Electrochemical characterization of surface-immobilized metal nanostructures: stability, atomic level doping, catalysis, and sensing applications.

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ELECTROCHEMICAL CHARACTERIZATION OF SURFACE-IMMOBILIZED METAL NANOSTRUCTURES: STABILITY, ATOMIC LEVEL DOPING, CATALYSIS, AND SENSING APPLICATIONS

By

Badri Prasad Mainali

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

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Department of Chemistry

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ELECTROCHEMICAL CHARACTERIZATION OF SURFACE-IMMOBILIZED METAL NANOSTRUCTURES: STABILITY, ATOMIC LEVEL DOPING, CATALYSIS, AND SENSING APPLICATIONS

By

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A Dissertation Approved on

July 21, 2021

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Dr. Craig A. Grapperhaus

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Dr. Gamini Sumanasekera
DEDICATION

This dissertation is dedicated to my lovely and wonderful parents:

my father Dilli Ram Mainali
my mother Tulasa Devi Mainali

my beloved wife and children:

my wife Asmita Parajuli
my son Arnab Mainali
my daughter Ayra Mainali

and all my supportive family members
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My special thanks go to my esteemed parents, beloved wife Asmita Parajuli, and my lovely children Arnab Mainali and Ayra Mainali who love, encourage, and support me in all the moments of my life.
ABSTRACT

ELECTROCHEMICAL CHARACTERIZATION OF SURFACE-IMMOBILIZED METAL NANOSTRUCTURES: STABILITY, ATOMIC LEVEL DOPING, CATALYSIS, AND SENSING APPLICATIONS

Badri Prasad Mainali

July 21, 2021

This dissertation has two main themes. The first theme involves voltammetric analysis of the stability of Au nanoparticles (NPs) under electrochemical and thermal treatment as a function of size, ligand stabilizer, and atomic composition. The second theme involves the use of Au NPs, electrophoretic deposition (EPD), and anodic stripping voltammetry (ASV) for electrochemical detection of analytes.

The electrochemical size stability of 4.1, 15.1, and 50.3 nm average diameter Au NPs upon treatment with multiple electrochemical oxidation-reduction cycling in acidic electrolyte is monitored by observing changes in the peak oxidation potential \( (E_p) \) in ASV and the electrochemically measured surface area-to-volume ratios (SA/V) of the Au NPs. The Au NPs exhibit size-dependent size stability. The ripening rate depends on cycling scan rate, NP coverage on the electrode, and anodic polarization. Also, the NPs take part in a combination of anodic dissolution and electrochemical Ostwald ripening as the
mechanism for ripening. The rate and extent of thermal ripening also depends on the Au NP diameter. Au NPs of 0.9 nm and 1.6 nm diameter begin to sinter at 70-80 °C while 4.1 nm diameter Au NPs remain stable when heated up to 400 °C for 60 minutes. The $E_p$ in ASV tracks the Au NP size changes, where the ratio of peak currents for sintered size and original size as a function of temperature provides the sintering transition temperature, which is 109, 132, and 509 °C for 0.9 nm, 1.6 nm, and 4.1 nm diameter Au NPs, respectively.

The stability of citrate-coated Au NPs against electrooxidation increases with increasing size of the NPs. This trend becomes opposite when the NPs are coated with alkanethiolate self-assembled monolayers (SAMs). The Au oxidation current measured by CV and chronocoulometry (CC) follows the order of 50.3 nm > 15.1 nm > 4.1 nm Au NPs, and this result is supported by UV-Vis combined with CC experiments. The NP composition plays an important role in the catalytic activity and stability towards the oxygen reduction reaction (ORR) in alkaline solution. Atomic level doping of 1.6 nm diameter Au NPs with 1-2% Ag by anti-galvanic replacement (AGR) dramatically improves the ORR of the Au NPs to a level similar to Ag NPs, but also dramatically improves the stability. In terms of synthesis, the work on AGR shows successful atomic level doping of 1.6 nm Au NPs with 1-2% Ag and Cu, where the cluster size remains stable during doping and the Ag or Cu atoms can be removed and put back on the clusters multiple times.

Another important discovery in this dissertation involves the development of a unique electrochemical sensor that employs 4.1 and 15.1 nm diameter Au NPs, EPD, and ASV as the signal for the detection of aqueous Cr(III) and melamine. Sensing is based on
the selective binding of analyte to the citrate-stabilized Au NPs, which causes a decreased electrophoretic mobility of the Au NPs. This leads to a decreased amount of EPD of the Au NPs, which is detected by ASV. The decrease in peak current relative to the peak current with no analyte is linear with analyte concentration. The method detects Cr(III) and melamine with detection limits of 15 and 45 ppb, respectively and even 1 ppb by decreasing the concentration of Au NPs relative to analyte concentration.
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CHAPTER I

INTRODUCTION

1.1. Research Goals and Overview

The primary goal of this research was to study the electrochemical and thermal stability of Au nanoparticles (NPs) as a function of size, ligand stabilizer, and metal composition by anodic stripping voltammetry (ASV), cyclic voltammetry (CV), chronocoulometry (CC), and/or combination of them. This goal also involves the study of stability towards oxygen electroreduction by AuAg nanostructures formed by atomic level doping of sub-2 nm Au NPs with Ag. A second goal was to combine electrophoretic deposition (EPD) and ASV for electrochemical sensing of analytes (trivalent chromium and melamine) in aqueous medium by using Au NPs.

We studied electrochemical and thermal stability under a variety of electrochemical conditions\(^1\) and temperatures. Our previous work showed that the oxidation potential of Au NPs decreases with decreasing size.\(^2\)-\(^3\) This can be monitored by ASV and can therefore act as an electrochemical size analysis tool. Also, the combination of CV and ASV for electrode-attached Au NPs can provide the surface area-to-volume ratio (SA/V), which also allow electrochemical size determination using simple geometry.\(^4\) In these projects, we are using those size analysis tools to study size transformations (size stability) that can occur in electrochemical environments and at high temperature. We focus on sub-4 nm
diameter Au NPs/NCs, which generally exhibit very high reactivity and instability. For stability study of metal (Au) NPs as a function of ligand stabilizer, weakly coated Au NPs are purposely coated with thiols which are common ligand stabilizers for metal NPs/NCs. Studying the role of thiol on electrochemical stability of metal NPs is important due to widespread employment of the thiol coated Au NPs/NCs in thin film applications, catalysis, and sensing where the electrochemical dissolution behavior of the NPs/NCs is crucial. For atomic level doping of Au with Cu and Ag, anti-galvanic replacement (AGR) reaction in thiol-coated Au clusters has been previously demonstrated by several researchers.\textsuperscript{5-6} Recently, our group looked at the AGR in weakly-coated Au clusters electrochemically due to the ease of electrochemical characterization of these clusters.\textsuperscript{7} The electrocatalytic activity and stability for weakly-coated clusters before and after atomic level doping can be easily studied by our methods and these clusters should be more reactive and highly promising for electrocatalysis applications. The electrochemical methods allow us to study these Au clusters directly on common electrode surfaces, which is not generally possible by most electron microscopy and spectroscopy methods.

We studied electrochemical sensing of trivalent chromium and melamine by a combination of ASV and EPD of Au NPs. ASV has for many years been used for electrochemical detection, mainly for trace metal analysis. Also, Au NP-analyte specific binding interactions has been used for many years as an optical based detection strategy. Here we develop a new sensing method that involves Au NP-analyte binding as with optical methods, but then utilized EPD to attach the Au NPs to an electrode and ASV to detect the amount of Au NPs that attach. This allows us to use an electrochemical method to detect analyte-Au NP binding rather than optical and the EPD part allows both
amplification of the signal and discrimination between different analyte concentrations. We directly compare the electrochemical method to optical detection, highlighting the benefits of not needing plasmonic NPs, and not being limited by size and type of NPs that can be used. Also, the method is fast, simple, cheap, and highly sensitive.

Chapter I of this dissertation provides the general background information, theory, and previous research findings related to metal NPs, along with the stability, catalytic, and sensing behavior of metal NPs. Chapter II describes the experimental procedures and common characterization tools and techniques used in this research work. Chapters III-V of this dissertation describe the use of CV, ASV, and CC to characterize the size stability of weakly-stabilized Au NPs under different electrochemical conditions, at different temperatures, and as a function of ligand stabilizers respectively. Particularly, Chapter III describes the size-dependent ripening of Au NPs through electrochemical surface oxidation-reduction cycling in acidic electrolyte. Chapter IV describes the thermal sintering behavior of sub-4 nm diameter weakly-stabilized Au NPs/NCs. Chapter V focuses on the size-dependent electrooxidation of citrate-coated Au NPs coated with alkanethiolate self-assembled monolayers (SAMs). Chapter VI deals with the electrochemical stability and reactivity of bimetallic AuCu and AuAg nanostructures formed by atomic level doping of sub-2 nm diameter Au NCs with Cu and Ag via AGR reaction. Chapter VII describes the use of Au NPs for sensing of Cr(III) and melamine by the combination of Au NP-analyte binding, electrophoretic deposition (EPD) and ASV analysis. Chapter VIII summarizes the research in this dissertation and discusses possible future directions.
1.2. Motivation and Objective

The motivation behind this research was aimed at better understanding of the electrochemical properties and chemical reactivities of weakly-stabilized ultra-small metal nanoparticles (NPs) or nanoclusters (NCs) by using spherical Au nanostructures as the model system. The issue of NP stability is very important as it has a direct impact on their various applications such as in catalysis, sensing, and nanoelectronic devices. Previously, the stability study of the metal NPs has been mostly carried out by using sophisticated microscopic and spectroscopic techniques which are often tedious, time consuming, unavailable, and costly. For most of these studies, NPs must be analyzed by mobilizing them on specific substrates which often requires complex sample preparation and analysis. Our goal was to perform these studies by the utilization and development of electrochemical techniques by directly attaching the NPs on the conventional electrode surfaces. Using the electrochemical techniques, a systematic study of the stability of surface-immobilized Au NPs was carried out under different conditions of electrochemical oxidation-reduction cycling\(^1\) and thermal treatment. Our findings provide useful information about the electrochemical stability and reactivities of these NPs upon different treatment conditions. This sort of information provides fundamental understanding about the behavior of metal NPs, which is useful for promoting the real-life applications of metal NPs.

