochemical oxidation by linear sweep voltammetry (LSV) in a similar manner as described in our previous studies.^{37,38,51} Figure 5.1 shows the UV-visible spectra for the first 30 min of the reaction. This figure shows the formation of a plasmon band and the plasmon band changed in wavelength from 483 nm to 512 nm as a result of the change in the reaction time from 30 sec to 30 min.

Figure 5.1. UV-visible spectra of citrate-coated Au NPs reduced for 0.5 to 30 min as indicated. The more intense plasmon band at 512 nm is indicative of larger Au NPs after 30 min of reduction compared to the sample reduced at 1.0 min, which is consistent with smaller average diameter determined by TEM (Figure 5.3.C) and the more negative oxidation potential in the linear sweep voltammograms (Figure 5.2.A black solid plot).

Figure 5.2. shows a comparison between three LSVs. The black solid plot is for the sample containing 1.5 nm average diameter Au NPs (1 min reaction time and higher pH), the blue dashed plot is for the 2.3 nm average diameter Au NPs (15 min reaction time), and the red solid plot for the sample containing 4.2 nm average diameter Au NPs. The average size is based on transmission electron microscopy (TEM) image. (Figure 5.3) The LSV for 1.5 nm diameter (black solid plot) showed a peak near 664 mV along with 15 peaks in the 295 to -85 mV range, which is between 555 to 935 mV negative of the bulk Au oxidation peak. Au can be oxidized in the presence of halides by the following reactions:¹¹⁸

The three-electron (3e) oxidation is thermodynamically most favorable, but our group previously reported an average oxidation of 1.5 electrons, while others reported 1.9 electrons.¹¹⁸ This could be due to a combination of the direct 3e and one electron (1e) oxidation or the third chemical step shown above. We previously described the oxidation of < 4 nm diameter Au nanoparticle (NPs) attached to indium tin oxide-coated glass electrodes in Br⁻ solution.⁵¹ The Au oxidation potential of citrate-coated Au NPs is in the 300-500 mV range for 2.3 nm average diameter.

Figure 5.2. (A) LSVs for Au NPs with diameter 1.5 nm (black solid plot), 2.3 nm (blue dashed plot), and 4.2 nm (red solid plot) in 0.1 M HClO_4 + 0.01 M KBr from -0.2 to 1.0 V. (B) Expanded view of the region from -0.1 to 0.31 V

Figure 5.3. TEM and histogram for Au NPs with diameter (A) 4.2 nm, (B) 2.3 nm, and (C) 1.5 nm

Figure 5.2. B shows an expanded view of the LSV from -100 to 310 mV. The ultra-sharp peaks observed belong to the oxidation of Au NPs with diameter ranging from < 1.0 nm to 3.0 nm. No peaks exist in this low potential range for the 4.2 nm and 2.3 nm diameter samples due to their larger size sample population. On the basis of these three plots and the TEM size analysis, we attribute the peak at 664 mV to the oxidation of Au NPs from 3- 5 in diameter, which agrees with the sample population of the 4.2 nm diameter Au NPs and Plieth equation.

The peaks from 293 to -86 mV correspond to the oxidation of 0.5 nm to 2.0 nm diameter Au NPs. Figure 5.3. shows the TEM and histogram size analysis for these three different samples, Figure 5.3.A, 5.3.B and 5.3.C belong to 4.2 nm, 2.3 and 1.5 nm NPs respectively. The comparison between TEM data and electrochemical data in this study show first a clear evidence of the evolution on size of Au NPs at different times. Second the size evolution is tracked by linear sweep voltammetry (LSV). The three plots on figure 5.2.A show the response to the oxidation of Au NPs from sizes that go from 0.9 nm to 4.2 nm diameter. For the 1.5 nm average diameter LSV black solid plot, we observed ultra-sharp peak at negative shifted of the Au bulk value of 850 mV. The formation of these sharp-peaks is the result of the stripping of singular narrow NPs sizes in the range of 0.9 to 1.4 nm. These results are in good agreement with the Plieth's theory. Plieth predicted a $1/r$ -dependent negative shift in the oxidation potential relative to the bulk metal for metal NPs with radius r .⁵⁴ The Plieth equation is as follow:

$$E_{\text{particle}} = \left(-\frac{2\gamma V_m}{ZF} \right) \left(\frac{2}{d} \right) + E_{\text{bulk}} \quad (5.4)$$

Where E_{bulk} is the oxidation potential of the bulk metal (taken as 850 mV on the basis of the oxidation of ≈ 50 nm diameter Au NPs under our conditions), γ is the surface tension (1880 erg cm^{-2}),⁵⁴ V_m is the molar volume ($10.21 \text{ cm}^3 \text{ mol}^{-1}$),⁵⁴ Z is $1 e^-$, F is Faraday's constant, and d is the NP diameter. It should be noted that surface stress, instead of surface tension, is more appropriate for the calculation, so the use of γ could be a potential source of error.^{110,162} In Figure 5.2. the low-potential region (-86 to 293 mV), corresponding to 1.4 to 0.9 nm diameter Au NPs according to eq 5.4 Taking the Plieth's equation, a bulk value of 850 mV for the oxidation of Au, and the LSVs for the electrochemical oxidation of Au NPs in Br^- solution.

We made histograms base on the size obtained from E_p value applied on Plieth's equation and counts base on to the total charge for each peak from the LSVs in Figure 5.2. Figure 5.4. shows simulated histograms for 4.2 nm, 2.3 nm and 1.5 nm average diameter. These histogram are in decent agreement with the data obtained from the TEM size analysis in Figure 5.3. The sharp shape and separation of each peak in the LSVs that belong to the 1.5 nm diameter sample is in agreement with the change of E_p value when the NPs decrease in size. The higher potential region between (650 to 700 mV), corresponding to 3-4 nm diameter Au NPs. The set of histograms shown in Figure 5.4. are made taking in consideration a $Z = 1$. The comparison between the simulated histograms in Figure 5.4. and the actual histograms in Figure 5.3. shows the agreement between made a size analysis by TEM image and made a size

Figure 5.4. Histogram made base on the E_p and total charge for each peak from the LSV for Au NPs with (A) 4.2 nm, (B) 2.3 nm and (C) 1.5 nm average diameter.

analysis taking in consideration E_p values and total charge from the electrooxidation of Au NPs with Br⁻ solution. It is important to emphasize that the Plieth's equation describe the E_p shift for NPs with sizes above 1 nm.

Figure 5.5. shows Linear sweep voltammograms for the synthesis of citrate-coated Au NPs (High pH) obtained in 10 mM KBr plus 0.1 M HClO₄ from 2 to 1.2 V versus Ag/AgCl (3 M KCl) at a scan rate of 0.01 V/s. A, B, C, and D correspond to 4 different samples. The intensity of the Au peaks varied due to different coverages of Au NPs on the electrode, but the peak potentials were highly reproducible. Additionally Figure 5.6. shows the comparison of two LSVs for samples synthesized at higher pH (blue solid plot) and a lower pH (red dashed plot). These two experiments show the difference between the synthesis with KOH and without KOH. We attached the citrate coated Au NPs synthesized without KOH onto the electrode and performed the stripping oxidation from -0.2 to 1.2 V, The scan shows a noticeable oxidation peak at 714 mV, which we attribute to the oxidation of 4.0 nm diameter NPs. Overall, the synthesis without KOH had 68% with peaks below 0.6 V and synthesis with KOH had 88% with peaks below 0.6 V. The total charge for no KOH was 7.89×10^{-6} C and with KOH was 7.54×10^{-5} C, showing higher amount of small Au NPs with KOH.

Previously we reported the synthesis of <4 nm citrate coted Au NPs. We found that a short reaction time allowed the capture of small NP sizes. Applying the same concept in the present study, we attached citrate-coated Au NP s after a 1 min reaction time. LSV and UV-visible spectroscopy allowed us to track the change of citrate-coated Au NPs size with reaction time. The presence of sharp

Figure 5.5. Linear sweep voltammograms for the synthesis of citrate-coated Au NPs (High pH) obtained in 10 mM KBr plus 0.1 M HClO₄ from -0.2 to 1.2 V versus Ag/AgCl (3 M KCl) at a scan rate of 0.01 V/s. A, B,C, and D correspond to 4 different samples. All the plots were obtained after 1 minute reaction time and 1 minute of glass-ITO/APTES soaking time. The intensity of the Au peaks varied due to different coverages of Au NPs on the electrode, but observation of sharp peaks from -0.1 to 0.4 V was highly reproducible. A1, B1, C1 and D1 correspond to the expanded view of the region from -0.2 to 0.4 V, marked by the dotted box in A,B,C, and D. Violet and green dotted lines indicated the location of the main stripping peaks in these 4 samples.

Figure 5.6. Linear sweep voltammograms for the synthesis of citrate-coated Au NPs with KOH (blue solid plot), and without KOH (red dotted plot) obtained in 10 mM KBr plus 0.1 M HClO₄ from -0.2 to 1.2 V versus Ag/AgCl (3 M KCl) at a scan rate of 0.01 V/s.

peaks at low E_p for 1 min of reaction time and the absence of a plasmon band during the first minutes of the reaction are in direct correlation with our findings. The short reaction time allowed the quenching of small NP sizes. As a result of our findings in the synthesis of citrate-coated Au NPs in the range of few nanometers. We decided to test the reactivity of this citrate-coated Au NPs in the electrocatalytic reduction of CO_2 . Kauffman and co-workers demonstrated that Au_{25} (0.9 nm average diameter) enhanced electrocatalytic activity for the reduction of CO_2 .¹⁶³ They shown that the electrochemical reduction of CO_2 in aqueous 0.1 M KHCO_3 under unstirred condition display a reduction peak at -0.7 V vs RHE. We synthesized 1.5 nm diameter citrated-coated Au NPs in solution, chemically attached them to functionalized glass/indium tin oxide (ITO) electrodes, and studied the reduction of CO_2 by cyclic voltammetry (CV).

We found that our 1.5 nm average diameter citrate-coated Au NPs display a reduction peak at -0.35 V vs Ag/AgCl (3 M KCl) or -0.54 V vs RHE (by calculation). Figure 5.7. shows the comparison of the CVs for the CO_2 reduction under unstirred condition for citrate coated Au NPs 1.5 nm, 4 nm and Au bulk. These CVs demonstrate that just only the 1.5 nm Au NPs sample is electrocatalytic active for the reduction of CO_2 at potentials close to -0.35 V vs Ag/AgCl (3M KCl). These set of result indicated that our Au nanoparticles of 1.5 nm are active for CO_2 reduction in similar way as the Au_{25} cluster (0.9 nm diameter) without the requirement of a previous activation step that imply the removal of the cluster's ligands.

Figure 5.7. CVs for the electrochemical reduction of CO₂ in 0.1 M KHCO₃ at scan rate of 0.01 V/s in a electrochemical cell where the RE is Ag/AgCl (3 M KCl), the CE is platinum wire and the WE is as follow, 1.5 nm average diameter Au NPs glass-ITO/APTES (blue solid plot), 4.0 nm Au NPs glass-ITO/APTES (red dashed plot) and Au bulk (green dashed plot).

5.4. Conclusions

In summary, we have reported for the first time the electrooxidation of Au NPs in the sub 2 nm size regime. We validate LSV as a powerful technique for size analysis of bare metal NPs in the range of 1 to 4 nm (and up to 50 nm), and for the first time ultra sharp peaks for the electrooxidation of Au NPs with average diameter 0.5 to 1.5 nm. We think that more studies must be done in order to correlate magic number clusters with the location of their E_p values. Additionally we found that CO₂ reduction is enhancement by Au NPs below 4 nm.

mV full width at half height) stripping peaks in the LSV, which we attribute to a low coverage of small, uniformly sized Au NPs, whose peak oxidation potentials shifts negative dramatically as the particle dissolves and becomes smaller.