Our other motivation involved the size-dependent electrochemical oxidation behavior of weakly coated Au NPs in presence of stronger thiol ligands. The weakly coated ligands such as citrate, phosphines, and phosphoniums offer easy size-dependent electrooxidation behavior of the metal NPs. Contrary to this, the stronger thiol ligands in
the form of self-assembled monolayers (SAMs) on the NPs surface strongly prevent them from the electrooxidation due to strong nature of Au-S bond. Also, the stability of thiol SAMs is greater on roughened Au surfaces and smaller NPs compared to 2-dimensional (2D) smooth films suggesting greater SAM stability on highly curved structures. However, there is lack of study carried out on the stability of thiol SAMs on the 3D Au NPs. It would be interesting to study the size-dependent electrooxidation behavior of Au NPs as a function of thiolate binding due to widespread applications of thiolates as stabilizers for Au NPs. Our group has developed electrochemical methods to study the stability of Au NPs against oxidative dissolution, electrochemical ripening, and oxidation-reduction cycling. We wanted to employ those techniques to compare the stability of thiolate-coated Au NPs to citrate-coated Au NPs but also compare the size-stability for the two different stabilizers. Our prior work shows a clear decrease in stability with decreasing size but prior SAM work suggested increasing stability with decreasing size. The relative stabilities as a function of ligand stabilizers can be studied by electrochemical methods, including ASV, CV, and CC, and combination of ultraviolet visible spectroscopy (UV-Vis) and CC. Several applications of metal NPs and clusters involve alkanethiol coatings. It is important to understand how the size affects the stability in terms of dissolution of NPs coated with alkanethiolates. Fundamental knowledge about size-dependent stability against oxidative dissolution is important to further promote applications of metal NPs.

Another motivation for this study was to understand the controlled doping of sub-2 nm Au NPs with Cu and Ag via AGR reaction. Galvanic exchange is a mild and facile way of synthesizing bimetallic alloyed or core/shell nanostructures by which their optical and electrochemical properties can be altered easily. Previously, the atomic level doping of
metal NPs/NCs was mostly carried out by co-reduction of metal ion precursors with suitable reducing agent.\textsuperscript{14} Also, the doped nanostructures were mostly characterized by scanning transmission electron microscopy (STEM), transmission electron microscopy (TEM), X-ray methods, and mass spectrometry (MS). These characterization techniques are very expensive, tedious, and not widely available. Our motivation was to dope Au clusters at the atomic level, determine if AGR could do atomic level doping without altering the size of the clusters, and determine if ASV could be used as a tool for size and composition analysis, potentially as a substitute for TEM, MS, and X-ray methods. Then we could correlate ASV with any interesting properties, such as catalytic activity or improved stability.

Besides these, our motivation involves the use of citrate-stabilized Au NPs for sensing of Cr(III) and melamine in aqueous medium by a new electrochemical approach. We observed previously that aggregated NPs lead to a dramatic change in the ASV.\textsuperscript{15} We thought we could use this as a method to detect aggregation in aggregation-based sensing assays. The idea was to add analyte which caused the Au NPs to aggregate selectively in the presence of that analyte. Then we detect the aggregation by ASV as the signal instead of using UV-Vis. This allows smaller and non-plasmonic NPs to be used in the aggregation-based assay, broadening the type of metal for sensing. We later added the EPD to concentrate the Au NPs on the electrode for ASV analysis since it is easier than binding through linker. The EPD step is an important step for speeding up the reaction, determining analyte concentration, improving reproducibility, and lowering the detection limit. With controlled addition to colloidal citrate-coated Au NPs, the analytes limit the amount of Au NPs deposited onto the electrode during EPD by partial charge...
neutralization and/or aggregation of the Au NPs. The electrochemical signal response obtained from the electrooxidation or stripping of the Au NPs deposited on to the electrode during ASV is proportional to the analyte concentration which is useful for the selective, sensitive and reproducible detection of the analytes.

1.3. Introduction to Nanoparticles

Nanoparticles (NPs) are the particles of a matter whose size normally ranges from 1 to 100 nanometer (nm) in one dimension (length, width, diameter).\textsuperscript{16-17} NPs are generally comprised of metals, metal oxides, semiconductors, carbon, ceramics and polymers.\textsuperscript{18} NPs are available in various shapes such as nanospheres,\textsuperscript{4} nanochains,\textsuperscript{19} nanostars,\textsuperscript{20} nanoflowers,\textsuperscript{21} and nanofibers,\textsuperscript{22} which is possible due to the intrinsic crystal forming properties of the nanomaterials under various environments during synthesis. Metal NPs can be further categorized as individual or alloyed or core/shell NPs depending upon the nature of constituent atoms, composition, and atomic arrangement.\textsuperscript{23} Being at the transition level between bulk materials and atomic or molecular structures, NPs often exhibit phenomena that are not observed at either scale and therefore have markedly different optical,\textsuperscript{24} electrochemical,\textsuperscript{2} thermal,\textsuperscript{25} and magnetic\textsuperscript{26} properties as compared to their bulk counterparts. Such properties of metal NPs and their applications depend upon the nature of the metal, composition, size, shape, and stabilizing ligands.\textsuperscript{27} NPs in solution often have surfactant, polymer, or ligand stabilizers that affect oxidation potential and improve stability by preventing aggregation via interparticle electrostatic interaction or steric hindrance.\textsuperscript{28} Smaller-sized metal NPs (< 1 nm), also called nanoclusters (NCs), often show unique electrochemical and chemical reactivity compared to larger ones due to high surface area,
overall increase in the number of low coordination surface atoms and higher surface free energy.\textsuperscript{29,30} Also these NPs often tend to grow into the bigger and more stable ones by the lowering of surface free energy.\textsuperscript{30} Such a change in size and morphology of metal nanostructures leads to a substantial change in their electrochemical,\textsuperscript{30-31} thermal,\textsuperscript{32} plasmonic,\textsuperscript{33} and many other important properties.

\subsection*{1.4. Importance of Research on Metal Nanoparticles}

The behavior of metal NPs are totally different as compared to their bulk counterparts due to their high surface area-to-volume ratio (SA/V) and relatively large number of surface-active sites. Due to this, the optical,\textsuperscript{34} magnetic,\textsuperscript{35} thermal,\textsuperscript{36} chemical,\textsuperscript{37} and electrochemical\textsuperscript{2} properties of metal NPs are usually very different from the bulk materials and are strongly related to their size, shape, and morphology. The observation of such size effects raised expectations for the superior performance of nanomaterials compared to their bulk counterparts in many applications, if the size and the shape of the particles can be optimized in a rational way. Most of the alterations in properties of materials with the decrease in size are beneficial for various applications, such as CO\textsubscript{2} reduction,\textsuperscript{38} oxygen reduction reaction (ORR),\textsuperscript{39} CO oxidation,\textsuperscript{40} hydrogen evolution reactions (HER),\textsuperscript{41} nanoelectronics,\textsuperscript{20} photovoltaic applications,\textsuperscript{42} and numerous other electrocatalytic processes and biomedical applications.\textsuperscript{43} Due to these reasons, metal NPs have been of great scientific interest in regards of their shape, size, and composition-controlled synthesis with different stabilizers.\textsuperscript{44-45}
Metal NPs exhibit size and shape dependent electrochemical properties and reactivities which determine their catalytic and sensing applications accordingly.\textsuperscript{46-47} Sensing applications of Au NPs based on photoluminescence is pronounced as the size of a metal NP decreases from nanoparticle size to a cluster with few to tens of atoms.\textsuperscript{48} Au NPs also exhibit size-dependent optical properties such as fluorescence quenching.\textsuperscript{34, 49} Au NPs exhibit size dependent aggregation in various pH conditions as shown by Allen \textit{et al.} and Pattadar \textit{et al.}\textsuperscript{3, 15} Researchers have employed several NPs treatment strategies such as chemical and thermal treatment,\textsuperscript{50} ozone cleaning,\textsuperscript{51} and electrochemical oxidation-reduction cycling\textsuperscript{52} prior to their applications for removing the ligands and unwanted impurities from the surface. However, these cleaning strategies could cause alteration in the size and morphology of metal NPs affecting their desired reactivities and applications.

Because of the enormous application of metal NPs in various fields, the accurate characterization of these NPs is crucial to further broaden their applications. In literature, the most common NPs characterization techniques include scanning electron microscopy (SEM),\textsuperscript{4} transmission electron microscopy (TEM),\textsuperscript{53} X-ray photoelectron spectroscopy (XPS),\textsuperscript{54} energy dispersive X-ray (EDX) spectroscopy,\textsuperscript{7} X-ray diffraction (XRD),\textsuperscript{55} extended X-ray fine structure (EXAFS),\textsuperscript{56} X-ray absorption near edge structure (XANES),\textsuperscript{57} and mass spectrometry.\textsuperscript{58} These sophisticated high-vacuum characterization techniques are very costly and often time consuming, and not convenient for the routine analysis of metal NPs.\textsuperscript{59} Also, they do not provide some of the important information, such as the oxidation related properties. Understanding the oxidation relevant properties of metal NPs is very important as it would address the stability and reactivity of the NPs during their applications.\textsuperscript{3} The stability of metal NPs is also equally important as it determines
the reactivities towards oxidation and dissolution along with aggregation and size-dependent size transformations under various conditions. Therefore, developing simple and accurate electrochemical methods to better understand the metal NPs stability, reactivities, and sensing applications would be very helpful.