The assembly of metallic or semiconductor nanostructures on solid surfaces is of tremendous interest in many areas of science and technology due to the important applications of nanostructures in sensing, optical, electronic, photovoltaic, biomedical, and catalytic devices. Many assembly methods exist, including drop-cast deposition,³⁸ chemical assembly,⁵¹ and electrophoretic deposition.^{38,70-72}

In the case of negatively-charged, citrate-coated Au nanoparticles (NPs), as described here, most methods employ chemical attachment to thiol (SH)-functionalized surfaces³⁸ or electrostatic attachment to positively charged amines ($-\text{NH}_3^+$).³⁸ In this type of approach the particle transport is governed solely by Brownian motion, resulting in completely random particle-particle and particle-substrate collisions. Also, the size and shape of deposited nanostructures is not selective if the solution contains particles with dispersity.

Electrophoretic deposition (EPD) is an alternative assembly method previously employed to deposit metallic,^{3,4} semiconducting,¹ and insulating² nanoparticles on conductive substrates. Several studies involve EPD of Au NPs. For example, Giersig and Mulvaney prepared highly ordered 2D films of Au NPs from aqueous and organic media onto transmission electron microscopy (TEM) grids by EPD.^{4,73} Hupp *et al.* prepared patterned thin films of colloidal gold by EPD.³ They described the application of an electric field to drive the movement of the colloidal Au NPs from the solution to the surface of

the substrate.³ Poelsema *et al.* studied the potential dependence on the EPD of nanocolloidal Au particles by spectroscopic ellipsometry. At low voltage, the deposition of 8.6 nm octadecylamine coated Au NPs did not occur, while at higher voltage, a strong increase in the deposition rate occurred.⁷⁵ David *et al.* studied EPD of colloidal Au NPs on a silicon wafer by scanning electron microscopy. They found a dense and uniform distribution of NPs with no aggregation over the surface.⁷⁶

Interestingly, none of the previous reports closely examined the dependence of Au NP size on EPD. Since the electrophoretic mobility of ions or particles increases with increasing charge/size ratio, we hypothesized that EPD would be different for different-sized Au NPs. Here we explored the effect of Au NP size on the EPD process for diameters ranging from about 1 nm to 33 nm. We observed that the voltage applied controls the size of the Au NPs that are deposited, acting as a low pass Au NP size deposition filter. An important aspect of this work was that we directly analyzed the size and coverage of the Au NPs deposited by EPD by monitoring the peak potential of oxidation (E_p) and the peak area in a linear sweep voltammogram (LSV) of the electrode/Au NP assembly. Our previous work showed that the E_p for Au oxidation in bromide solutions strongly depends on the size in the range of diameters from 1 nm to 50 nm, which is critically important to the fast analysis of the EPD process in this work by LSV.⁵¹ We also determined that H_2O_2 in solution greatly increased the coverage of Au NPs attached during EPD. This led us to conduct 3-electrode electrochemical deposition of Au NPs by precipitation where oxidation of H_2O_2 lowers the pH near the electrode and promotes Au NP attachment. We

observed a similar size dependence and determined both deposition mechanism to be electrochemical instead of electrophoresis.

6.2. Experimental

We synthesized 33, 17, 4 and <4 nm diameter citrate-coated Au NPs in solution, added H₂O₂ to each solution, and performed EPD by applying a positive voltage to a glass/ITO electrode relative to a Au foil second electrode. We measured the size and coverage of the Au NPs by electrochemical oxidation using linear sweep voltammetry (LSV) in a similar manner as described in our previous studies.^{36-38,51}

6.2.1. Electrodeposited solutions for 4, 17, and 33 nm diameter citrate-coated Au NPs and the mixture of 4 and 33 nm Au NPs

The composition of the solution for the 4 nm Au NPs was 2 mL of Au NPs, 3.6 mL of H₂O₂ and 9.4 mL of H₂O. The composition of the solution for the 17 nm Au NPs was 4.69 mL of Au NPs, 3.60 mL of H₂O₂ and 6.71 mL of H₂O. The composition of the solution for the 33 nm Au NPs was 0.85 mL of Au NPs, 3.6 mL of H₂O₂ and 10.55 mL of H₂O. The mixture for separation was 0.4 mL of 4 nm Au NPs, 0.34 mL of 33 nm, 3.6 mL of H₂O₂ and 10.66 mL of H₂O.

6.3. Results and Discussion

Figure 6.1. shows LSVs as a function of EPD for citrate-coated 4 nm Au NPs. When performing EPD at 2.5, 2.0, and 1.5 V for 90 s, we observed deposition of 4 nm Au NPs on the surface of bare glass/ITO. In contrast at 1.0, 0.5, and 0.0 V for 90 s, we observed little or no deposition of 4 nm Au NPs.

Figure 6.2. shows the coverage as a function of potential for the electrophoretic deposition of citrate-coated 4 nm, 17 nm and 33 nm diameter

Figure 6.1. LSVs of 4 nm diameter citrate-coated Au NP after electrophoretic deposition. LSVs were performed in 0.1 M HClO₄ + 0.01 M KBr from -0.1 to 1.0 V, at a scan rate 0.001 V/s. The red dashed line, blue dashed line and brown dashed line show the stripping peaks for 4 nm diameter Au NPs electrophoretically deposited at 2.5 V, 2.0 V, and 1.5 V for 90 secs, respectively. The light purple line, light green line and dark blue line show LSV for 4 nm diameter Au NPs electrophoretically deposited at 1.0 V, 0.5 V and 0.0 V for 90 secs, respectively.

Figure 6.2. Coverage vs EPD potential Profile of 4 nm, 17 nm and 33 nm diameter Au NPs. The X-axis shows the potential of deposition. The Y-axis shows the total charge when stripping the Au NPs from the surface of the glass/ITO electrode in 0.1 M HClO_4 + 0.01 M KBr from -0.1 to 1.0 V at a scan rate of 0.001 V/s. Red squares represent a single stripping replicate of the 4 nm diameter Au NPs, yellow squares represent the average of two single stripping replicates. Blue circles represent a single stripping replicate of the 17 nm diameter Au NPs, brown circles represent the average of two single stripping replicates. Dark green triangles represent a single stripping replicate of the 33 nm diameter Au NPs, black triangles represent the average of two single stripping replicates.

Au NPs. When performing EPD at 2.5 V for 90 s, we observed deposition of all three different sizes. At 1.5 V, we observed the deposition of mostly 4 nm Au NPs; 17 nm and 33 nm only show very low deposition. At a deposition potential of 1.0 V, 0.5 V, and 0.0 V, we observe little to no deposition of Au NPs with diameters >4 nm NPs. Below 1.0 V, none of the Au NP sizes deposit appreciably by EPD.

Figure 6.3 shows LSVs of glass/ITO after EPD at different potentials of a mixture of 4 nm and 33 nm diameter citrate-coated Au NPs containing 6.47×10^{-6} M and 1.30×10^{-5} M Au respectively. Since the total Au for 33 nm is double the 4 nm, the concentration in terms of particles/mL is about 250 times greater for the smaller 4 nm diameter Au NPs. We decided to keep the total Au double for 33 nm in comparison to 4 nm since the LSV stripping analysis measures the total Au for each size. After EPD at 2.5 V for 90 s, we observed stripping peaks for both the 33 nm and 4 nm Au NPs as labeled in Figure 6.3, indicating they both deposited onto glass/ITO during EPD. The coverage is higher for the 33 nm Au NPs, indicating a larger amount of Au atoms compared to that for 4 nm NPs. At 2.0 V, we also observed stripping peaks for both 33 and 4 nm diameter Au NPs, but the coverage in terms of total Au is now lower for the 33 nm Au NPs compared to the 4 nm Au NPs. At 1.5 V, we only observed deposition of 4 nm Au NPs. This shows that small particles can be separated from larger Au NPs by EPD.

Figure 6.4. shows SEM images of the glass/ITO electrode after EPD of the mixture of 4 nm and 33 nm diameter Au NPs at 1.0 V, 1.5 V, and 2.0 V, in Frames A-C as indicated. Consistent with the LSVs, the SEM images show both 4 nm

Figure 6.3. LSVs plots of citrated-coated Au NPs with 33 nm and 4 nm diameter size after electrophoretic deposition. Black dashed line (33 and 4 nm Au NPs) at 2.5 V for 90 s. Blue dashed line (33 nm and 4 nm Au NPs) at 2.0 V for 90 s. Red solid plot (33 nm and 4 nm Au NPs) at 1.5 V for 90 s. All LSVs were performed in 0.1 M HClO₄ + 0.01 M KBr from -0.1 to 1.0 V at a scan rate of 0.001 V/s.

Figure 6.4. SEM images of Glass/ITO electrodes after EPD in a mixture of 4 nm and 33 nm diameter citrate-coated Au NPs for 90 s at (A) 1.0 V, (B) 1.5 V, and (C) 2.0 V.

and 33 nm diameter Au NPs after EPD at 1.5 V and 2.0 V, but only 4 nm diameter Au NPs (no 33 nm) after EPD at 1.0 V. These images represent the appearance of the entire surface. Additional SEM images are presented in Figure 6.5.

We added H_2O_2 to all of the Au NP solutions after their synthesis and before EPD because we found that it enhanced the attachment of the 4 nm diameter Au NPs. This was discovered by accident, since the longer Au NPs were synthesized in the presence of H_2O_2 . To keep conditions the same, we added H_2O_2 to the 4 nm diameter Au NPs and found greatly increased attachment (coverage). Figure 6.6. shows the LSV of of glass/ITO following EPD of citrate-coated 4 nm diameter Au NPs at 1.5 V for 90 s in the presence and absence of H_2O_2 . The LSV shows a clear stripping peak at 647 mV with 3.03×10^{-5} C of charge for 4 nm diameter Au NPs after EPD in the presence of H_2O_2 but no Au stripping peak after EPD in the absence of H_2O_2 . H_2O_2 clearly plays an important role in the EPD process.

We hypothesized that oxidation of H_2O_2 to form H^+ ions caused a drop in pH near the electrode leading to Au NP deposition. To confirm this, we ran LSVs in solution of 4 nm diameter citrate-coated Au NPs with H_2O_2 , H_2O_2 with citrate only, and H_2O_2 only in solution, from -0.2 to 1.2 V at a scan rate of 0.01 V/s in a three electrode cell. The working electrode was bare glass/ITO, the counter electrode was a Pt wire, and the reference electrode was a Ag/AgCl (3 M KCl) with the real reference we could control H_2O_2 oxidation as see if it correlates with Au NP deposition. Figure 6.7. shows the LSVs in these three solutions. With H_2O_2 only, the current is very low at all potentials, mainly due to high

Figure 6.5. SEM images of citrated-coated Au NP after electrophoretic deposition at 1.0 V (A), 1.5 V (B) and 2.0 V (C) by 90 secs.

Figure 6.6. LSV plots of citrate-coated 4 nm diameter Au NPs in 0.1 M HClO₄ + 0.01 M KBr from -0.2 to 1.0 V at a scan rate of 0.001 V/s after the electrophoretic deposition in the presence or absence of H₂O₂. The red dashed line shows the stripping of Au NPs deposited on the surface of glass/ITO at 1.5 V for 90 s in the presence of H₂O₂. The blue solid line shows the stripping of Au NPs deposited on the surface of glass/ITO at 1.5 V for 90 secs in the absence of H₂O₂.

Figure 6.7. LSVs plots of H_2O , H_2O_2 , and citrated-coated Au NPs 4 nm in diameter (red dashed plot), H_2O , H_2O_2 and citrate (blue dashed plot), and H_2O and H_2O_2 (black solid plot) .All experiments were performed from -0.2 to 1.2 V at a scan rate of 0.01 V/s.

solution resistance, with H₂O₂ and citrate added, some H₂O₂ oxidation occurs near 0.6 V. With H₂O₂, citrate, and Au NPs, H₂O₂ oxidation appears near 0.4-0.5 V and the current is much larger due to the Au NPs catalyzing H₂O₂ oxidation as shown in equation 6.1.

We hypothesized that the formation of H⁺ at the surface of the NPs causes neutralization of the negative charge of the citrate-coated Au NPs. As a consequence of the neutralization, the NPs lose stability and precipitate on the glass/ITO surface.