1.5. Chemical Synthesis of Metal Nanoparticles

1.5.1. Chemical Synthesis of Water-Soluble 4-50 nm Diameter Au NPs.

Metal NPs are generally prepared in the solution phase by reducing the metal salt solution as metal precursor in presence of a suitable stabilizing agent. Common reducing agents for reduction of Au ions to metallic Au during the synthesis are \(\text{NaBH}_4\), \(\text{H}_2\text{O}_2\), and citrate.\(^{62}\) The stabilizing ligand plays a critical role to control size, shape, and surface chemistry of the metal NPs. The stabilization is mainly achieved through electrostatic or steric repulsion between the NPs. Polymers or surfactants are commonly used as stabilizers for metal NPs. Besides these, ions and ligands, such as citrate,\(^{60}\) thiols,\(^{63}\) amines,\(^{64}\) phosphines,\(^{65}\) and biomolecules also act as stabilizing agents of metal NPs.\(^{66}\) Sometimes a desired ligand could be incorporated into the as-prepared metal NPs to alter the properties and functionality of NPs via ligand exchange.\(^{67}\) In certain cases, compounds used as ligands play a dual role of stabilizing agent and reducing agent. For example, citrate is used as reducing agent and stabilizer in the synthesis of 12-40 nm diameter Au NPs during the chemical synthesis at elevated temperature.\(^{62}\)

For last several decades, scientists have carried out the chemical synthesis of Au NPs with fine control in size, shape, and morphology. Efforts have also been carried out to modify the ligands and NP functionality. The most convenient and widely used
chemical synthesis of Au NPs dates back to 1951 by the so-called citrate route developed by Turkevich et al. Turkevich method was later modified for the synthesis of different sized spherical Au NPs by simply changing the citrate to Au salt ratio. A higher citrate-to-Au ratio produces smaller sized Au NPs due to faster nucleation. In addition to the citrate route, many other approaches have been developed to synthesize Au NPs in specific organic solvents or in the presence of different types of surfactants and reducing agents to fine-tune the morphology from nanocubes to hexagonal shapes, nanorods, and nanostars.

The chemical synthesis of Au NPs was further developed by different researchers with fine tune in size using different reducing agents. For example, Murphy and coworkers synthesized citrate-coated ~4 nm diameter Au NPs by the reduction of Au salt with sodium borohydride and extended their work on the seeded growth synthesis of Au NPs up to 40 nm in diameter using ascorbic acid. Later this method was modified to synthesize Ag, Pd, and Cu NPs. Many other researchers synthesized Au NPs using strongly bound thiol ligands as stabilizers, producing relatively smaller sized particles (<1 nm), which are also referred to as nanoclusters (NCs). With thiol ligand stabilizers, it is possible to produce Au NCs containing variable Au atoms such as Au₁₁, Au₂₅, Au₃₈, Au₁₄₄, and so on. In some cases, more weakly bound phosphine ligands are also utilized for the synthesis of ultra-small Au NPs or Au NCs.

1.5.2. Synthesis of Water-Soluble Weak Ligand Protected 1-2 nm Diameter Au NPs. Weakly-stabilized 1-2 nm diameter Au NPs are of special importance for many electrocatalytic applications due to: i) easy access of core Au atoms, ii) water solubility, and iii) low or null toxicity for biological applications. In 1993, Duff and coworkers carried out chemical synthesis of sub-2 nm diameter Au NPs that are stabilized with
tetrakis(hydroxymethyl)phosphonium chloride (THPC) ligands in water with narrow size distribution.\textsuperscript{77} In this method, the Au(III) salt was mixed with THPC in NaOH solution with a specific Au(III)/THPC ratio. When THPC reacts with NaOH, it generates HCHO, which reduces Au(III) ions to Au(0), forming Au NCs instantly (Figure 1.1). This method of synthesis has been used for various biological and chemical applications. After Duff’s work, several scientists have developed the synthetic strategy of weakly coated Au clusters with variable Au atoms. For example, Yao and coworkers more recently have reported the synthesis of Au\textsubscript{11} clusters using triphenylphosphine monosulfonate (TPPS) as a stabilizer and NaBH\textsubscript{4} as a reducing agent. Characterization of the Au NCs was carried out by mass spectrometry.\textsuperscript{78} Electrochemical characterization of these Au NCs was recently carried out Pattadar \textit{et al.} in our group.\textsuperscript{10}

\textbf{1.6. Characterization of Metal Nanoparticles}

A size analysis of metal NPs can be performed by several techniques such as UV–Vis spectroscopy,\textsuperscript{79} SEM,\textsuperscript{4} atomic-force microscopy (AFM),\textsuperscript{80} transmission electron microscopy (TEM),\textsuperscript{81} and dynamic light scattering (DLS).\textsuperscript{82} Microscopic methods suffer
from certain limitations such as they involve complicated sample preparation, high cost, long analysis time and they may also suffer from sample damage, especially for contact AFM or electron microscopies. UV–Vis spectroscopy is only useful for plasmonic NPs and provides a rough estimate of the size. DLS suffers from dominance of bigger-sized NPs over the smaller ones. Electrochemical methods benefit from simple operation, low cost, high sensitivity to size, and quick analysis times. This allows high throughput, the potential for good statistical analysis, and improved size resolution as well, especially for electrode-attached metal NPs, compared to electron microscopes. Previously, our group reported on the use of ASV to determine the size-dependent oxidation potential of Ag and Au NPs with the size range of 8-40 and 4-250 nm diameter, respectively, where smaller sized NPs are oxidized at lower potential. In addition, the combination of surface-sensitive electrochemical reactions as measured by CV and ASV can be used as an analytical tool to measure the electrochemical SA/V. Combined or individually, these techniques are ultimately useful to determine NP size, aggregation state, electrode-nanoparticle interactions, composition, and atomic arrangement. Recently, we showed that ASV is excellent for analyzing the effect of various electrochemical and chemical treatments, such as ozone treatment, oxidation-reduction cycling, and electrochemical Ostwald ripening, on the size stability of sub-2 nm diameter Au NPs. Thus, we can use electrochemical techniques to monitor the fate of NPs during these common NPs treatment processes. Electrochemistry also offers information relevant to the oxidation and stability of metal NPs while assembled on an electrode support, where the catalysis occurs. This is very challenging with electron microscopy.
For the last several years, the analysis of metal NPs by electrochemical methods has become more important and widespread. Electrochemical techniques allow cheap and simple operation, high throughput and fast method of analysis. A tremendous amount of information about metal NPs can be obtained by electrochemical approaches. Various electrochemical studies have been reported in the literature for metal NP analysis, including oxidation, electrodeposition, and single particle collisions. Besides this, electrochemical methods are also utilized for the controlled synthesis of individual or alloyed metal NPs such as electrochemical synthesis and electrophoretic deposition of Au NPs. This dissertation focuses on electrochemical studies of ultra-small weakly stabilized metal NPs in regards to their electrochemical and thermal ripening behavior under a variety of conditions, stability against oxidative dissolution when coated with different ligands, electrochemical reactivity, and stability following atomic-level doping, and electrochemical sensing applications.

1.7. Stability of Metal NPs

Stability of metal NPs is an important parameter to be studied as it determines several important electrochemical, chemical, and optical properties of them for applications such as in catalysis, sensing, and nanoelectronics. Under these NPs treatment and applications conditions, NPs cannot work as intended due to their reported size change. The most common mechanisms that NPs undergo during these changes include NPs dissolution, surface oxide formation, aggregation, and/or ripening. In some other instances, the NPs stability could be enhanced by change of stabilizing ligands and alloying. These studies were mostly carried out by sophisticated
microscopy or spectroscopy techniques. Our approach to study the NPs stability involves the use of electrochemical techniques as a substitute of the sophisticated microscopic or spectroscopic techniques. Results obtained from the electrochemical approach and the fundamental insights provided from these stability studies will be very important to extend the further applications of the NPs in several important areas of material science, and nanotechnology.

1.8. Oxidation of Metal Nanoparticles

Because of widespread applications of metal NPs in different areas of modern science, study of the oxidative properties of the NPs is very important. Oxidation is the chemical or electrochemical process by which a metal NP forms an insoluble surface oxide or is converted into soluble metal ion species in different oxidative environments or in the presence of different metal etching agents. Oxidation occurs during the corrosion of metal, and chemical synthesis of metal NPs. Oxidation of metal also takes place during electrocatalysis, and electrochemical sensing. This leads to the loss in desirable properties of the metal NPs. A better understanding of metal NP oxidation is needed to control their stability and promote their long-term use in heterogeneous catalysis and a wide spectrum of other nanotechnologies. For example, understanding metal NP oxidation properties could be useful to synthesize corrosion-resistant nanomaterials and design of NPs undergoing minimal sintering during catalysis.

The amount of oxidation of metal NPs is directly related to the Nernst equation, which correlates the half-cell potential to the standard potential and to the activities of the
electroactive species. For a redox couple \( \text{M(Ox)} + \text{ne} \rightarrow \text{M(Red)} \), the Nernst equation assumes the form of equation 1.1.

\[
E = E^\circ - (0.0592/n)\log\left(\frac{a_{\text{M(Red)}}}{a_{\text{M(Ox)}}}\right) \tag{1.1}
\]

where, \( n \) is the number of electrons transferred during the redox process, \( E \) is the half-cell potential (V), \( E^\circ \) is the standard redox potential of the metal, \( a_{\text{M(Ox)}} \) is the activity of the oxidized form of the metal and \( a_{\text{M(Red)}} \) is the activity of the reduced form of the metal.

Since the standard electrode potential is different for different metal/metal ion combinations, the oxidation potential of metal NPs is a function of the nature of the metal as well as the oxidative environment. The Nernst equation does not take into account the size of the metal NPs, which is another important factor that alters the \( E^\circ \).

1.9. Methods of NPs Assembly on the Electrode and Analysis by Stripping Voltammetry

Analysis of NPs by stripping voltammetry involves their oxidation at a certain applied potential in the presence of a suitable electrolyte. The current due to electrooxidation as a function of potential or time is recorded by a potentiostat. By proper analysis of the electrical signal, size, composition, aggregation and size transformation information of the metal NPs can be obtained. Before analysis, NPs are first immobilized onto the electrode surface by different approaches. The common approach for NPs attachment onto the electrode surface including the stripping voltammetry of metal NPs is as shown in Figure 1.2. The metal NPs can be attached to the electrode surface by four major approaches: (a) via molecular linker, (b) by direct drop casting on the electrode
Figure 1.2. Attachment of metal NPs to the electrode surface, (A) through molecular linker, (B) drop cast method, (C) electrophoretic deposition and (D) electrochemical deposition on electrode surface for stripping voltammetric analysis.
interactions via the linker while NPs can be mobilized on to the electrode simply by drop-casting the colloidal solution of the NPs on to the electrode surface. NPs can also be attached to the electrode surface by electrophoretic deposition while NPs can be directly synthesized on the electrode surface via electrochemical synthesis method. The different assembly methods of the metal NPs on the electrode surface determine many important electrochemical properties of metal NPs such as electrochemical oxidation potential and surface-to-volume ratio (SA/V).

After metal NPs are attached onto the electrode surface, their electrochemical characterization can be characterized by using linear sweep voltammetry (LSV). In LSV, the potential on working electrode is linearly increased with respect to a reference electrode in a 3-electrode set up. The blue curve in Figure 1.3 is a typical voltammogram for the oxidation of metal NPs. As the potential on the working electrode is linearly increased with time in presence of a suitable electrolyte, the NPs attached on to the electrode surface undergo electrochemical dissolution or stripping. Since the dissolution takes place due to oxidation of the NPs, LSV is also referred to as anodic stripping voltammetry (ASV). In case of Au NPs using Br$^-$ as oxidizing/etching agent, the electrochemical dissolution is represented by equations 1.2-1.3, where Au undergoes electrochemical dissolution into soluble Au complexes.

\[
\begin{align*}
\text{Au}^0 + 4\text{Br}^- &\rightarrow \text{AuBr}_4^- + 3e^- \quad (E^0 = 0.85 \text{ V vs NHE}) \quad (1.2) \\
\text{Au}^0 + 2\text{Br}^- &\rightarrow \text{AuBr}_2^- + e^- \quad (E^0 = 0.96 \text{ V vs NHE}) \quad (1.3)
\end{align*}
\]
Under a set of conditions, the peak oxidation potential (E<sub>p</sub>) in ASV as shown in Figure 1.3 is dependent upon the NPs size with smaller NPs showing lower E<sub>p</sub> as compared to the bigger ones (discussed in more details later). In case of Au NPs subjected to stripping in halide (Br<sup>-</sup>) containing electrolyte as in equations 1.2–1.3, the number of electrons transferred due to oxidation of Au is proportional to the area under the voltammogram of Figure 1.3C. The integrated area under the voltammogram peak (Figure 1.3C, yellow region) is called peak area which in turn is proportional the amount of Au present on the electrode surface that is dissolved during ASV.

**Figure 1.3.** Showing linear sweeping of potential on working electrode with time (A), typical linear sweep voltammogram (B), and voltammogram for stripping analysis of Au NPs (C).
1.10. Size Dependent Electrochemical Oxidation of Metal NPs

The oxidation potential ($E_p$) of metal NPs is primarily related to their size which is an important parameter to determine their stability. Besides size, $E_p$ also depends on the scan rate and electron transfer kinetics during electrochemical process. For a long span of time, both theoretical and experimental explanations have been reported for the study of size-dependent metal nanoparticle oxidation. In 1977, Henglein observed the standard potential of Ag clusters containing 1 and 2 Ag atoms to be -1.8 V and -1.0 V vs RHE respectively which is way below the oxidation potential of bulk Ag (+0.799 V vs RHE).\textsuperscript{96} After Henglein, Pleith in 1982 predicted the size-dependent oxidation potential of metal NPs based on the theoretical calculations and experimental observations (equation 1.4).\textsuperscript{30}

\begin{equation}
E_{\text{particles}} = \left( -\frac{2\gamma V_m}{ZF} \right) \left( \frac{2}{d} \right) + E_{\text{bulk}} \tag{1.4}
\end{equation}

where $\gamma$ is the surface stress of Au (1880 erg cm$^{-2}$), $V_m$ is the molar volume of Au (10.21 cm$^3$ mol$^{-1}$), $Z$ is the number of electrons transferred per atom oxidized, $F$ is Faraday’s constant, and $d$ is the diameter of the NP. The equation is derived based on the theoretical considerations of the changes in standard free energy ($\Delta G$) of a substance on moving from bulk form to nanoscale form and its correlation to the standard electrode potential. The equation predicts the oxidation potential of metal NPs to be decreasing with decreasing NP diameter by an amount proportional to 1/d. The size-dependent oxidation potential is an important parameter to characterize metal NPs as it directly relates to their stability against oxidative dissolution. Several other scientists also studied metal NP oxidation, mainly for NP arrays on electrode surfaces, in theory and experiment.\textsuperscript{97-101} For example, Compton and coworkers reported theoretically and experimentally the effect of Ag NPs size and coverage for the shift in oxidation potential.\textsuperscript{100} Sieradzki and their group reported both
theoretically and experimentally the size dependent stability of Pt NPs towards oxidation in acidic solution.\textsuperscript{101} It was found that Pt NPs size smaller than 4 nm were directly oxidized to \( \text{Pt}^{2+} \) whereas those higher than 4 nm in size formed Pt oxide. Brainina group studied the size dependent oxidation of Au, Ag and Bi NPs and compared their findings with the microscopic studies.\textsuperscript{97-98} In their work, the different metal NPs were immobilized on the surface of different carbon containing screen printed electrodes. Based on theoretical calculations and experimental studies, they found a negative shift in \( E_p \) with maximum current on transition from macroparticles to NPs, whereby they obtained good agreement between experiment and theory.

Based on Plieth theory\textsuperscript{30} and electrochemical Ostwald ripening studies on Ag by Brus and co-workers,\textsuperscript{102} Ivanova and Zamborini firstly observed the size dependent electrochemical oxidation of Ag NPs using ASV.\textsuperscript{46} They observed a negative shift in \( E_p \) of citrate-coated Ag NPs from 391 mV to 278 V when the size of Ag NPs decreased from \(~40\) nm to \(~8\) nm in diameter. The size of Ag NPs was also correlated with SEM and AFM imaging which were in general trend with the NPs determined based on \( E_p \). Later, Ivanova and Zamborini reported an approximately 100 mV negative shift in \( E_p \) for Au NPs as the size of the NPs decreased from 250 nm to 4 nm in diameter.\textsuperscript{2} The small sized 4 nm Au NPs were attached electrostatically to glass/ITO through an APTES linker while 8, 13, 23, and 249 nm average diameter NPs were directly synthesized on the electrode surface electrochemically. The oxidation of Au NPs was caused by halide containing acidic electrolyte solutions (equation 1.2 -1.3) and was found to follow size- dependent behavior. The shift in \( E_p \) was by 179 mV as the size of Au NPs decreased from 250 nm to 4 nm in diameter while the shift was 88 mV when the size was decreased from 8 nm to 4 nm. The
more significant decrease in $E_p$ between 8 nm and 4 nm Au NPs (i.e. difference in size by 4 nm in diameter) as against between 250 nm and 4 nm Au NPs (i.e. difference in size by 246 nm in diameter) in these two cases demonstrates the more dramatic shift in $E_p$ of Au NPs as the size of Au NPs becomes smaller and smaller. This observation is in accordance with Plieth prediction of the decrease in $E_p$ with decreasing NPs size. Masitas and Zamborini also studied the shift in the $E_p$ of citrate-coated Au NPs in less than 4 nm diameter range and observed a shift of ~850 mV from bulk Au $E_p$ with halide containing acidic electrolyte.\textsuperscript{103} In 2013, Buttry group studied highly purified different sized water soluble 2,2’-Bicinhoninic acid-capped Pd NPs using ASV in 0.1 M HClO\textsubscript{4} and 10 mM NaCl.\textsuperscript{99} They found that the $E_p$ shifted as a function of NPs size where bulk Pd oxidized at 0.70 V vs Ag/AgCl, while 1 nm diameter Pd NPs oxidized at 0.34 V. All these size-dependent studies for various metal NPs with their respective different sizes were fairly consistent with the $1/radius$ dependence as predicted by Plieth. More recently, Pattadar \textit{et al.} showed the size-dependent $E_p$ of Au NPs ranging from 1 nm to 50 nm in diameter\textsuperscript{10} where they observed a dramatic decrease in $E_p$ for NPs smaller than 4 nm i.e. ~0.45 V and ~0.22 V for 1.6 nm and 0.9 nm respectively (Figure 1.4).
This result also shows a good general agreement with Plieth prediction regarding dramatic decrease in $E_p$ of metal NPs with decreasing size. Besides size, NPs coverage, linker used for attaching NPs to the electrode surface, aggregation state, and method of attachment of NPs onto the electrode surface also determine the electrooxidation behavior of metal NPs to different extents.

**Figure 1.4.** Showing size-dependent electrochemical oxidation of Au NPs attached to glass/ITO via APTES linker in 10 mM KBr plus 0.1 M KClO₄.

1.11. Electrochemical SA/V for Size Analysis of Metal NPs

The peak oxidation potential ($E_p$) of metal NPs cannot always provide complete information about size of metal NPs. This is because besides size, $E_p$ also depends on the NPs coverage on the electrode surface, scan rate of ASV, and aggregation state of metal NPs. Additionally, $E_p$ remains the same for metal NPs above a certain size. For example, Au NPs assume almost similar $E_p$ (~0.9 V vs Ag/AgCl in Br⁻ containing
electrolyte) which is close to the $E_p$ for bulk Au as the size goes above 25-30 nm in diameter. To address these issues, NP size can also be alternatively tracked based on the electrochemically-measured surface area-to-volume ratio (SA/V) (equation 1.5) where

$$\text{SA/V} = \frac{(4\pi r^2)}{(\frac{4}{3}\pi r^3)} = \frac{3}{r} \text{ and } r = \text{radius of } \text{NPs.}^4 \quad (1.5)$$

SA of the Au NPs can be calculated by integrating the $\text{Au}_2\text{O}_3$ reduction peak area measured from CV in acidic solution (equation 1.6). Performing CV of Au NPs in acid containing electrolyte, Au is oxidized to $\text{Au}_2\text{O}_3$ during oxidation process (1st half cycle) while $\text{Au}_2\text{O}_3$ is reduced back to Au (2nd half cycle) during reduction process. After CV, the total volume of Au NPs can be obtained by integrating the peak representing the oxidation of Au during ASV in halide containing electrolyte as given by equations 1.2-1.3 (Figure 1.5).

$$\text{Au}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Au} + 3\text{H}_2\text{O} \quad (1.6)$$

Sharma et al. in our group recently measured the SA/V of a metal NPs for the size analysis of spherical metal NPs. The NPs size of several different sized metal NPs measured by this method shows pretty close agreement with the NPs size measured by SEM showing the validity of the method for NPs size analysis. They also reported that the NPs size measured by this method is independent of the NPs coverage on the electrode surface. Also, the method can work for a wide NPs size ranging from 4 nm to 70 nm in diameter. Electrochemical SA/V is thus a good alternative approach to $E_p$ as it provides information about surface area contribution besides the volume of the NPs. Measuring the size of metal NPs based on the SA/V ratio measurements is very useful for stability study of metal NPs.
as the size transformation of electrode attached metal NPs can be easily monitored by this method.