Figure 6.8. shows two LSVs of citrate-coated 4 nm diameter Au NPs with H₂O₂ in solution. The red dotted plot is for a LSV with a scan from -0.2 to 1.2 V (Total time 140 s) and the blue solid plot is for a LSV with a scan from -0.2 to 0.35 V (Total time 55 s). The blue LSV intentionally was ended at -0.35 V before the rise of the anodic current that comes from the oxidation of H₂O₂. The stripping of these two samples in 10 mM KBr and 0.1 M HClO₄ are presented in the Figure 6.9. The red dotted plot shows the stripping of citrate-coated 4 nm diameter Au NPs at 654 mV as a result of the electrochemical deposition of the NPs on the surface of bare glass/ITO (LSV from -0.2 to 1.2 V, Figure 6.8). The blue solid plot in Figure 6.9. does not show a Au stripping peak at 654 mV due to the absence of electrochemical deposition of NPs on the surface of the electrode (LSV from -0.2 to 0.35 V Figure 6.8.), since H₂O₂ oxidation was not

Figure 6.8. LSVs of glass/ITO in H₂O, H₂O₂, and citrated-coated 4 nm diameter Au NPs with a potential scan from -0.2 to 1.2 V (red dashed plot) and in H₂O, H₂O₂ and citrate-coated 4 nm diameter Au NPs with a scan from -0.2 to 0.35 V (blue solid plot). All experiments were performed at a scan rate of 0.01 V/s.

Figure 6.9. LSVs of glass/ITO in 0.1 M HClO₄ + 0.01 M KBr from -0.2 to 1.2 V at a scan rate of 0.01 V/s after scanning from -0.2 to 1.2 V in the presence of 4 nm diameter citrate-coated Au NP and H₂O₂ (Red dashed line) and from -0.2 to 0.35 V in the presence of 4 nm diameter citrate-coated Au NP and H₂O₂ (Blue dashed line).

applied in that solution. Interestingly, we observed the presence of sharp stripping peaks at -103 mV for the sample that was stopped at -0.35 V. The potential of oxidation for these peaks belong to citrate-coated Au NPs of approximately 1 nm diameter. This suggests that in the resulting synthesis of citrate-coated Au NPs (2 hr. reaction time) remains NPs < 4 nm. The presence of H₂O₂ and the high catalytic reactivity of citrate-coated Au NPs (sizes below 4 nm) are making possible the precipitation of NPs close to 1 nm at potentials below the E^0 for the oxidation of H₂O₂. More experiments must be done to understand this interesting result.

In order to discard the influence of time during the electrochemical deposition of citrate-coated Au NPs, we ran similar experiments as shown in Figure 6.8. Figure 6.10. shows two LSVs for 4 nm diameter citrate-coated Au NPs with H₂O₂ in solution. The blue solid plot is for a LSV with a scan from -0.2 to 0.35 V (total time of 55 s), and the red dotted plot is for a LSV with a potential scan from -0.2 to 0.35 V (total time of 140 s). The red LSV intentionally was paused at -0.35 V for 85 s before the rise of the anodic current that comes from the oxidation of H₂O₂ in order to keep the total time the same as the scan to 1.2 V. The stripping of these two samples in 10 mM KBr and 0.1 M HClO₄ are presented in the Figure 6.11. The blue solid plot and the red dotted plot do not show a stripping peak at 654 mV for oxidation of citrate-coated 4 nm Au NPs. This shows that the electrochemical deposition of citrate-coated 4 nm diameter Au NPs did not occur on the surface of the electrode. This is consistent with the hypothesis that H⁺ formation during the oxidation of peroxide at potentials

Figure 6.10. LSVs of glass/ITO in H_2O , H_2O_2 , and citrated-coated 4 nm diameter Au NPs with a potential scan from -0.2 to 0.35V and total time of 55 s (blue solid plot) or 140 s (red dashed plot). All experiment were performed at a scan rate of 0.01 V/s.

Figure 6.11. LSVs of glass/ITO in 0.1 M HClO_4 + 0.01 M KBr from -0.2 to 1.2 V at a scan rate of 0.01 V/s after scanning from -0.2 V to 0.35 V at 0.01 V/s (55 s total, red-dashed plot) or from -0.2 V to 0.35 V and pausing at 0.35 V for 85 s (140 s total, blue solid plot) in a solution of H_2O , H_2O_2 , and 4 nm diameter citrate-coated Au NPs. There is no peak near 0.65 V for oxidation of 4 nm diameter Au NPs, but several sharp peaks from -0.2 to 0.5 V corresponding to the oxidation of smaller Au NPs.

higher than 0.35V is responsible for the electrochemical precipitation of citrate-coated Au NPs.

The particle velocity in an electric field is defined as its electrophoretic mobility. According to the equation describe previously³, mobility plays an important role in the electrophoretic deposition of citrate-coated Au NPs. The electrophoretic mobility and zeta potential are related by the following equation:

$$U_E = 2 \epsilon z f(ka) / 3\eta \quad (6.2)$$

Where U_E is electrophoretic mobility, z is the zeta potential, ϵ is the dielectric constant, η is the viscosity of the solution and $f(ka)$ is Henry's function.¹⁶⁴ The electrophoretic mobility is defined as the migration rate of the particle measured in $\mu\text{m}/\text{sec}$ under a potential gradient of 1 V/cm. In this study, we measure all NP samples under the same experimental conditions. This electrophoretic mobility depends on the size, shape, and electric charge of the Au NPs. The electrophoretic mobility also depends on pH, composition of the conducting media, concentration, the presence of additional substances such as H_2O_2 and viscosity. The particle will migrate according to its electric surface charge as it moves towards the electrode of opposite charge.

Table 6.1 shows Z and the electrophoretic mobility for citrate-coated Au NPs of 4 nm, 17 nm, and 33 nm average diameter. Z and electrophoretic mobility were obtained for citrate-coated Au NPs with total Au of 3.24×10^{-5} M and without H_2O_2 . The results indicate that 4 nm, 17 nm, and 33 nm Au NPs follow the trend in electrophoretic mobility of 4 nm > 17 nm > 33 nm.

NP size	Zeta potential Zp (mV)	Zp Std Dev	Mobility ($\mu\text{mcm/Vs}$)	Mobility Std Dev
4	-35.88	2.25	-2.80	0.18
17	-22.00	2.77	-1.72	0.22
33	-8.45	1.68	-0.66	0.13

Table 6.1. Zeta potential and electrophoretic mobility of the citrate-coated Au NPs of different size.

In a similar way Z follows the same trend of 4 nm > 17 nm > 33 nm. These results are in agreement with the migration of negatively charged citrate-coated Au NPs from the solution to the surface of the glass/ITO electrode.

To confirm these results, we applied a positive potential to pre-deposited Au NPs to determine if we could remove them from the electrode surface of Glass/ITO. Figure 6.12 shows that the stripping peak for Au NPs decreases after applying -0.7 V for 90 s, suggesting that it is possible.

The addition of the H₂O₂ decreases the pH value of all three solutions of 4 nm, 17 nm, and 33 nm Au NPs to values of pH 5.8, pH 5.7, and pH 5.5, respectively. These values of pH result in a similar level of deprotonation of the trisodium citrate for the three different sizes. Trisodium citrate has 3 pK values (6.4, 4.8 and 3.2).¹⁶¹ This result confirms the negative charge nature of the Au NPs at similar pH values for these three different sizes. In order to confirm if the Au NPs retain the same size and are stable, we performed UV-Vis spectroscopy of each sample before and after the addition of H₂O₂. Figure 6.13. and Table 6.2 shows the results. There is no change in the size of the citrate-coated Au NPs after the addition of H₂O₂ and no precipitation.

In Figure 6.14., we used electrophoretic deposition to attach citrate-coated Au NPs of < 4 nm. The synthesis of citrate-coated Au NPs < 4 nm was performed as reported previously by our group.³⁸ Citrate-coated Au NPs < 4 nm were synthesized using borohydride reduction of AuCl₄⁻ in the presence of citrate with a reaction time of 5 min instead of the standard 2 h reaction time. This short reaction time allowed us to synthesize smaller Au NPs by stopping the reaction stage of the nucleation and growth process. Figure 6.14. shows

Figure 6.12. Deposition and removal of 4 nm diameter citrate-coated Au NPs by a potential change. The blue solid line shows the stripping LSV of glass/ITO after Au NPs were deposited at 1.5 V for 90 s. The red dashed line shows the stripping LSV of glass/ITO after deposition of Au NPs at 1.5 V for 90 s and then removal of Au NPs by applying -0.7 V for 90 s.

Figure 6.13. UV-Vis spectra before and after addition of H_2O_2 to solution of 4 nm, 17 nm, and 33 nm Au NPs.

Au NP size	pH before addition of H ₂ O ₂	pH after addition of H ₂ O ₂	Wavelength before addition of H ₂ O ₂ (nm)	Wavelength after addition of H ₂ O ₂ (nm)
4 nm	8.44	5.80	510	511
17 nm	6.06	5.65	517	518
33 nm	6.04	5.52	530	530

Table 6.2. pH values and wavelength before and after addition of H₂O₂ to solutions of 4 nm, 17 nm, and 33 nm Au NPs.

Figure 6.14. LSVs of glass/ITO in 0.1 M HClO₄ + 0.01 M KBr from -0.1 to 1.2 V at a scan rate of 0.001 V/s after electrophoretic deposition at a potential of 0.0 V for 180 s (blue dashed plot) and at 0.4 V for 180 s (red solid plot) in a solution of Au NPs synthesized for 5 min.

the LSV obtained in 0.01 M KBr + 0.1 M HClO₄ for the glass/ITO after EPD at 0.4 V for 180 s in a solution of citrate-coated Au NPs synthesized for a 5 min reaction time. There is one oxidation peak at 180 mV, while the LSV for glass/ITO 4 nm diameter Au NPs prepared by reduction for 2 h (Figure 6.6., red dashed plot at the same voltage and time) does not show an oxidation peak from -200 to 640 mV. The LSV for the 4 nm diameter Au NPs exhibits one main peak at 647 mV with no discernible peaks at the lower potential. We also performed a LSV for a control glass/ITO sample where we applied 0.0 V for 180 seconds in similar solution of citrate-coated < 4nm Au NPs, (5 min reaction time) and did not observe any Au oxidation peaks at potential of -0.1 to 1.0 V. This indicates that these Au NPs do not deposit on glass/ITO without applying a positive potential.

The absence of a peak near 0.65 V on both the LSV of citrate-coated 4 nm diameter Au NPs and the LSV of the control experiment (Figure 6.14. blue dashed plot) and the presence of peaks at lower potentials <640 mV indicates the oxidation of <4 nm diameter citrate-coated Au NPs. This result confirms that the 5-min reaction time and low 0.4 V successfully allowed the attachment (EPD) of a large population of <4 nm Au NPs on the glass/ITO surface.

6.4. Conclusions

In summary, we report a size selection for attachment of citrate-coated Au NPs on a glass/ITO by electrophoretic deposition on Glass/ITO. We used an electric field cut-off of ~2.0 V/cm for the deposition of both citrate-coated Au NPs with ≤33 nm, and ≤4 nm diameter respectively, and ~1.5 V/cm for the deposition of ≤4 nm diameter Au NPs. If the applied electric field and H₂O₂ is

absent, we did not observe any measurable deposition of 4-33 nm diameter Au NPs on glass/ITO. The lowest deposition potential of 0.4 V led to the electrophoretic deposition of Au NPs of <4 nm without H₂O₂. We believe that future studies should be performed in order to understand more details about this phenomenon. Here, in this study we clearly show the attachment of different size Au NPs by varying the deposition potential. These results provides an excellent opportunity for the development of an alternative method for the synthesis and attachment to electrodes of Au NPs <4 nm without the use of organic capping ligands. Moreover, we believe that electrophoretic deposition of <4 nm diameter citrate-coated Au NPs and metallic NPs (no organic capping ligands) will enable electrocatalysis studies and applications of bare metal NPs of very small size.