**Figure 1.5.** Schematic illustration of the principle involved in the electrochemical determination of SA/V of Au NPs for determining their sizes.

### 1.12. Ripening of Metal Nanoparticles

Metal NPs are widely used for catalysis and sensing purposes because of their high surface area-to-volume ratio (SA/V) and large number of surface active sites.² As the NPs are subjected to repetitive oxidation-reduction cycling and heating, analogous to the case when they are used for catalytic and other useful applications, they undergo transformation in size and morphology due to particle dissolution, movement, aggregation or deposition onto other bigger-sized particles.¹⁰⁶ During these processes, smaller sized NPs grow into
bigger ones due to a thermodynamic driving force to lower the SA/V.\textsuperscript{107} Thermodynamically, NPs tend to achieve stabilization by the reduction of interfacial area, which leads to the transformation in size and morphology of the NPs. It has been reported in the literature that metal NPs undergo size transformation (increase) when used in various catalytic applications such as CO$_2$ reduction,\textsuperscript{87} CO oxidation,\textsuperscript{108} and the hydrogen evolution reaction.\textsuperscript{109} This increase, also referred to as ripening or sintering, significantly reduces or alters the optical,\textsuperscript{110} catalytic,\textsuperscript{111} and electronic\textsuperscript{112} behavior of the metal NPs. The decrease in electrocatalytic activity of the NPs is primarily due to significant loss of surface area and surface-active sites with an increase in particle size.\textsuperscript{113-114}

The stability of the metal NPs, which is critical for their widespread applications, is mainly determined by the surface free energy, which is proportional to the exposed interfacial area.\textsuperscript{107} There are number of reports where metal NPs undergo sintering when subjected to catalytic applications. For example, Manthiram and coworkers reported the dendritic assembly of carbon-supported Au NPs during electrocatalysis for CO$_2$ reduction and hydrogen evolution.\textsuperscript{115} They believe that such an assembly is because of diffusion, collision and fusion of the NPs with carbon and chemical binders under reductive polarization. Such particle movement and collision are favored more for reactions that give gaseous products. Goodman \textit{et al.} and Wang \textit{et al.} proved by molecular dynamics simulations and experimental approaches that the sintering of NPs is driven by surface thermodynamic fluctuations and atomic interaction forces.\textsuperscript{116-117} The sintering phenomenon was also explained by Ouyang and coworkers in which smaller NPs having high chemical potential and surface energy diffuse on the support and attach to the larger particles having lower chemical potential and lower surface energy, tending to make the
system more stable. In most of the instances, the sintering phenomenon is divided into several phases in which the particles undergo fast ripening at the initial stages, which later decreases as the NPs tend to larger, more stable structures.

The two main modes of nanoparticle ripening are broadly classified as Ostwald ripening and Smoluchowski ripening (Figure 1.6). In Ostwald ripening (Illustration A), smaller-sized NPs in a sample with size dispersity oxidize and dissolve into solution and redeposit onto larger-sized NPs. This is driven by a difference in the standard potential as well as surface free energy of the different-sized NPs. In Smoluchowski ripening (Illustration B), two or more NPs combine together via particle movement and coalescence. Along with the two modes of ripening, NPs could also undergo aggregation, precipitation, dissolution, growth, digestive ripening, and galvanic replacement which are the important factors causing the loss of stability of metal NPs. The modes of sintering or the loss in stability of metal NPs are dependent upon the nature of the NPs and their environment. As an example, Hu and coworkers noticed that small sized Au NPs/NCs (Au$_{561\pm13}$ and Au$_{923\pm20}$) undergo a drastic particle size increase via Ostwald ripening when used for catalytic CO oxidation while the bigger ones (Au$_{2057\pm45}$) undergo Smoluchowski ripening. Similarly, Tindell et al. observed that 2 nm diameter citrate-capped Au NPs were converted to ~6 nm during catalytic reduction of CO$_2$ to CO. Kang et al. reported the size transformation of Pt NPs embedded in membrane electrode assemblies from 2.2 nm of initial average diameter to a final diameter of 10.3 nm when used for proton exchange membrane fuel cell (PEMFC). Not only NPs size transformation but also a substantial decrease in electrochemical active surface area (ECSA) of the Pt NPs was observed when the NPs were cycled up to 10,000 times in the
PEMFC. This made it impossible to correlate the size of the Au NPs with their catalytic behavior, since the NP size changed during the catalytic reaction.

1.12.1. Electrochemical Ripening of Metal NPs

The electrochemistry of metal NPs involves electrochemical treatment for cleaning, electron transport mediation, electrocatalysis, and sensing. Studying the size stability of NPs under these treatments is important fundamentally to better understand their reactivity and also practically to increase their stability for long term use. When metal (Au) is subjected to electrochemical oxidation-reduction cycling in presence of an electrolyte, it undergoes a number of changes on the surface as reported previously by several researchers.\textsuperscript{89, 118-119} Several groups studied the formation of AuO\textsubscript{x} when Au is subjected to anodic polarization from $\sim 1.3$ V to $\sim 2.0$ V vs SHE in acidic solution. For example, Nicol and coworkers observed the formation of reversible Au-Au$_2$O$_3$ (equation 1.6) on the
Au surface as evidenced by fast scan CV of polycrystalline Au performed in HClO$_4$. The observance of surface instability of 2D Au surfaces occurring during the electrochemical treatments leads us to a consideration that 3D Au nanocrystals also undergo similar effects by various modes of electrochemical treatments which are significant to be studied for the reasons already discussed.

The electrochemical cycling of metal NPs caused significant changes in the behavior of metal NPs. For example, Sagura and coworkers found a rapid loss in electrochemically active surface area (ECA) of Pt NPs in parallel with NP agglomeration when subjected to electrochemical oxidation-reduction cycling from 0.0 to 1.4 V vs Ag/AgCl in acidic solution. Blake and coworkers performed repetitive potential cycling of carboxylic acid stabilized Au NPs in acidic solution and observed a high level of surface defects due to AuO formation along with electrodissolution of Au. Rhieu et al. observed an insignificant change in the average size of citrate-coated Au NPs attached to glass/ITO following CV cycling in citrate buffer (4 nm transformed to 3.53 ± 0.27 nm whereas 20 nm transformed to 20.74 ± 2.31 nm). Brus and coworkers reported an electrochemical Ostwald ripening of thermally evaporated Ag NPs on a conducting surface in presence of water. They believed such a ripening process to occur spontaneously due to size dependence of standard electrode potential and work function. These studies were carried out by employing SEM, energy-dispersive X-ray analysis (EDX), and optical absorption spectroscopy as analytical tools. The observance of electrochemical ripening behavior metal NPs on a conductive surface inspired us to study the ripening behavior of metal NPs on a conductive surface under controlled electrochemical conditions.
As discussed earlier, the dependence of $E_p$ on the size of small metal NPs provides a way to monitor size transformations that may occur during oxidation-reduction cycling. The $E_p$ in ASV and SA/V is also sensitive to the aggregation state of Au NPs$^{15}$ and the composition and atomic arrangement of bimetallic Au-Cu NPs.$^{123}$ This shows the significance of ASV and electrochemical SA/V measurements to analyze electrode-attached metal NPs for the study of their ripening behavior. In this dissertation, under various conditions of multiple oxidation-reduction cycling in acidic electrolyte, we study the ripening behavior of surface-immobilized Au NPs where smaller NPs undergo faster ripening kinetics than the bigger ones, which shows good agreement with electron microscopy results. We also discuss the mechanism of the ripening process. Details of this study are provided in Chapter III.

### 1.12.2. Thermal Ripening of Metal NPs

The phenomenon of transformation in size and morphology of metal NPs upon heating is referred to as thermal ripening or sintering. Various groups have carried out the study of thermal sintering behavior of metal NPs when used for different applications. Study of thermal sintering behavior of metal NPs is important for their applications such as in high temperature catalysis and nanoelectronic devices.$^{124-125}$ For example, Hansen and coworkers showed that when subjected to high temperature catalytic processes such as exhaust conversion in automobiles and steam reforming ($\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$), Ni NPs undergo sintering.$^{124}$ Bowker et al. anchored one- and two-dimensional islands of Au NPs to alumina.$^{125}$ Upon heating above 300 $^\circ$C, they observed significant sintering of Au NPs. The restriction of the size of Au domains affected the sintering process and hence their
catalytic behavior. The sintering and catalyst deactivation behavior of thermally-treated Pt NPs was also analyzed by Larsson and coworkers using a kinetic model, showing their size-dependent sintering behavior proceeded via Ostwald ripening.\textsuperscript{114}

In order to exploit the metal NPs for various applications, it is important to study their thermal stability. Understanding the factors that affect thermal sintering/ripening of NPs is crucial as it would provide very useful information regarding proper selection of size and ligands for either inhibiting, controlling or causing sintering in NPs based on the desired application. With regard to the size of metal NPs in correlation to their thermal behavior, it is already well known that the melting temperature decreases with a decrease in NP size.\textsuperscript{126-127} The plot of melting point of NPs as a function of NPs diameter as shown in Figure 1.7 shows that the melting point of the NPs gradually decreases with the decrease in size of the NPs and drops down more significantly below ~ 500 °C for Au NPs below 4 nm in diameter.\textsuperscript{126} The calculation of the melting point is based on the equation $f(x) = -1509/d + 1338$, where $f(x)$ = the melting temperature and $d$ = the diameter of the NP diameter (assuming a sphere shape).\textsuperscript{127} NPs smaller than about 1.1 nm in diameter have negative melting points (in °C) indicating that the melting point of these NPs is significantly low (Figure 1.7). This is indicative of the role of NP size on thermal stability and sintering of the Au NPs since metal atoms are expected to be mobile and rearrange well before their melting point.\textsuperscript{127} Also, the various applications of metal NPs are partly determined by their thermal stability. For example, NPs with low to moderate temperature stability are good at forming electrically conducting thin film structures while those with high temperature stability are desirable for catalytic and sensing applications.\textsuperscript{51} The
smaller sized Au NPs (< 4 nm) are drawing more interest for our work as they demonstrate better catalytic activities, such as for fuel cell applications.\textsuperscript{128}