7.1. Introduction

Here we demonstrate that galvanic replacement between surface-attached metallic Au nanoparticles (NPs) and PtCl_4^{2-} strongly depends on the size of the Au NPs, which was varied to be 4 nm, 15 nm, 50 nm, and 128 nm in diameter. With the Au surface area held constant in order to keep the amount of Au exposed to PtCl_4^{2-} constant, the galvanic replacement reactivity increased as the Au NP diameter decreases, being strongest for the 4 nm diameter Au NPs. The extent of reactivity was determined by the catalytic oxidation of Br^- , oxygen reduction reaction, hydrogen evolution reaction and CO stripping analysis, which all depend on the presence of surface Pt. Au stripping analysis and UV-vis spectroscopy provides supporting evidence for the different amount of reactivity. Scanning electron microscopy images reveal no noticeable morphological changes in the Au NPs after exchange with PtCl_4^{2-} . The size-dependent behavior is likely a result in the negative shift in oxidation potential as the Au NP size decreases, making it more susceptible to exchange with PtCl_4^{2-} . Galvanic exchange with very small nanoparticles may lead to new reactivity and alloy nanostructures not possible in bulk systems, opening up the possibility for new properties and applications.

It is well-known that the properties of nanoscale metals are different from their bulk properties and tunable by their size over the range of 1 to 10s of nm. These properties and their small size has led to a wide range of applications in catalysis,⁵⁰ sensing,¹⁶⁵ plasmonics,¹⁶⁶ drug delivery,¹⁶⁵ therapeutics,¹⁶⁷ imaging,¹⁶⁸ and detection.⁶⁴ Monometallic nanoparticles have a variety of uses, but often bimetallic or multimetallic systems have distinct advantages, depending on the application. With so many potential applications, it is important to have good control over the size, shape, and composition of metallic nanostructures and a full understanding of their reactivity as a function of these three variables. These issues are important in terms of the properties and applications of the nanomaterials, but also in terms of their stability and potential toxicity.

The most common method of forming monometal or alloy nanoparticles with controlled size and shape is by the reduction of metal ion or metal complexes in the presence of some stabilizer. This can be performed in one step with one or more metal precursors or in multiple steps to form core/shell type alloy nanoparticles. Three less common strategies that allow both morphological and chemical changes to preformed metal nanoparticles by chemical reactions⁸⁷ are the Kirkendall effect,⁸⁸⁻⁹⁰ anion exchange,⁹¹ and galvanic replacement (or exchange) reactions.^{92,93} These versatile reactions allows the formation of complex morphologies and variable compositions of metal nanoparticles. For example, the Kirkendall effect has been used to prepare rod-shaped gold nanorattles with improved plasmon sensitivity and catalytic activity. Anion exchange reactions on ZnO nanoparticles with molecular sulfur

precursors produced ZnS hollow nanoparticles. Galvanic replacement reactions between Ag nanostructures and Pd(II), Au(III), and Pt(II), for example, has led to unique structures with tunable optical properties and a variety of applications.

Our group has recently been studying the oxidation of Au and Ag NPs as a function of their diameter by voltammetry. We recently showed that the oxidation potential of Ag and Au NPs electrochemically deposited or chemically-synthesized and electrostatically attached to indium tin oxide coated glass (glass/ITO) electrodes decreases as the diameter of the nanoparticle decreases.^{36,37} The decrease is about 200 mV from bulk size (>60 nm) to 4 nm average diameter for Au NPs electrochemically-synthesized, for example.³⁷ The oxidation potential shifted by as much as 850 mV negative for citrate-coated Au NPs electrostatically attached to amine-functionalized glass/ITO electrodes that are estimated to be in the 1-2 nm diameter range, which is the largest shift in E_p observed to date and correlates fairly well with the 1/radius dependence predicted by Plieth.⁵¹ We also recently described the effect of electrode surface charge and electrode material on the oxidation of surface-attached Au and Ag NPs.³⁸ The NP diameter is the most important factor, but the surface charge can also lead to a significant shift for larger NPs. The electrode material has a relatively smaller effect. Other groups have also observed size dependent metal NP oxidation. For example, Giovanni et al. studied the size-dependent oxidation of Ag NPs of 10-107 nm in diameter,¹⁵⁹ while Buttry and co-workers showed a negative shift in the oxidation potential of Pd NPs with decreasing size by voltammetry.¹⁶⁰ Sieradzki and co-workers

reported the early oxidation of < 4 nm diameter Pt NPs at potentials well below the bulk value.¹⁶² They developed size-dependent potential-pH diagrams and imaged dissolving Pt NPs by scanning tunneling microscopy (STM).¹¹⁰ Del Popolo et al.¹⁶⁹ reported the oxidation of small Pd NPs at more negative oxidation potential relative to the bulk, while Compton and co-workers observed no change in the oxidation potential for Ag NPs from 25 to 100 nm diameter range.⁵⁶ Finally, Brainina and co-workers described the size dependent oxidation of metal NPs theoretically⁶⁰ and later compared theory to experimental data for the oxidation of Au in chloride solution.⁶⁶

Galvanic replacement is a simple oxidation-reduction reaction that occurs when the oxidized form of one metal reacts with the reduced form of another metal. The reaction is spontaneous if the metal in the oxidized form has a more positive standard reduction potential than that of the metal in the reduced form. Since it is more energetically favorable in the reduced form compared to the other metal, the two metals will spontaneously exchange with one another. During this replacement reaction, the oxidation and reduction of the two metals involves the intermediate steps of alloy formation and dealloying as follows (assuming the same number of electrons in the oxidation and reduction):

The galvanic replacement reaction has been utilized in recent years to synthesize pure metal and alloy nanomaterials with structures not easily obtainable by other methods. Examples include the synthesis of hollow single and multi-walled metal nanotubes,⁹⁴ nanoframes,¹⁷⁰ nanorattles,⁹⁴ and nanocages.⁹⁵ These materials usually exhibit unique optical, electronic, or catalytic properties that are tunable,⁹⁰ improve catalysis,^{171,172} and in some cases are useful for cancer treatment.¹⁷³ Interestingly, there have not been any studies to our knowledge exploring the effect of NP size on the galvanic replacement reaction.

Here, we describe the role of metal NP size on the galvanic replacement reaction between aqueous PtCl_4^{2-} and surface-attached citrate-coated Au NPs of 4 nm, 15 nm, 50 nm, and 128 nm average diameter. There are two reasons to suspect that this reaction would be size dependent. First, since galvanic exchange involves the oxidation of one metal (Au in this case), decreasing the size of the metal is likely to facilitate the galvanic replacement based on previous studies showing that the oxidation potential shifts negative as the NP size decreases.^{36,37,51,160} In addition, the reduction of the metal complex (PtCl_4^{2-} in this case) may be catalyzed by smaller Au NPs, since they typically act as nucleation sites for growth. On the other hand, the reaction may not be affected since the standard reduction potential of both the Au and Pt would change in a similar fashion as a function of size. We chose to study the exchange of Au^0 with Pt(II) because this is usually not a favorable reaction based on their standard reduction potentials. The small size of the Au NPs could change the thermodynamics of the system in a way that would make it favorable, allowing

new reactivity not observed in the bulk. The results show large differences in the reactivity depending on the size of the Au NPs. The reaction was more strongly favored as the Au NP size decreased, as hypothesized.

7.2. Experimental

7.2.1. Attachment of Citrate-coated Au Nanoparticles to Functionalized Electrodes

The glass/ITO/APTES electrodes were soaked in solutions of the different-sized Au NPs (see Table 7.1., where the concentration is in term of Au atoms), rinsed thoroughly with nanopure water, and dried under N₂ prior to galvanic exchange and electrochemical analysis. The soaking time was chosen to obtain a similar Au surface area for the different Au NP sizes.

7.2.2. Surface area analysis of Citrate-coated Au NPs

The surface area of citrate-coated Au NPs was measured electrochemically by monitoring the surface oxidation and reduction of the Au NPs that is well-known to occur when cycling the potential in acid. Briefly, the electrochemical cell consisted of the glass/ITO/APTES/AuNPs as the working electrode, a Pt wire counter electrode, and an Ag/AgCl (3 M KCl) reference electrode. Cyclic voltammograms (CVs) were obtained with a CH Instruments model 620 electrochemical analyzer in 0.5 M H₂SO₄ electrolyte at a scan rate of 0.5 V/s.

7.2.3. CO Stripping Voltammetry

An electrochemical cell was constructed with the glass/ITO/APTES/AuNPs(Pt Exch) as the working electrode, Pt wire counter

Au NPs (nm)	Concentration (mM)	Soaking Time
4 ±1	0.0243	90 to 120 sec
15±4	0.0909	110 to 150 sec
50±8	0.1015	10 to 12 min
128±14	0.2936	22 to 27 min

Table 7.1. Soaking time chosen to obtain a similar Au surface area

electrode, Ag/AgCl (3 M KCl) reference electrode, and 0.5 M H₂SO₄ electrolyte solution in a glass cell. CO was purged through the H₂SO₄ solution at room temperature for at least 1.0 h to allow complete adsorption of CO onto any available surface Pt while maintaining a constant voltage of 0.35 V. Excess CO was then purged with N₂ for at least 1.0 h. The amount of CO adsorbed was evaluated by integration of the CO stripping peak during a stripping voltammogram performed by sweeping the potential from -0.2 to 1.0 V at a scan rate of 0.02 V/s in the same 0.5 M H₂SO₄ solution with a CH Instruments model 660E electrochemical analyzer. Since CO only adsorbs to Pt, the charge under the CO stripping peak is indicative of the amount of Pt exchange.

7.2.4. Cyclic Voltammetry of the Oxygen Reduction Reaction (ORR) and Hydrogen Evolution Reaction (HER)

The glass/ITO/APTES/AuNPs(Pt Exch) working electrodes were cycled from 0.4 to -0.8 V in 0.5 M H₂SO₄ solution at a scan rate of 0.01 V/s with a Pt wire counter electrode and an Ag/AgCl (3 M KCl) reference electrode with a CH Instruments model 660E electrochemical analyzer. O₂ and N₂ were purged into the cell for at least 15 min to allow O₂ or N₂ saturation of the electrolytic solution prior to obtaining the voltammograms. Improved catalytic activity for ORR and HER is indicative of Pt on the surface.

7.2.5. UV-visible spectroscopy

Citrate-coated Au NPs of 4, 15, 50 and 128 nm were evaluated for galvanic replacement reaction with PtCl₄²⁻ in solution. The total surface area for these 4 different sizes is constant similar to the experiments with the glass/ITO/APTES substrate. The total surface area for each specific Au NPs size used in this

experiment was $7.5 \times 10^{16} \text{ nm}^2$ and the total amount of moles of PtCl_4^{2-} used was 1×10^{-7} moles. The different Au NP sizes were mixed with PtCl_4^{2-} solution for a period of 3 min and 24 hr before acquiring the UV-visible spectra. UV-visible spectra for 128 nm Au NPs (24 hr) was not acquired due to precipitation. Figure 7.1. and Table 7.2. show the UV-visible spectroscopy data and the number of moles used for each specific Au NP size in this experiment, respectively.

7.3. Results and Discussion

In this work, we focused on the galvanic replacement of Au in the form of Au NPs of different size with Pt from a PtCl_4^{2-} complex. The overall reaction and experimental set-up is shown in Figure 2.9., where we hypothesized that smaller Au NPs would show greater reactivity for galvanic replacement with Pt based on their more negative oxidation potential and ability to catalyze Pt deposition. The first step in the experimental procedure was to synthesize citrate-coated Au NPs of different diameter (4 nm, 15 nm, 50 nm, and 128 nm) and attach them electrostatically to 3-(aminopropyl)triethoxysilane (APTES)-functionalized glass/ITO electrodes as described by our group previously.³⁸ In these experiments, we decided to keep the Au surface area constant for the different sized Au NPs so that the PtCl_4^{2-} would see the same amount of total surface Au atoms for each size Au NPs.