Over the past decade the thermal stability and sintering phenomenon of Au NPs has been studied by several researchers by monitoring the change in optical properties, microscopic size change or by different spectroscopic methods. For example, King and coworkers studied the role of different stabilizers on the thermal sintering of 2-6 nm diameter Au NPs by thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).\textsuperscript{129} They observed that stabilizers with high thermal stability, such as 1-pyrenebutanethiol, can prevent sintering of up to 390 °C. Sub-2 nm diameter Au NPs are typically synthesized with thiol stabilizers in organic media and the thermal behavior of these NPs has been extensively studied.\textsuperscript{129-130} Thiols form a strong Au-S bond with the Au surface, providing high thermal stability.\textsuperscript{8} However, little attention has been paid to the thermal properties of ultrasmall (<2 nm) Au NPs stabilized with water-soluble, weakly

\begin{figure}[h]
    \centering
    \includegraphics[width=\textwidth]{Figure_1.7.png}
    \caption{Size-dependent melting curve of Au NPs}
\end{figure}
bound ligands (citrate, phosphines, phosphoniums), despite their potential applications in
the field of catalysis.\textsuperscript{131-132} In this dissertation, we describe an electrochemical approach to
monitor the thermal ripening of sub-4 nm diameter Au NPs coated with weak stabilizers.
We discuss the low temperature thermal sintering kinetics of surface-immobilized Au
NPs/NCs by an electrochemical approach and compare the sintering transition temperature
to the theoretical and experimental melting points in the literature. The electrochemical
study of the thermal stability of ultra-small metal nanostructures by using ASV is a unique
aspect of our work discussed in Chapter IV of this dissertation.

1.13. Size-Dependent Electrochemical Oxidation of Au Nanoparticles
Coated with Alkanethiol Self-Assembled Monolayers

The stability of metal NPs is a key factor that is usually determined by the type of
ligand or surfactant stabilizer used in the synthesis. One common way to increase the
stability is by direct adsorption of ordered organic molecules on the NPs surface, forming
self-assembled monolayers (SAMs).\textsuperscript{133-136} The order and orientation of these molecular
assemblies play an important role in NP stability.\textsuperscript{133, 136-137} In spite of the presence of
stabilizing agents, there are many examples where NPs cannot be used as intended due to
their inadequate stability.\textsuperscript{138-139} The low stability of metal NPs can cause the alteration in
their electrocatalytic applications, such as in fuel cells.\textsuperscript{140} For example, Trindell \textit{et al.}
reported that 2 nm diameter Au NPs stabilized by citrate and sixth generation hydroxy-
terminated polyamidoamine (G6-OH) dendrimers rapidly grew into bigger sizes when used
for electrocatalytic CO\textsubscript{2} reduction. Several other reports have shown that metal NPs <10
nm exhibit superior catalytic performance over bigger sizes under a wide variety of
Success for these applications requires strategies to enhance the stability of smaller-sized metal NPs without negatively affecting their catalytic properties. The change of ligand stabilizers could be a good alternative approach to stabilize the smaller NPs. However, change of stabilizing ligands in turn could affect the catalytic activity of the NPs. Therefore, a rational strategy to address the trade-off between the stabilizing effect and the catalytic activity is necessary.

Organomercaptan SAMs have long been utilized by several researchers for enhancing the stability of metal (Au) surfaces. As an example, Porter et al. carried out the assembly of alkanethiols with different chain lengths onto bulk two-dimensional (2D) Au surfaces showing that longer chain alkanethiols form more ordered and densely-packed SAMs compared to shorter ones. This was accompanied by the enhancement in surface coverage, increased packing density, and capacity to block electron transfer with longer carbon chain alkanethiols. Büttner et al. studied the stability of thiol-protected Au NPs against thermal treatment at temperatures up to 160 °C, where they found that longer chain alkane thiols offer more stability at elevated temperatures as evidenced by X-ray photoelectron spectroscopy (XPS).

Based on the notion developed behind the enhancement in surface stability of 2D or planar Au in the presence of thiol SAMs, we were interested in what would happen to the electrochemical stability when it is extended to Au NPs with 3D morphology. The nature and type of ligand stabilizer is crucial in determining the electrochemical stability of Au NPs. Thiol ligand stabilizers are well known for providing stability against aggregation, ripening, and oxidation (corrosion), especially for Au NPs, due to the high strength of the Au-thiolate bond. Accordingly, different researchers have been able to
develop synthetic strategies for preparing thiolate-coated Au clusters, ranging from 1 nm to about 5 nm in diameter. As an example, Negishi et al. found that the growth of Au clusters during the synthesis can be suppressed by passivation with thiolates, indicating improved stability of small Au clusters with thiolates. The effect of thiol binding to Au NPs in the form of SAMs on the relative stability of different sized Au NPs would be an important field to study to extend their further applications in catalysis and sensing. Accordingly, we were interested in the size-dependent electrochemical stability of Au NPs when coated with alkanethiolates (strong binding ligands) compared to size-dependent stability of Au NPs coated with weaker binding ligands (citrate, phosphine, phosphonium). Since there are several applications of metal clusters and NPs involve alkanethiol coatings, a detailed fundamental understanding on how the size affects the stability in terms of dissolution of NPs coated with alkanethiolates is very important to further promote the applications.

In this dissertation, we describe the electrochemical oxidation of electrode-attached, citrate-stabilized different sized Au NPs coated with alkanethiol SAMs. The study is carried on 4.1, 15.1, and 50.3 nm average diameter citrate-coated Au NPs treated with butanethiolate (C4S), decanethiolate (C10S), and hexadecanethiolate (C16S) SAMs. We compare the oxidative dissolution of the citrate- and alkanethiolate-modified Au NPs as a function of size in acidic Br⁻ electrolyte by cyclic voltammetry (CV), chronocoulometry (CC), and UV-Vis spectroelectrochemistry. Details of this study are provided in Chapter V of this dissertation.
1.14. Electrochemical Oxygen Reduction Reaction

The oxygen reduction reaction (ORR) is one of the most important reactions in energy converting systems, such as fuel cells and many life processes in the biological world. In proton exchange membrane (PEM) fuel cells, ORR is the reaction occurring at the cathode.\textsuperscript{161} The common products of ORR are H\textsubscript{2}O, OH\textsuperscript{-} or HO\textsubscript{2}\textsuperscript{-} depending upon the reaction conditions. ORR can be carried out in acidic or basic solutions, where the reaction proceeds via a 2-electron pathway or 4-electron pathway (equations 1.7-1.14).\textsuperscript{162}

**ORR Pathways in Acidic Media:**

4 electron pathway: \( O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \) \hspace{1cm} (1.7)

2+2 electron pathway: \( O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \) \hspace{1cm} (1.8)

\[
H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O
\] \hspace{1cm} (1.9)

\[
2H_2O_2 \rightarrow 2H_2O + O_2
\] \hspace{1cm} (1.10)

**ORR Pathways in Basic Media:**

4 electron pathway: \( O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \) \hspace{1cm} (1.11)

2+2 electron pathway: \( O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \) \hspace{1cm} (1.12)

\[
HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \hspace{1cm} (1.13)
\]

\[
2HO_2^- \rightarrow 2OH^- + O_2 \hspace{1cm} (1.14)
\]

The most common electrode materials used for electrocatalysis of ORR are metals, transition metal oxides, and perovskites, each having different advantages and drawbacks.\textsuperscript{163} Out of these, Pt is reported to be the best material for ORR in acidic medium in term of several parameters.\textsuperscript{164} However, Pt degradation, poisoning and carbon corrosion
in acidic fuel cells has led to research on alkaline fuel cells. Further, the high cost of Pt has led to the search for a replacement of Pt catalysts. Ag is a promising candidate as a substitute for Pt as it has a similar reaction mechanisms and kinetics for ORR compared to Pt when in basic medium.\textsuperscript{165-166} Compared to Ag, Au NPs are poor catalysts for ORR in basic medium. Ag NPs are also used for improving the electrical conductivity and catalytic activity of transition metal oxides such as MnO\textsubscript{x}. Alloying of Au NPs with Ag is alternatively found to significantly improve the ORR activity in basic medium, where the reaction proceeds by the 4e- pathway.\textsuperscript{167} In this dissertation, we describe the atomic level doping of sub-2 nm diameter Au NCs with 1-2\% of Ag by AGR and study the effect of Ag composition on oxygen electroreduction.

1.15. Galvanic Replacement Reaction of Metal NPs

Galvanic replacement reactions (GRR) of metal NPs, where atoms from a metal nanoparticle can undergo exchange with more noble metal ions, are often used for the preparation of novel heteroatomic nanostructures with varied composition and tailored optical and catalytic properties.\textsuperscript{167-168} The change in behavior of the NPs as a result of GRR is useful to improve the NPs for catalytic and sensing applications.\textsuperscript{169} When the replacement occurs in the opposite direction of what is predicted thermodynamically, then that is called anti-galvanic replacement (AGR). It is not thermodynamically favored for bulk sizes, but as the nanoparticle size becomes smaller than about 4 nm for Au NPs, the AGR process becomes spontaneous.\textsuperscript{170} AGR (or GRR) is a simple and facile way of engineering various nanomaterials, including hollow nanocubes,\textsuperscript{171} and nanocages.\textsuperscript{172} The properties of these nanomaterials can be tuned accordingly.\textsuperscript{173-174}
As a result of doping via AGR, a significant change in the behavior of the alloy nanostructures occurs. For example, Young et al. reported that AuAg NCs after galvanic replacement of Au with Ag showed significantly improved electrocatalytic behavior towards ORR in alkaline media as compared to Au-Ag alloys prepared by other methods.\textsuperscript{167} The AGR of thiol-stabilized Au NCs with Cu and Ag and the electrocatalytic behavior was explained by several researchers. AGR with Ag NPs has been described by Xia,\textsuperscript{175} while Kurashige\textsuperscript{176} described galvanic replacement of selenoate-stabilized Au\textsubscript{25} clusters.

In addition to the study on controlled doping of Au NCs by some specific metals via GRR, several researchers studied the stability of nanostructure after the doping process. For example, the study of stability, geometric, and electronic structure of Cu doped Au\textsubscript{25} clusters was carried out by Negishi.\textsuperscript{13} Ghosh\textsuperscript{177} carried out Ag doping into thiol coated Au\textsubscript{25} and studied the stability and catalytic applications of the resultant nanocluster.\textsuperscript{178} Doping and stability testing of different sized Au NCs by controlled doping of metal nanostructures can also be carried out by co-reduction of the metal precursors as per the literature work reported previously.\textsuperscript{177} However, co-reduction generates a complex mixture of undoped and doped NCs with variable composition and one needs to use complicated techniques such as size-exclusion chromatography to isolate them.\textsuperscript{179} In this dissertation, we will discuss in detail about electrochemical study of the AGR of weakly coated sub-2 nm Au NPs with Cu and Ag. We also study the effect of atomic percentage doping of Ag onto 1.6 nm Au NPs for ORR in basic medium. Details of this work is provided in Chapter VI.
1.16. Electrophoretic Deposition of Metal Nanoparticles

Electrophoretic deposition (EPD) is a technique where charged species in a colloidal solution or suspension migrate and deposit on to the conductive surface under the influence of an electric field. Deposition of the migrating species is caused by several different mechanisms, depending on the experimental conditions. The thickness of the film or amount of material deposited during EPD depends on several different variables, including the concentration of particles in solution, electric field, electrophoretic mobility of the depositing particles (their charge and size), and time of deposition.\textsuperscript{180}

The use of EPD is highly advantageous in solar cell fabrication because of the facilitation of deposition of uniform films and thickness control on large surface area of the substrates. There are extensive research works involving EPD of rare earth oxide materials on the conductive surfaces to enhance the photovoltaic performance of solar cell materials.\textsuperscript{181-182} Masitas \textit{et al.} carried out the size-dependent electrophoretic deposition of Au NPs in the presence of H\textsubscript{2}O\textsubscript{2}.\textsuperscript{86} This was later modified by Allen \textit{et al.} to facilitate the deposition process via hydroquinone (HQ) mediation.\textsuperscript{183} ASV allows the determination of the size and amount of the deposited Au NPs during the selective deposition process, which is enabled by a drop in pH at the electrode surface due to release of H\textsuperscript{+} when H\textsubscript{2}O\textsubscript{2} or HQ are oxidized. In this dissertation, EPD in combination with ASV is utilized for the detection of trivalent chromium and melamine which is discussed in Chapter VII.

1.17. Sensing Applications of Metal Nanoparticles

There is a great interest in the electrochemical sensing of different substances using metal NPs due to the demand of new and advanced methods to detect various
biomolecules and inorganic species of human interest. The great interest on the sensing applications of metal NPs is primarily due to several factors including the selective binding or interaction of metal with analyte of interest, plasmonic, and fluorescence properties, and metal dependent electrochemical behaviors. Different electrochemical methods are available for biosensing based on resistance,\textsuperscript{184} impedance,\textsuperscript{185} amperometry,\textsuperscript{186} potentiometry,\textsuperscript{187} and voltammetry.\textsuperscript{188} In voltammetry, the most common methods for biosensing are CV, differential pulse voltammetry (DPV), and ASV. Amongst these techniques, ASV has been extensively used in combination with metal NPs due to strong interactions of metal NPs with the biomolecules (proteins, antibodies, DNA, RNA) upon derivatization/ modification of the analytes. The noble metal NPs are used in this case due to their high conductivity,\textsuperscript{189} high SA/V,\textsuperscript{4} biocompatibility,\textsuperscript{190} and modification possibility for hybridization.\textsuperscript{191} Different metal NPs that are routinely used for biosensing are Au, Ag, Cu, Pb, and Cd. The role of metal NPs in ASV for sensing is that electrochemical current is measured by stripping analysis of the metals, which is related in some way to the concentration of the analyte of interest, usually through metal NP surface binding in the presence of analyte. The analyte/biomolecule to be analyzed is first tagged on metal NPs which are then immobilized to the electrode surface by interaction between the analyte on the NP and their complementary recognition sites on the electrode (Figure 1.8 A). The NPs are then stripped in ASV and the stripping signal is monitored which helps to analyze the analyte attached to the NPs quantitatively and qualitatively by ASV (Figure 1.8 B). ASV analysis can be carried out by direct stripping or dissolution of the metal followed by redeposition on to the electrode surface under potential. Depending upon the mode of analyte-NPs
interaction, the detection strategy by using ASV could also be altered. One way of such a detection is to monitor the aggregation behavior of metal NPs in presence of the analyte.\textsuperscript{192} By monitoring the change in ASV signal of aggregated metal NPs for different analyte concentration, the detection of the analyte is carried out. Another possibility is the alteration in EPD of the metal NPs on to the electrode surface in the presence of the analyte which in turn could affect the ASV signals. ASV with metal NPs has the benefits

\textbf{Figure 1.8.} General scheme for sensing application of metal NPs by using ASV.

a) Immobilization of the analyte on the electrode surface via molecular linker to which the corresponding metal tagged antibody is attached forming a sandwich type structure.

b) Stripping analysis of metal NPs tagged analyte (i) by direct stripping (ii) by dissolving the metal in solution first followed by its redeposition under potential.
of low-cost operation, high sensitivity, high selectivity, enhanced signal transduction, and potential for automation and ease of operation.\textsuperscript{193}

Several researchers have employed Au NPs for the selective and sensitive detection of chromium and melamine. Chromium is widely used in electroplating, dyestuff, leather tanning, metallurgy and catalysis.\textsuperscript{194-195} As a consequence, chromium is often released to the environment, causing a serious threat to human health.\textsuperscript{196-197} Out of the most common forms of Cr, Cr(VI) is biotoxic, while Cr(III) is important in the activation of glucose and metabolism of proteins and lipids.\textsuperscript{194, 198} However, the presence of excess Cr(III) in the body causes oxidation of cellular components, such as DNA, proteins, and lipids, leading to an increased risk of cardiovascular diseases, diabetes, and cancer.\textsuperscript{199-200} Studies also show that Cr(III) is highly bioaccumulative and bioconvertible in nature, which causes considerable cell and tissue damage.\textsuperscript{201-202} Also, interconversion of the two ionic forms of Cr is common via simple oxidation-reduction processes.\textsuperscript{195, 203-204} For these reasons, the detection of Cr(III) is necessary for environmental monitoring, including water and food safety.

Melamine (C\textsubscript{3}H\textsubscript{6}N\textsubscript{6}) has applications as water-reducing agents, fire retardants, plastics, laminates, paints, and fertilizer mixtures.\textsuperscript{205} Some food processing companies use melamine as a food additive to enhance the protein content. The recommended minimum melamine concentration level in food with safe use is 2.5 ppm.\textsuperscript{206-208} However, since melamine is biotoxic in nature, it can cause many food borne diseases associated with the urinary tract and kidney malfunction.\textsuperscript{207, 209-210} Therefore, there is an increasing demand for feasible, reliable, and sensitive methods to detect the melamine concentration in food and the environment.
In this dissertation, we describe Cr$^{3+}$ and melamine detection by the combination of EPD and ASV based on analyte-induced alteration in electrophoretic mobility of citrate-coated Au NPs. Our method involves selective interactions between Cr$^{3+}$/melamine and citrate-stabilized Au NPs followed by EPD of the Au NPs and finally ASV. The peak current or peak oxidation potential in the ASV of the Au NPs depends on the analyte concentration since the analyte binding alters the EPD and also potentially the aggregation state of the Au NPs. The ASV depends on the rate of EPD of the Au NPs, which depends on the charge and size of the Au NPs, both of which can be altered by the analyte of interest. This sort of alteration in peak current or peak potential in ASV provides useful information for the quantification of the analytes.

1.18. Summary and Accomplishments

Chapter I and II of this dissertation provide an introduction to NPs and general background about electrochemical studies of metal NPs and previous work relevant to the research. Chapters III-VI describe the stability of Au NPs following electrochemical surface oxidation-reduction cycling, oxidative dissolution, electrocatalysis, or thermal treatment as a function of size, ligand stabilizer or atomic level doping by AGR. Chapter VII describes a unique strategy for sensing of Cr(III) and melamine by combining Au NP-analyte binding, EPD and ASV. Chapter VIII summarizes the results, significance, and potential future directions.

In Chapter III, we report on the electrochemical stability of surface-immobilized Au NPs with size ranging from 1.6 nm to 15 nm diameter upon treatment with multiple electrochemical surface oxidation-reduction cycles in acidic solution. Smaller sized NPs
are prone to undergo faster size transformation, or ripening kinetics, as compared to the bigger sizes. These results are confirmed by monitoring the positive shift in peak oxidation potential ($E_p$) and decrease in SA/V ratio of NPs, which indicates an increase in NP size. Some NPs dissolve and others increase in size by Ostwald ripening during electrochemical oxidation-reduction cycling.

In Chapter IV, we report on the thermal size ripening behavior of weakly-stabilized sub-4nm diameter Au NPs by using $E_p$ in ASV and electrochemically determined SA/V as an indicator of the size. The ratio of the peak currents in ASV at the two potentials after and before heating (for example $I_{0.70}/I_{0.45}$ for 1.6 nm Au NPs) increases with an increase in temperature and heating time which is utilized to determine the NPs thermal ripening transition temperature, which was 109, 132 and 509 °C for 0.9, 1.6 and 4.1 nm Au NPs, respectively. This shows close agreement with the melting point of the corresponding sized NPs as predicted in the literature, except that the temperature for 0.9 nm diameter Au NPs was high. SEM images confirm the electrochemical and UV-Vis size analysis as a function of temperature.

Chapter V describes the size-dependent electrooxidation of citrate-coated Au NPs as compared to the same sizes after coating with various chainlength alkanethiol SAMs. CV, CC, and spectroelectrochemistry assess the amount of Au dissolution at various potentials for the different sized Au NPs stabilized with citrate or alkanethiol SAMs. CV shows that the oxidative dissolution of Au NPs by Br⁻ is hindered significantly for 4.1 nm, 15.1 nm, and 50.3 nm diameter Au NPs when coated with butanethiolate (C₄S), decanethiolate (C₁₀S) and hexadecanethiolate (C₁₆S) ligands as compared to citrate-stabilized Au NPs and the passivation of Au increases with increasing chainlength. When comparing sizes, the 4.1 nm thiol-coated Au NPs show greater resistance to oxidative
dissolution compared to the 15.1 nm and 50.3 nm diameter Au NPs coated with the same thiols. This is further supported by CC and CC combined with UV-Vis experiments. The stability of the Au NPs against oxidative dissolution shows a reverse size-dependence for thiol-coated Au NPs compared to the trend for citrate-stabilized Au NPs, where the resistance to dissolution increases with increasing Au NP size.