The attachment of Au NPs to the surface of glass/ITO/APTES allowed control over the total amount of Au and surface area for each specific nanoparticle size by controlling the immersion time in the Au NP solution as discussed in the experimental section. This is important because we wanted to

Figure 7.1. UV-visible spectra obtained for citrate-coated Au NPs in solution before (blue solid) and after (red solid) galvanic replacement with PtCl_4^{2-} , (A) 4 nm Au NPs, (B) 15 nm Au NPs, (C) 50 nm Au NPs, and (D) 128 nm Au NPs.

Nanoparticle size (nm)	Au moles	Ratio : Total moles/Total moles (4 nm) Theory	Ratio : Total moles/Total moles (4 nm) Practice	Surface Area (nm ²)	PtCl ₄ ²⁻ moles
4	2.42x10 ⁻⁶	1	1	7.54x10 ¹⁶	1.0x10 ⁻⁷
15	9.03x10 ⁻⁶	3.8	3.7	7.58x10 ¹⁶	1.0x10 ⁻⁷
50	3.02x10 ⁻⁵	12.5	12.5	7.54x10 ¹⁶	1.0x10 ⁻⁷
128	7.74x10 ⁻⁵	32.0	32.0	7.53x10 ¹⁶	1.0x10 ⁻⁷

Table 7.2. Moles of Au used in the solution of citrate-coated Au NPs in order to keep the surface area constant relative to the moles of PtCl₄²⁻ in the galvanic replacement reaction in solution.

study the effect of size on the galvanic exchange reaction while keeping the surface area constant. Figure 7.2. shows the electrochemical analysis of 4, 15, 50 and 128 nm diameter Au NPs attached to glass/ITO/APTES without performing any galvanic exchange. The linear sweep voltammograms (LSVs) in Frame A in 0.01 M KBr + 0.1 M HClO₄ provide the total amount of Au on the surface and the cyclic voltammograms (CVs) in Frame B performed in 0.5 M H₂SO₄ at 0.5 V/s provide the Au surface area. It is clear that the Au reduction peak in Frame B at about 0.8 V is similar for all sizes, while the Au stripping peak in Frame A near 0.7 V increases with increasing Au NP size. The Au reduction peak corresponds to the reduction of surface Au oxide and is indicative of the surface area. The Au stripping (oxidation) peak corresponds to the dissolution of all the Au from the surface by formation of AuBr₄⁻ or AuBr₂⁻ and is therefore indicative of the total amount of Au. The larger sizes have a larger total amount of Au, which is necessary to have a similar surface area compared to smaller sizes. It can be shown mathematically that the ratio of the total Au/surface area is directly proportional to the NP diameter. Therefore, to keep the surface area constant, the 128 nm diameter Au NPs should have 32 times more Au on the surface compared to the 4 nm diameter Au NPs.

Table 7.3. shows the total charge under the reduction peak for the analysis of surface area and the total charge from the oxidative stripping of Au. The table also shows the stripping charge to surface charge ratios and the ratios of those values between the different sized Au NPs (theoretical and actual). The 128 nm diameter Au NP sample is only about 11 times greater than the 4 nm diameter Au NPs, instead of the theoretical 32 times greater. We are not sure

Figure 7.2. (A) Linear Sweep Voltammograms (LSVs) in 0.1 M HClO_4 plus 0.01 M KBr solution and Cyclic voltammograms (CVs) in 0.5 M H_2SO_4 of glass/ITO/APTES/Au NP electrodes with 4, 15, 50 and 128 nm diameter Au NPs.

Nanoparticle Size (nm)	Total Charge Under The Reduction Peak in H ₂ SO ₄ (Coulombs)	Total Charge Under The Stripping Peak in KBr and HClO ₄ (Coulombs)	Ratio : Stripping charge/Stripping charge (4 nm) Theory	Ratio : Stripping charge/Stripping charge (4 nm) Practice
4 ± 1	1.17 ± 0.23x10 ⁻⁶	4.49 ± 1.65x10 ⁻⁶	1.0	1.0
15 ± 4	1.26 ± 0.22x10 ⁻⁶	1.03 ± 0.26x10 ⁻⁵	3.8	2.3
50 ± 8	1.29 ± 0.51x10 ⁻⁶	3.27 ± 0.98x10 ⁻⁵	12.5	7.3
128 ± 14	1.34 ± 0.36x10 ⁻⁶	4.82 ± 1.58x10 ⁻⁵	32.0	10.7

Table 7.3. Total charge under the reduction peak for surface analysis and total charge under the stripping peak for total content of Au.

why we have this discrepancy. It could be that the larger Au NPs are not fully dissolved during the LSV or that the surface oxide formation is very different on the 4 nm diameter Au NPs, leading to a lower charge for the surface reaction. More work will be needed to better understand this interesting result. In Figure 7.3.A, we also note that the peak potential for Au oxidation in Br⁻ shifts negative with decreasing Au NP size as shown previously by our group and others.^{37,38,51} The experimental shift in E_p is due to a size-dependent change in E^0 for the Au oxidation reaction.^{37,51}

Citrate-coated Au NPs from 4 to 128 nm were synthesized chemically and attached to glass/ITO/APTES electrodes as just described. Then the glass/ITO/APTES/Au NPs were placed in 1.0x10⁻⁵ M PtCl₄²⁻ solution for 180 s before removing, rinsing with nanopure water, and drying under N₂. The resulting AuPt NPs were characterized by SEM, LSV, CO stripping oxidation, and by monitoring the oxygen reduction reaction (ORR) and hydrogen reduction to characterize the content of Pt over the surface of the Au NPs after galvanic displacement. Before showing the results, we calculated theoretically the extent to which the reaction should proceed based on the standard reduction potential of bulk Au and Pt and assuming reversible electrochemical kinetics under the experimental conditions.

The reaction between PtCl₄²⁻ and Au bulk metal is not thermodynamically favorable under standard conditions. The net equation between Au⁰ and PtCl₄²⁻ has a standard cell potential of -0.264 V as follows:

Figure 7.3. Linear sweep voltammetry (LSV) in 10 mM KBr and 0.1 M HClO_4 for Au NPs (A) 4 nm, (B) 15 nm, (C) 50 nm, and (D) 128 nm before (blue) and after (red) galvanic exchange for 180 s with 1.0×10^{-5} M PtCl_4^{2-}

However, since E^0 shifts negative as the Au NP size decreases, we hypothesized that the reaction would be more favorable on smaller Au NPs. In our experiments we did not work at standard conditions. Since there is no AuCl_4^- in solution initially, we cannot accurately calculate the cell potential, but the total reaction will be pushed to the right according to Le' Chatelier's Principle. The equilibrium concentration of AuCl_4^- expected for Au placed in a solution of $1.0 \times 10^{-5} \text{ M}$ PtCl_4^{2-} according to the K_{eq} determined by the E^0 of the reaction above is as follows:

$$K_{\text{eq}} = 10^{nE/0.0592} = 10^{-26.76} = [\text{AuCl}_4^-]^2 [\text{Cl}^-]^4 / [\text{PtCl}_4^{2-}]^3 \quad (7.7)$$

At equilibrium,

$$[\text{PtCl}_4^{2-}]_{\text{eq}} = 1.0 \times 10^{-5} - x = 9.9 \times 10^{-6} \text{ M} \quad (7.8)$$

$$[\text{AuCl}_4^-]_{\text{eq}} = 2/3x = 7.1 \times 10^{-8} \text{ M} \quad (7.9)$$

$$[\text{Cl}^-]_{\text{eq}} = 4/3x = 1.4 \times 10^{-7} \text{ M} \quad (7.10)$$

Solving for x ($1.1 \times 10^{-7} \text{ M}$) from K_{eq} gives the above equilibrium concentrations by the following analysis. At equilibrium, we know the following.

$$E_{\text{Anode}} = E_{\text{Cathode}} \quad (7.11)$$

$$E_{\text{Au}}^O - \left(\frac{0.0592}{6}\right) \log \frac{[\text{Cl}^-]^8}{[\text{AuCl}_4^-]^2} = E_{\text{Pt}}^O - \left(\frac{0.0592}{6}\right) \log \frac{[\text{Cl}^-]^{12}}{[\text{PtCl}_4^{2-}]^3} \quad (7.12)$$

$$E_{\text{Au}}^O - E_{\text{Pt}}^O = \left(\frac{0.0592}{6}\right) \log \frac{[\text{Cl}^-]^8}{[\text{AuCl}_4^-]^2} - \left(\frac{0.0592}{6}\right) \log \frac{[\text{Cl}^-]^{12}}{[\text{PtCl}_4^{2-}]^3} \quad (7.13)$$

$$0.264 = \left(\frac{0.0592}{6}\right) \log \frac{[\text{PtCl}_4^{2-}]^3}{[\text{AuCl}_4^-]^2 [\text{Cl}^-]^4} \quad (7.14)$$

$$\left(\frac{0.264 \times 6}{0.0592}\right) = \log \frac{[\text{PtCl}_4^{2-}]^3}{[\text{AuCl}_4^-]^2 [\text{Cl}^-]^4} \quad (7.15)$$

$$26.7 = \log \frac{[\text{PtCl}_4^{2-}]^3}{[\text{AuCl}_4^-]^2 [\text{Cl}^-]^4} \quad (7.16)$$

$$1/K_{eq} = \frac{[\text{PtCl}_4^{2-}]^3}{[\text{AuCl}_4^-]^2 [\text{Cl}^-]^4} = 10^{26.7} \quad (7.17)$$

Initial	1×10^{-5}	0	0
Final	$1 \times 10^{-5} - X$	$\frac{2}{3}X$	$\frac{4}{3}X$

$$K_{eq} = \frac{[\text{AuCl}_4^-]^2 [\text{Cl}^-]^4}{[\text{PtCl}_4^{2-}]^3} = 1.995 \times 10^{-27} \quad (7.19)$$

$$\left(\frac{2}{3}X\right)^2\left(\frac{4}{3}X\right)^4/(1 \times 10^{-5} - X)^3 = 1.995 \times 10^{-27} \quad (7.20)$$

$$\left(\frac{4}{9}X^2\right)\left(\frac{256}{81}X^4\right)/(1 \times 10^{-5} - X)^3 = 1.995 \times 10^{-27} \quad (7.21)$$

$$\left(\frac{1024}{729}X^6\right)/(1 \times 10^{-5} - X)^3 = 1.995 \times 10^{-27} \quad (7.22)$$

$$X^6 = \frac{(729)(1.995 \times 10^{-27})(1 \times 10^{-5} - X)^3}{1024} \quad (7.23)$$

$$X^6 = \frac{(729)(1.995 \times 10^{-27})(1 \times 10^{-15})}{1024} \quad (7.24)$$

$$X^6 = 1.42 \times 10^{-42} \quad (7.25)$$

$$X = 1.06 \times 10^{-7} \text{ M}$$

	[PtCl ₄ ²⁻]	[AuCl ₄ ⁻]	[Cl ⁻]
Initial	1 × 10 ⁻⁵ M	0 M	0 M
Final	1 × 10 ⁻⁵ - 1.06 × 10 ⁻⁷ M	7.1 × 10 ⁻⁸ M	1.4 × 10 ⁻⁷ M
	9.89 × 10 ⁻⁶ M		

Considering that the volume of the vial is 10 mL, this would lead to 7.1×10^{-10} moles of total Au oxidized if the entire solution reached equilibrium with the electrode. Table 7.4. shows the total amount of Au oxidized and the percentage of Au that this would amount to for each size of Au NPs based on the total amount of Au originally on the surface in each sample.

These values are not indicative of the true experiment, however, since we only perform the reaction for 180 s. It will not have enough time to equilibrate with the entire solution. We therefore have to determine how much Au would theoretically oxidize in that time. To do that, we need to determine the diffusion layer thickness after 180 s which is given by

$$\delta = (2Dt)^{1/2} \quad (7.26)$$

where δ is the diffusion layer thickness, D is the diffusion coefficient of PtCl_4^{2-} ($\sim 1.0 \times 10^{-5} \text{ cm}^2/\text{s}$),¹⁷⁴ and t is time. This gives a δ of 0.060 cm. The volume of solution affected by the electrode reaction is then given by

$$V = \delta A \quad (7.27)$$

where A is the electrode area, in this case 1.2 cm^2 . This gives a volume of 0.072 cm^3 . The concentration of AuCl_4^- at the electrode surface ($C_{\text{AuCl}_4^-(x=0)}$) is $7.1 \times 10^{-8} \text{ M}$ as determined from the calculated equilibrium concentration and there will be a gradient where the concentration drops from $7.1 \times 10^{-8} \text{ M}$ at the

Nanoparticle size in nm	Total Amount of Au in moles, from the LSV analysis	AuCl ₄ ⁻ moles considering 10 cm ³ (Total volume)	% after galvanic replacement (Considering total volume)	AuCl ₄ ⁻ moles considering 0.072 cm ³ (Diffusion layer volume)	% after galvanic replacement (Considering diffusion layer volume)
4	3.10x10 ⁻¹¹	7.10x10 ⁻¹⁰	2290	3.70x10 ⁻¹²	11.9
15	7.12x10 ⁻¹¹	7.10x10 ⁻¹⁰	997	3.70x10 ⁻¹²	5.2
50	2.26x10 ⁻¹⁰	7.10x10 ⁻¹⁰	314	3.70x10 ⁻¹²	1.6
128	3.33x10 ⁻¹⁰	7.10x10 ⁻¹⁰	213	3.70x10 ⁻¹²	1.1

Table 7.4. Theoretical amount of Au oxidized for each Au NP size based on theoretical calculation and the total amount of Au.

electrode ($x=0$) to the bulk concentration of $C_{AuCl_4^-}^* = 0$ at $x=\delta$, 0.060 cm. The average concentration in this volume next to the electrode is given by

$$C_{AuCl_4^-(ave)} = (C_{AuCl_4^-(x=0)} - C_{AuCl_4^-}^*(x=\delta))/2 = 3.6 \times 10^{-8} \text{ M} \quad (7.28)$$

The theoretical moles of Au oxidized then after 180 seconds at open circuit conditions is given by

$$\begin{aligned} C_{AuCl_4^-(ave)} * V &= (3.6 \times 10^{-8} \text{ mol/L})(1\text{L}/1000 \text{ cm}^3)(0.072 \text{ cm}^3) \quad (7.29) \\ &= 2.6 \times 10^{-12} \text{ mol Au} \end{aligned}$$

This analysis assumes reversible electrochemical kinetics, a linear concentration gradient at the electrode surface, linear diffusion, and a constant bulk value for E^0 . The E^0 is likely not constant throughout the reaction due to alloy formation as an intermediate structure, which would be more stable than the monometal, and the kinetics are also likely not reversible, not only because of the bond breaking needed, but alloy formation and dealloying processes. Our estimate would be the upper limit for the amount of Au oxidized in this reaction during 180 s. We purposely estimated the amount of Au oxidized based on the upper limit. Table 7.4. provides the theoretical amount of Au oxidized for each Au NP size based on the theoretical calculation and total amount of Au on the electrode from the stripping analysis. It is clear that the theoretical amount of Au oxidized is very small in all cases ($< 10\%$). Also, these values are for the Au oxidized relative to total Au available. The Au oxidized relative to the amount of surface Au available would be constant for all sizes.

Figure 7.3. shows LSVs of the 4, 15, 50 and 128 nm diameter Au NPs before (blue plots) and after (red plots) galvanic exchange for the 180 s in PtCl_4^{2-} solution. The stripping of 4 nm diameter Au NPs before galvanic exchange (Figure 7.3. A) shows a Au oxidation peak at about 0.6 V. After galvanic exchange, however, the Au stripping peak disappeared and the peak near 1.1 V grew dramatically. This suggests that Pt replaced Au to a large extent, consistent with no Au stripping peak. Also, the peak at 1.1 V is due to Br^- oxidation, which is catalyzed by Pt,¹⁷⁵ also indicating Pt exchange.

Figure 7.3. B shows the same data for 15 nm diameter Au NPs. In this case, there is still a Au stripping peak after galvanic exchange that is similar in size to the peak before exchange, but the peak potential is shifted positive by about 0.1 V. In addition, the Br^- oxidation peak near 1.1 V is enhanced by 3.5 times in comparison with a similar sample without galvanic exchange. We believe that the shift in the Au stripping peak and small increase in Br^- oxidation indicates some Pt exchange, but to a smaller degree compared to 4 nm diameter Au NPs. Figure 7.3. C and 7.3. D show the LSVs before and after galvanic exchange for samples with 50 nm and 128 nm diameter Au NPs, respectively. Similar to the 15 nm diameter Au NPs, the Au stripping peak did not change noticeably in size, but did shift about 0.1 V positive. In contrast to the 15 nm diameter Au NPs, the current due to oxidation of Br^- was not increased at all significantly above the average of those measured without galvanic exchange. This lower current is likely indicative of less Pt exchange on the surface, but could also be due to the effect of NP size on catalytic activity.

The notorious absence of an Au stripping peak for 4 nm diameter Au NPs after galvanic exchange for similar surface area (Figure 7.3. A) confirms the larger amount of Pt on the surface of small Au NPs, which is the main reason for enhancement of Br⁻ oxidation.

In addition to the comparison of the galvanic exchange reaction between different size NPs with similar surface area, we also tested 15 nm and 4 nm diameter Au NPs with similar total coverage (similar amount of Au) but different surface area. Our results indicate that even with a similar total Au coverage for the 4 nm and 15 nm NPs, the 4 nm Au NPs are more prone to the galvanic exchange reaction (Figure 7.4. A and B). In Figure 7.4. A the stripping peak for 4 nm diameter Au NPs disappears after the galvanic exchange reaction, which is not the case for the 15 nm diameter Au NPs. Also, the peak current for Br⁻ oxidation was much higher for the 4 nm diameter Au NPs.

This is the same type of behavior observed with samples with similar surface area but different total charge. This result strongly supports a NP size dependence in the galvanic exchange reaction. Figure 7.4. B shows enhanced Br⁻ oxidation as a result of the galvanic exchange reaction.

A complementary experiment was also performed in order to evaluate the level of galvanic exchange for the samples with similar coverage. An analysis of electrochemical surface area for 4 nm Au NPs before and after galvanic exchange (Figure 7.5 A) showed a dramatic reduction in the surface Au reduction peak and appearance of oxygen reduction for the 4 nm diameter Au NPs after galvanic exchange. In the sample of 15 nm diameter Au NPs (Figure

Figure 7.4. (A) LSVs in 0.01 M KBr and 0.1 M HClO₄ of 4 nm and 15 nm Au NPs before and after galvanic exchange with similar total Au coverage prior to exchange. (B) The same plots as A, but over a wider potential range.

Figure 7.5. CVs in 0.5 M H_2SO_4 at 0.5 V/s for 4 nm diameter Au NPs (A) and 15 nm diameter Au NPs (B) before (blue solid) and after (red dash) galvanic exchange.

7.5. B), though, no change in the Au surface reduction occurred, providing more evidence of the size dependence in the galvanic exchange reaction.

Figure 7.6 shows scanning electron microscopy images for 4, 15, 50 and 128 nm average diameter Au NPs before galvanic exchange (A1, B1, C1 and D1) and after galvanic exchange (A2, B2, C2 and D2). We obtained the average size and standard deviation of the Au NPs from a population of 100 NPs, which was 4 nm $\pm$ 1 nm, 15 nm $\pm$ 4 nm, 50 nm $\pm$ 8 nm and 128 nm $\pm$ 14 nm.

Another way to make an evaluation of platinum exchange is by the quantification of the electrochemical surface area (ESA) of Pt.¹⁷⁶ The ESA of Pt was obtained by the CO_{ad} stripping analysis on samples of Au NPs after galvanic exchange. This analysis allows quantification of the surface area of Pt. The electrochemical surface area of PtAu NPs was measured electrochemically by oxidation of preadsorbed carbon monoxide (CO_{ad} stripping). The CO oxidation charge can be converted into surface area by a conversion factor of 420 μ C/cm².¹⁷⁷ Figure 7.7.A and 7.7.B shows the CO stripping of CO bonded to the surface of Au NPs. We chose 4 and 50 nm Au NPs to determine the amount of Pt on these surfaces after exchange. In Figure 7.7. A we show two CVs in blue (scan 1 and 2) for the stripping of CO on the surface of 4 nm diameter Au NPs after galvanic exchange and two in red (scan 1 and 2) for CO stripping of 50 nm Au NPs after exchange. For the 4 nm diameter Au NPs, there is clearly a CO stripping peak on the first scan, which is gone on the second scan, since it was removed and diffused away from the surface. This conclusively indicates Pt is on the surface of these exchanged Au NPs. In contrast, there is no noticeable CO stripping wave for the 50 nm

Figure 7.6 Scanning electron microscopy (SEM) images of glass/ITO/APTES electrodes coated with Au NPs (A1 before galvanic exchange reaction – A2 after galvanic exchange reaction) 4 nm, (B1 before galvanic exchange reaction – B2 after galvanic exchange reaction) 15 nm, (C1 before galvanic exchange reaction – C2 after galvanic exchange reaction) 50 nm, and (D1 before galvanic exchange reaction – D2 after galvanic exchange reaction) 128 nm radius.

Figure 7.7. (A) Cyclic voltammetry for CO_{ad} stripping in 0.5 M H₂SO₄, 4 nm Au NPs after galvanic exchange reaction (red solid plot, 1 first CV and 2 second CV). 50 nm Au NPs after galvanic exchange reaction (blue dashed plot, 1 first CV and 2 second CV). (B) Cyclic voltammetry for Co_{ad} stripping in 0.5 M H₂SO₄, 4 nm Au NPs after galvanic exchange reaction (red solid plot, 1 first CV and 2 second CV). 4 nm Au NPs before galvanic exchange reaction (blue dashed plot, 1 first CV and 2 second CV).

diameter Au NPs after Pt exchange on the first or second scan, indicating no significant Pt exchange on this surface. The resulting Pt ESA for the 4 nm diameter Au NPs after galvanic exchange is $3.45 \times 10^{-3} \text{ cm}^2$. Considering the original Au ESA, this gives an estimated 69% of the Au surface coated with Pt after exchange. These results conclusively show size-dependent galvanic exchange between citrate-coated surface-confined Au NPs and PtCl_4^{2-} . Figure 7.7. B shows the CO stripping experiment for 4 nm diameter Au NPs before and after galvanic exchange with PtCl_4^{2-} . It is clear that there is no CO stripping on Au NPs only, further confirming that the peak observed after Pt exchange is due to CO stripping from the surface Pt.

We also qualitatively characterized the Au NP size dependence of the galvanic exchange reaction with PtCl_4^{2-} by monitoring the oxygen reduction reaction (ORR) and H^+ reduction, or hydrogen evolution reaction (HER) in acidic solutions for samples before and after galvanic exchange. Since both of these reactions are catalyzed by Pt, the potential and current measured give an indication of the amount of surface Pt. Figure 7.8.A and 7.8.B show CVs in 0.5 M H_2SO_4 under O_2 for 4 nm diameter Au NPs before and after galvanic exchange while Figure 7.8.C and 7.8.D show CVs in 0.5 M H_2SO_4 under N_2 for 4 nm Au NPs before and after galvanic exchange. In Figure 7.8.A, the large current beyond -0.4 V is due to Pt-catalyzed HER for the 4 nm Au NPs after Pt exchange. The sample before exchange shows comparably much lower current. The blow up in Figure 7.8.B shows Pt-catalyzed ORR starting around 0.2 V, which again is not observed in the Au NPs before exchange. Under N_2 (Figure 7.8.C and 7.8.D), the current observed in the exchanged samples is

Figure 7.8. CVs in 0.5 M H₂SO₄ at scan rate 0.01 V/s for 4 nm Au NPs before and after galvanic exchange with PtCl₄²⁻ under O₂ (A and B) and under N₂ (C and D).

strictly due to Pt-catalyzed HER, which is comparably much smaller without exchange. There is also no ORR current starting at 0.2 V since O₂ was removed from the solution. We performed a similar analysis with 15 nm diameter Au NPs before and after galvanic exchange. Figure 7.9.A and 7.9.B shows CVs under O₂ and N₂ conditions for 15 nm Au NPs before and after galvanic exchange with PtCl₄²⁻.

We performed a similar analysis with 15 nm diameter Au NPs before and after galvanic exchange. Figure 7.9.A and 7.9.B shows CVs under O₂ and N₂ conditions for 15 nm Au NPs before and after galvanic exchange with PtCl₄²⁻. In Figure 7.9.A, 15 nm diameter Au NPs with galvanic exchange show only a small increase in current for ORR relative to no exchange and no shift in potential. CVs under N₂ saturated solution for similar samples show no cathodic current for 15 nm Au NPs without galvanic exchange, confirming that the cathodic current was due to ORR. The CV of 15 nm Au NPs after galvanic exchange under N₂ condition displayed a small cathodic current likely due to a small amount of HER due to a minimal amount of Pt exchange. In this case the current is low because there is less galvanic exchange between 15 nm Au NPs and PtCl₄²⁻ due to the size dependence on the galvanic exchange reaction.

Additionally we tested by UV-visible spectra the change in the Au localized surface resonance (LSPR) band absorbance before and after galvanic replace reaction. We observed a large change in absorbance for 4 nm diameter citrate-coated Au NPs after galvanic replacement in comparison with Au NPs of 15, 50 and 128 nm. The reduction in the absorbance of 4 nm Au

Figure 7.9. CVs in 0.5 M H_2SO_4 at scan rate 0.01 V/s for 15 nm Au NPs before and after galvanic exchange with PtCl_4^{2-} . (A) under O_2 and (B) under N_2

NPs compared to the other sizes is again consistent with small sizes being more prone to galvanic replacement. In Figure 7.1., the blue solid plot is for 4 nm Au NPs before galvanic replacement the red solid plot is after galvanic replacement 3 min and the black dotted plot is after galvanic replacement 24 hr. There is a clear change in the Au LSPR band after exchange. In contrast, Frames B, C, and D, corresponding to the UV-vis spectra of 15, 50 and 128 nm Au NPs, respectively, do not show any significant changes to the optical properties following galvanic replacement.

7.4. Conclusions

In summary, we have described a strong size dependence on galvanic replacement reactions, using exchange of citrate-coated Au NPs with PtCl_4^{2-} as a model system since it is not generally favored. Citrate-coated 4 nm diameter Au NPs are more prone to the galvanic replacement reaction as compared to 15 nm, 50 nm, and 128 nm diameter Au NPs. We believe the driving force for this reaction is the decrease in Au oxidation potential with decreasing NP size and the ability of small metal NPs to catalyze metal deposition. While more details must be worked out, this study clearly shows that metal NPs have unique reactivity that is not observed in bulk systems. This fact could result in new strategies for modification of the composition of metallic NPs, especially for metal systems whose galvanic replacement is not thermodynamically favorable in bulk systems.

8.1. Summary

This dissertation focused on oxidation of highly unstable <4 nm diameter gold nanoparticles 800 mV negative of the bulk oxidation potential, effect of surface charge and electrode material on the size-dependent oxidation of surface-attached metal nanoparticle, a large negative potential shift and ultra sharp voltammetry of 1.5 nm diameter citrate-coated Au nanoparticle, a size-dependent electrochemical precipitation of citrate-coated Au NPs, and a size-dependent galvanic replacement reaction.

The key conclusions from the research in Chapter III are:

- The dramatic negative thermodynamic shift in the oxidation potential for <4 nm diameter Au NPs. The oxidation was as large as 850 mV negative of the value for bulk Au for the smallest NPs synthesized. The lowest oxidation potentials observed are consistent with 1–2 nm diameter Au NPs on the basis of the Plieth equation. While the details of the oxidation reactions involved (3e, 1e, and chemical) are not well understood, the data fit best with the Plieth equation for a process involving one or an average of 1.5 electrons.
- The oxidation of the smallest Au NPs in the presence of Br⁻ and Cl⁻ exhibits less dependence on the halide used, which is very different from bulk Au

behavior. While more details must be worked out, this study clearly shows the remarkable difference in reactivity and large decrease in stability for small metallic nanostructures.

The key conclusions from the research in Chapter IV are:

- This study shows two very different and important electrode effects that can significantly alter the oxidation potential of metal NPs. First, the presence of the positively charged APTES linker on glass/ITO/APTES electrodes at low pH (1–3) greatly decreased the peak oxidation potential for Au (as much as 155 mV) and Ag NPs that were greater than about 10 nm in diameter relative to the more neutral glass/ITO, glass/ITO/MPTMS, and glass/ITO/APTES (pH 7) electrodes.
- For smaller Au NPs of 4–6 nm in diameter and Ag NPs of 9 nm diameter, the E_p value was independent of surface charge.
- The increased stability for Au NPs directly on glass/ITO occurred similarly for both electrodeposited Au NPs and chemically synthesized, drop-cast deposited Au NPs, confirming that the method of Au NP synthesis does not play a role in the E_p value; electrostatic effects dominate.
- The third important finding from this work is that the underlying electrode material has an effect on the oxidation potential of metal NPs even when there is a similar linker present. For Ag NPs of 9 nm average diameter attached to various electrodes electrostatically through similar amine-terminated linkers, the oxidation order follows as Au ~ Pt > GC > glass/ITO. This follows the order of work function, except that the Au and Pt are reversed. Electrostatic effects were ruled out in this case, since the E_p of 9

nm diameter Ag NPs is independent of surface charge. Inter Alloying and aggregation was also ruled out due to the presence of the linker and well-dispersed, separated NPs on the surface.

The key conclusions from the research in Chapter V are:

- We have reported for the first time the electrooxidation of Au NPs in the sub 2 nm regimen.
- We are validating LSV technique as a powerful technique in the size analysis of citrate coated nanoparticles in the range of 1 to 4 nm.
- We are showing for the first time sharp peak shape for the electrooxidation of Au NPs with average diameter of 1.5 nm. We think that more studies must be done in order to correlate magic number clusters with the location of their E_p values.
- We are showing the enhancement of CO₂ reduction on 1.5 nm average diameter Au NPs

The key conclusions from the research in Chapter VI are:

- We have reported a size selection of citrate-coated Au NPs by electrochemical deposition on glass/ITO. We used an electric field cut-off ~2.0 V/cm for the deposition of both citrate-coated Au NPs with ≤ 33 nm, and ≤ 4 nm diameter, and ~1.5 V/cm for the deposition of ≤ 4 nm diameter. If the applied electric field is absent, we did not observe any measurable deposition of 4-33 nm diameter Au NPs on glass/ITO.
- The lowest deposition potential tested in this study of 0.4 V was applied to obtain the electrochemical deposition of Au NPs sizes < 4 nm. We believe

that future studies should be performed in order to understand more details about this phenomenon.

- Here, in this study we clearly show size selective deposition by controlling EPD potential. These results provide an excellent opportunity for the development of an alternative method for the attachment of Au NPs <4 nm without the use of capping organic ligands. Moreover, we believe that EPD of <4 nm diameter citrate-coated Au NPs and metallic NPs will open up new studies and applications in electrocatalysis.

The key conclusions from the research in Chapter VII are:

- We have described a strong size dependence on galvanic replacement reactions, using exchange of citrate-coated Au NPs with PtCl_4^{2-} as a model system since it is not generally favored. Citrate-coated 4 nm diameter Au NPs are more prone to the galvanic replacement reaction as compared to 15 nm, 50 nm, and 128 nm diameter Au NPs.
- We believe the driving force for this reaction is the decrease in Au oxidation potential with decreasing NP size and the ability of small metal NPs to catalyze metal deposition. While more details must be worked out, this study clearly shows that metal NPs have unique reactivity that is not observed in bulk systems. This fact could result in new strategies for modification of the composition of metallic NPs, especially for metal systems whose galvanic replacement is not thermodynamically favorable in bulk systems.

8.2. Future Directions

Future projects should include studies on the electrochemical oxidation of Au MPCs, Au₁₄₄ (1.6 nm) and Au₂₅ (0.9 nm). We believe that since these clusters are coated with an organic layer, it could be possible to remove it from the metallic core by ozone treatment. This procedure should oxidize the organic layer making possible the electrooxidation of a metallic bare NP. Having the bare NPs will allow the study of the electrooxidation of these small-sized NPs making an analytical ruler to better understand the relationship between E_p and the size of Au NPs.

In addition, we believe it would be important to pursue further studies on the Ostwald ripening of non-organic-ligand Au MPCs by LSV. Since bare Au NPs below 4 nm are unstable and easily oxidized at low E_p values, the resulting Au ions produced are prompt to be reduced on the surface of the slightly bigger sizes of Au NPs. Therefore, if two NPs with close related size are mixed together, it could be possible to observe the Ostwald ripening phenomenon by electrochemical methods.

Based on our previous studies on electrophoretic deposition, we suggest the tracking of the evolution in size following the synthesis of Au NPs using the Turkevich method. Since this method does not require a strong reducing reagent, the isolation of different NP sizes is highly doable. We believe that using the method will allow the understanding of the growth of the NPs size and the isolation of bare NPs with specific sizes without the presence of organic ligands.

Using electrochemical deposition, it is possible to isolate specific size NPs with diameters below 4 nm. Once the specific sized Au NPs are isolated, we suggest the study of their catalytic activity towards reactions such as CO reduction on the surface of Au NPs. By varying the reaction time during Au NP synthesis and controlling the EPD potential, it is possible to capture specific sized Au NPs. We believe that it would be important to systematically study different Au NP sizes for CO reduction.

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APPENDIX

Title: Oxidation of Highly Unstable <4 nm Diameter Gold Nanoparticles 850 mV Negative of the Bulk Oxidation Potential

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Title: Effect of Surface Charge and Electrode Material on the Size-Dependent Oxidation of Surface-Attached Metal Nanoparticles

Author: Rafael A. Masitas, Irina V. Khachian, Bryan L. Bill, Francis P. Zamborini

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CURRICULUM VITAE

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University of Louisville Louisville KY 40217, USA
Louisville KY 40208, USA Cell Phone: (502) 345-9832
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Education:

University of Louisville, Louisville, KY, USA 2009-2015
Doctor of Philosophy in Chemistry December, 2015
Mentor: Professor Francis P. Zamborini
Dissertation Title: "THE UNIQUE ELECTROCHEMICAL REACTIVITY OF
SMALL METAL NANOPARTICLES"

Universidad Peruana Cayetano Heredia, LIMA, PERU 2001
Bachelor of Science, Chemistry

Publications:

1. "Oxidation of Highly Unstable <4 nm Diameter Gold Nanoparticles 800 mV Negative of the Bulk Oxidation Potential". Masitas, R. A.; Zamborini, F. P. *J. Am. Chem. Soc.* **2012**, *134*, 5014-5017
2. "Effect of Surface Charge and Electrode Material on the Size-Dependent Oxidation of Surface-Attached Metal Nanoparticles" Masitas, R. A.; Khachian, I.V.; Bill, B. L.; Zamborini, F. P. *Langmuir* **2014**, *30*, 13075-13084
3. "One-to-One Correlation between Structure and Optical Response in a Heterogeneous Distribution of Plasmonic Constructs" Fang, A.; White, S. L.; Masitas, R. A.; Zamborini, F. P.; Jain P. K. *J. Phys. Chem. C* **2015**, *119*, 24086-24094
4. "An electrophoretic low pass filter for assembling ultra-small gold nanoparticles onto an indium tin oxide electrode" (manuscript in preparation)
5. "A size-dependent galvanic replacement reaction" (manuscript in preparation)
6. "Large negative potential shift and ultra sharp voltammetry of sub 2 nm diameter Au nanoparticle" (manuscript in preparation)

Presentations:

1. "Selective Deposition of 1-2 nm Diameter Au Nanoparticle onto Electrode Surfaces by Migration" The Pittsburgh Conference, (Pittcon), New Orleans, LA, March 9, 2015 - TALK by Rafael Masitas
2. "Electrophoretic Deposition of Citrate Coated Au Nanoparticles on ITO Substrate and Enhancement of Voltammetric Size Analysis" Southeastern Regional Meeting American Chemical Society, (SERMACS), Nashville, Tennessee, October 19, 2014 – TALK by Rafael Masitas
3. "Effect of Synthesis Method and Electrode Material on the Oxidation Potential of Metal Nanoparticles" The Pittsburgh Conference, (Pittcon), Chicago, Illinois, March 3, 2014 - TALK by Rafael Masitas
4. "Exploring the Unique Electrochemical Reactivity of Metal Nanoparticles" Electrochemistry Gordon Research Seminar and Gordon Research Conference, Ventura, California, January 4 – 10, 2014 – POSTER by Rafael Masitas
5. "Voltammetric Observation of the Oxidation Potential of Au₂₅ and Au₁₄₄ Clusters" 246th American Chemical Society, (ACS), National Meeting & Exposition, Indianapolis, Indiana, September 9, 2013 – TALK by Rafael Masitas
6. "Oxidation of Highly Unstable < 4 nm Diameter Gold Nanoparticles 850 mV Negative of the Bulk Oxidation Potential". The Pittsburgh Conference, (Pittcon), Orlando, Florida, March 11, 2012 - TALK by Rafael Masitas

7. "Ag Nanoparticles Attached to ITO as an Electrocatalyst for Oxygen Reduction Reaction". 2011 Kentucky Statewide Workshop: Renewable Energy & Energy Efficiency, Louisville, Kentucky, March 14, 2011 – POSTER by Rafael Masitas
8. "Ag Nanoparticles Attached to ITO as an Electrocatalyst for Oxygen Reduction Reaction". American Chemical Society Regional Meeting, 42nd Central Regional Meeting, (CERM), Indianapolis, Indiana, June 8, 2011 – TALK by Rafael Masitas
9. "Altering the Electrocatalytic Activity of Au Nanoparticles by Organomercaptan Self-Assembly and Oxidative Stripping Processes". Southeastern Regional Meeting American Chemical Society, (SERMACS), Richmond, Virginia, November 15, 2011 – TALK by Rafael Masitas

Research Experience:

Graduate Research Assistant

University of Louisville, Department of Chemistry, Louisville, KY 2009-present

As a graduate research assistant, the main focus of my research was the study of the electrochemical properties of 1-4 nanometers diameter Au nanoparticles (NPs) and be the mentor of graduate and undergraduate students. The result of my research is summarized in two papers already published, the first one in *Journal of the American Chemical Society* and the second one in *Langmuir*. Also I have in this moment three additional papers in preparation to be

summitted. In my first paper published, I discovered the dramatic change of 850-450 mV negative of the bulk Au oxidation peak near to 850 mV in the oxidation potential (E_p) for Au NPs below 4 nm. The lowest oxidation potential observed are consistent with 1-2 nm diameter Au NPs on the basis of the Plieth equation. In my second paper published, I discovered the effect of surface charge and electrode material on the size dependent oxidation of Au and Ag NPs. This study show two different electrode effect. First, the presence of the positively charged APTES linker on glass/ITO/APTES electrodes at low pH (1-3) greatly decreased the peak oxidation potential for Au and Ag NPs that were greater than about 10 nm in diameter relative to the more neutral glass/ITO, glass/ITO/MPTMS and glass/ITO/APTES (pH 7) electrodes. The second finding from this work is that the underlying electrode material has an effect on the oxidation potential of metal NPs even when there is a linker present.

My three additional papers to be summited are focus in galvanic exchange reaction, electro oxidation of Au₂₅ and Au₁₄₄ and size selection of citrate coated Au NP by electrophoretic deposition. In the first paper I am describing the galvanic exchange reaction between PtCl₄²⁻ and Au NPs on base to the change of the E_p value when the Au NP decrease on size. Sizes below 12 nm are more prone to galvanic exchange reaction. In the second paper I found the E_p values for the electro oxidation of Au₂₅ (0.9 nm diameter) and Au₁₄₄ (1.6 nm diameter) clusters. The correlation between E_p value and NP size will make possible to develop an analytical tool for size analysis by potentiometric method. In the last paper, I am presenting electrophoretic deposition as a new approach to deposit different sizes of Au NPs, on base to the selection of potential. My result

indicated that I am able to deposit Au NPs below 4 nm on the surface of a Glass/ITO electrode.

As a mentor my work included the training of students on techniques such as Linear Sweep Voltammetry (LSV), Cyclic Voltammetry, Chronocoulometry (CC), UV-Vis spectroscopy, Scanning Electron Microscopy (SEM), synthesis of metallic NPs and functionalization of electrodes with organic linkers. My students were trained in the preparation of their own posters and in the presentation of their own research. The results of this mentoring activity include one Master student, two graduate students that are following my research, two Bachelors in chemistry applying to graduate school in chemistry and one paper with two of my students. Additional duties and responsibilities to my research include, webmaster and person in charge for the maintenance of two potentiostats, CHI 660E and 620A.

Technical Skills

Electrochemical methods: Voltammetry, Chronoamperometry, Chronocoulometry

Microscopy: Atomic Force Microscopy (AFM), and Scanning Electron Microscopy (SEM).

Optical Methods: Ultraviolet-visible Spectroscopy (UV-VIS), Fluorescence Spectroscopy, Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Atomic Absorption Spectroscopy (AAS), and Infrared (IR) Spectroscopy.

Others: Nuclear Magnetic Resonance (NMR), Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-TOF) and Gas Chromatography.

Analysis of Food Products: Mojonnier (Fat), Gerber, Soxhlet, MilkoScan S50 (TS, FT and NTS), Refractometers RFM 742, Color using Hunter L, A and B, Kjeldahl (Buchi system), Viscometer, Titration by Titrino-Metrohm and others.

Teaching Experience:

My teaching experience is divided mainly in two parts, my experience as an instructor and teaching assistant (T.A.) and my mentor activity with graduate and undergraduate students.

Instructor

University of Louisville at Panama, Panama Summer 2012

As an instructor at University of Louisville at Panama, my duties and responsibilities involved, preparing classes, exams, homework, labs practices, lecturing, grading of exams, homework and lab reports.

CHEM 201: General Chemistry I – Overseas program (Instructor) 2012

CHEM 207: Intro to Chem Analysis I – Overseas program (Instructor) 2012

Teaching Assistant and Guest Lecture

University of Louisville, Department of Chemistry, Louisville, KY 2009-2012

As a Teaching Assistant at University of Louisville, my duties and responsibilities involved, teach labs practices, office hours to meet with students, grading of lab report and quizzes. As a Guest Lecture, I did the lecturing of one class for Undergraduate level.

CHEM 529: Synthesis and Analysis II (Guest lecture) 2012

CHEM 209: Intro to Chem Analysis III (Teaching Assistant)	2010
CHEM 210: Intro to Chem Analysis IV (Teaching Assistant)	2010
CHEM 343: Organic Chemistry Lab I (Teaching Assistant)	2009

Universidad Peruana Cayetano Heredia (UPCH) 1999-2000

As a Teaching Assistant at Universidad Peruana Cayetano Heredia, my duties and responsibilities involved, teach labs practices and grading of lab reports.

Elements of Physical Chemistry (Teaching Assistant)	1999 -2000
Organic Chemistry I (Teaching Assistant)	1999 -2000

Mentoring Undergraduate and Graduate Students

University of Louisville, Department of Chemistry, Louisville, KY 2010-present

Undergraduate Students

David Greene III, Lyndsay Kissell, Phuong Lu, Nathan Hughes, Titay Ayano, Bryan Bill, Kevin Elmer, and Hannah Draver. They were trained in citrate-coated Au NPs synthesis, UV- Visible Spectroscopy and Linear Sweep Voltammetry. As a result of their research my students presented the next list of posters:

David Greene III - "Electrochemical Oxidation of Gold NPs Synthesized Directly on Indium-Tin-Oxide-Coated Glass Electrodes" – Undergraduate Symposium at University of Kentucky, Lexington, Kentucky, April 15, 2011

Titay Ayano (REU Student) – "Electrochemical and Optical Properties of Chemically-Synthesized Au NPs Ranging from Below 4 nm to 30 nm in Diameter" -Chemistry & Structural Biology Research Experience for Undergraduates University of Louisville, Louisville, Kentucky, July 31, 2012

Bryan Bill (REU Student) – “Effect of Electrode Material on the Oxidation Potential of 9 nm Diameter Ag NPs” – Chemistry & Structural Biology Research Experience for Undergraduates University of Louisville, Louisville, Kentucky, July 31, 2013. Additionally to the poster, He is co-author in the paper- “Effect of Surface Charge and Electrode Material on the Size-Dependent Oxidation of Surface-Attached Metal Nanoparticles” Masitas, R. A.; Khachian, I.V.; Bill, B. L.; Zamborini, F.P. *Langmuir* **2014**, 30, 13075-13084

Kevin Elmer (REU Student) - “Exploring the Effect of Gold Nanoparticle Concentration on the Electrooxidation Potential of Silver NPs” – Chemistry & Structural Biology Research Experience for Undergraduates University of Louisville, Louisville, Kentucky, July 31, 2014

Graduate Students

Irina Khachian, Dhruba Pattadar, and Stacy Allen. They were trained in citrate-coated Au NP synthesis, UV-VIS Spectroscopy, Linear Sweep Voltammetry, Cyclic Voltammetry and Scanning Electron Microscopy. As a result of their research my students are co-authors in the next list of papers.

Irina Khachian – “Effect of Surface Charge and Electrode Material on the Size-Dependent Oxidation of Surface-Attached Metal NPs” Masitas, R. A.; Khachian, I.V.; Bill, B. L.; Zamborini, F.P. *Langmuir* **2014**, 30, 13075-13084

Dhruba Pattadar – “A size-dependent galvanic replacement reaction” (In preparation)

Stacy Allen – “An electrophoretic low pass filter for assembling ultra-small gold nanoparticles onto an indium tin oxide electrode” (In preparation), and “Large

negative potential shift and ultra sharp voltammetry of sub 2 nm diameter Au nanoparticle” (manuscript in preparation)

Industrial Experience:

ALS LABORATORY GROUP

2008-2009

Marketing Executive in Environmental Division

- Responsible to develop new analytical techniques for solid, water and air samples on base to the requirements of the market.
- Responsible for the market grow of Environmental Division.

AJEGROUP

2007–2008

Chief of Quality Assurance

- Supervised the line of production of non alcoholic beverage, such as sodas, juices, isotonic beverage, and products based on soy.
- Audit team leader.

NESTLÉ, PERÚ

2002-2007

Quality Coordinator Analyst - Methods Specialist-Chemistry

- Responsible for the Physical Chemistry laboratory in the factory.
- Responsible for results of the Test Inter-laboratories.
- Responsible for the training of analyst at the production lines
- Technical analytical support in the division of applications and development in ice cream, spices, milk, candies, chocolates and cans.
- Validation of In-house methods. TS in Milk.

CAJAMARQUILLA REFINERY (VOTORANTIM METAIS)

2001

Co-op Main laboratory

- Analysis of metals and water with Inductively Coupled Plasma Mass Spectrometry (ICP), Atomic Absorption Spectroscopy (AAS) and Ultraviolet Visible Spectroscopy (UV / VIS).

IMARPE (National Institute of Sea of Peru)

2000

Co-op Division of evaluation of contamination of sea water.

- Analysis of metals in oil with Atomic Absorption Spectroscopy (AAS), liofilization and treatment of samples for microwave analysis.

Awards:

Research Tuition Award – University of Louisville, August 2014 to May 2015

Research Tuition Award – Conn Center for Renewable Energy Research, August 2011 to August 2013

Golden Key (International Honor Society) member

5 consecutive years with classification “A” Higher performance in Interlaboratories Test, Nestle P-test (522 factories and external laboratories around the word) from 2002 to 2006.

Languages:

English and Spanish