In Chapter VI, we report on the AGR of surface immobilized 1.6 nm diameter Au NPs with Ag\(^+\) and Cu\(^{2+}\). Based on ASV, the composition analysis of Au, Cu and Ag in the resulting alloyed NPs after AGR showed Ag or Cu ranging from \(~70\%\) down to \(~1\%\) atomic level doping. We observed significant better oxygen reduction reaction (ORR) catalytic activity for 9 nm Ag NPs compared to 1.6 nm Au NPs in 0.1 M KOH. After Ag doping via AGR down to even 1%, the Au NPs exhibited a peak reduction current for ORR that increased nearly 7-fold and was comparable to Ag NPs. Interestingly, the ORR activity of Ag-doped Au NPs was similar from 70% to 1%, suggesting that a very specific site is active for catalytic activity and that site exists at 1% doping level. Importantly, the ORR activity of Ag-doped Au NPs, even as low as 1%, was significantly more stable during ORR electrocatalysis compared to Ag NPs. Ag NPs were unstable even within 20 cycles while Ag-doped Au NPs remained stable for at least 100 cycles.

In Chapter VII, we combine Au NP-analyte binding, EPD and ASV to electrochemically detect aqueous Cr(III) and melamine. The EPD of citrate-stabilized Au NPs occurs on indium tin oxide (ITO)-coated glass electrodes by the release of protons upon electrochemical oxidation of hydroquinone (HQ). ASV allows the determination of the amount of Au deposition under specific conditions of potential and time. The binding of Cr\(^{3+}\) to the citrate stabilizer surrounding the Au NPs inhibits the EPD either by inducing
aggregation of the Au NPs or reducing the negative charge of the Au NPs, which could lower the effective NP concentration of the Au NPs for the former or the electrophoretic mobility for both. The lower oxidation charge in the ASV of Au accordingly acts as a signal for Cr$^{3+}$. The amount of Au measured by ASV decreases linearly with increasing Cr$^{3+}$ and melamine concentration with a limit of detection (LOD) of 21.1 ppb and 16.0 ppb when using 15.1 and 4.1 nm Au NPs, respectively. The LOD for melamine is 45.7 ppb with 4.1 nm Au NPs, which is below the EPA recommended level. The LOD can be improved for Cr$^{3+}$ down to 1 ppb when lowering the number of Au NPs in solution, which effectively increases the analyte/Au NPs ratio.
2.1. Chemicals and Reagents

We synthesized H\text{AuCl}_4\cdot3\text{H}_2\text{O} from metallic Au (99.99 % pure) in our lab by first dissolving it in aqua-regia followed by multiple distillation and crystallization. Sodium borohydride (≥98.5% reagent grade), hydrogen peroxide solution (30 wt.%), 2-propanol (ACS reagent), (3-aminopropyl)triethoxysilane (APTES, ≥98.0%), melamine (99%) silver nitrate (≥ 99.0%), potassium chloride (99.0-100.5%), and sodium citrate tribasic dihydrate (≥99.0 %) were purchased from Sigma Aldrich. Potassium perchlorate (99.0-100.5%, ACS) and perchloric acid (60%-62.0%) were purchased from Beantown Chemical. Nitric acid (68-70%, ACS grade), sulfuric acid (95-98%, ACS grade), hydrochloric acid (36.5-38%, ACS grade), and copper (II) sulphate were purchased from VWR, BDH Chemicals. Ethyl alcohol (ACS/USP grade) and acetone (ACS/USP grade) were purchased from Pharmco-AAPER. An 80% aqueous solution of tetrakis(hydroxymethyl)phosphonium chloride (THPC) and potassium bromide (>99.0%) were purchased from Acros Organics. Sodium hydroxide pellets and chromium nitrate were purchased from Fisher Scientific. Hydroquinone (HQ, 99%) was purchased from Alfa Aesar. All chemicals were used directly as received. A Barnstead NANOpure water purification system with a resistivity of 18.2 MΩ-cm was used for all aqueous solutions. Aqua-regia was prepared in lab by mixing concentrated HCl and HNO₃ in a ratio of 3:1 by volume. Piranha solution was
prepared in lab by mixing concentrated $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}_2$ in a ratio of 2:1 by volume. Aqua-regia and piranha solution were used for ultra-cleaning purpose of glassware and stirring bars and were handled with special precaution due to their highly hazardous nature. Nitrogen and oxygen gas cylinders were supplied by Welders Supply (Louisville, KY).

2.2. Substrate

The substrate used in our electrochemical studies is mostly composed of indium tin oxide (ITO) and glass where ITO acts as a conducting surface in the form of thin coating on the glass surface. We used unpolished float (soda-lime) glass coated ITO slides (Delta Technologies, LTD, Loveland, CO) as electrode material for electrochemical and UV-Vis measurements. These electrodes have surface roughness of resistance of 8-12 ohms. We cut the slides to a final size of 25 x 7 mm slices using a diamond cutter and cleaned them by sonication for 30-min in acetone, ethanol and isopropanol respectively. Finally, the slides were rinsed with water and dried under N$_2$ before use.

2.3. Synthesis of Different Sized Au Nanoparticles

2.3.1. Synthesis of THPC-Stabilized 1.6 nm Diameter Au NPs

Chemical synthesis of THPC-stabilized 1.6 nm diameter Au NPs was carried out by following the procedure developed by Duff et al.$^{77}$ A 15.5 mL aliquot of water in a clean vial with an ultra-clean stir bar was mixed with 400 µL of 0.1 M THPC and 500 µL of 0.1 M NaOH. On reaction with NaOH, phosphonium releases an aldehyde which serves as the reducing agent for Au(III) complex. After stirring for 2 min, 660 µL of aqueous 25
mM HAuCl₄·3H₂O was added, which immediately produced an orange-brown colored solution indicative of the formation of small Au NPs. The Au NPs were used from the solution they were prepared in with no further purification or isolation. The structure of THPC is as provided in Figure 2.1.

![Tetrakis (hydroxy methyl) phosphonium chloride (THPC) – Trisodium citrate (Tris)](image)

**Figure 2.1.** Structure of the stabilizing ligands (THPC and citrate) used in the chemical synthesis of Au NPs.

### 2.3.2. Synthesis of Citrate-Stabilized 4.1 nm Diameter Au NPs

We synthesized 4.1 nm average diameter Au NPs by the method described by Murphy and co-workers. It involved the preparation of a 19.5-mL aqueous solution of 0.25 mM HAuCl₄·3H₂O and 0.5 mL 0.25 mM trisodium citrate and mixing them together (Figure 2.2). It was then followed by the addition of 0.6 mL of ice-cold 10 mM NaBH₄ at once with rapid stirring for 2 hr. After addition of NaBH₄, the solution turned red immediately, indicating the formation of Au NPs. During the synthesis, first ultra-small lowly stable Au clusters were formed which continued to grow with time to produce around 4 nm Au NPs which is a thermodynamically stable size. The Au NPs were used from the solution as prepared with no further purification or isolation. The structure of tris used for the synthesis is provided in Figure 2.1.
2.3.3. Synthesis of Citrate-Stabilized 15.1 nm Diameter Au NPs

We synthesized 15.1 nm Au NPs by the reduction of HAuCl₄·3H₂O in boiling trisodium citrate, adopting the method originally developed by Turkevich.⁶² A mixture of 17.5 mL of nanopure water and 0.5 mL of 0.01 M HAuCl₄ was first boiled for 10 mins in a stirring vial. Then, 2.5 mL of 10 mM trisodium citrate was added, and the solution was continuously boiled for another 10 min (Figure 2.3). The appearance of a red color solution indicated the formation of the Au NPs. The Au NPs were used from the solution directly with no further purification or isolation.

\[
2 \text{AuCl}_4^- + \text{Na}_3\text{C}_6\text{H}_5\text{O}_7^- + 2\text{H}_2\text{O} \xrightarrow{\text{Boil}} 2\text{Au} + 3\text{CH}_2\text{O} + 8\text{Cl}^- + 3\text{Na}^+ + 3\text{H}^+ \tag{2.2}
\]

**Figure 2.3.** Synthesis of 15.1 nm diameter average diameter Au NPs by the citrate reduction method.
2.3.4. Synthesis of THPC-Stabilized 4.1 Diameter Au NPs

We prepared THPC-coated 4.1 nm diameter Au NPs by the ligand exchange method reported recently by Gulka and coworkers. Briefly, 500 µL of 100 µM THPC in water was added to 10 mL of citrate-coated 4.1 nm Au NPs solution synthesized by the method discussed above. After addition of THPC, the Au NPs immediately change from red to blue, indicating that NPs become aggregated immediately after the additions of THPC. The NP solution reverts back to a red color again after 24 hr, which indicates that the NPs spontaneously de-aggregate back to individual NPs. After that NPs were attached to the glass/ITO/APTES functionalized electrode by directly soaking the electrode in the Au NPs solution.

2.3.5. Synthesis of Citrate-Stabilized 50 nm Average Diameter Au NPs

We used the seed-mediated growth method reported by Wang and coworkers to prepare citrate-stabilized 50 nm average diameter Au NPs. This method is based on the growth of NPs on the surface of some other already prepared Au NPs, and so is called seeded growth method. In this method, first 18.0 mL of 30 wt% H₂O₂ was added to a mixture of 500 µL of 0.01 M HAuCl₄·3H₂O and 1.0 mL of 0.01 M trisodium citrate and stirred (equation 2.3). To this resultant mixture, was injected 500 µL of the as-prepared 15.1 nm Au NSs. After the addition of the 15.1 nm diameter Au seed NPs, the color of the solution changed to a pink-red color within a min, suggesting the formation of larger Au NPs (Figure 2.4).

\[
\text{AuCl}_4^- + \frac{3}{2}\text{H}_2\text{O}_2 \rightarrow \text{Au}^0 + 4\text{Cl}^- + 3\text{H}^+ + \frac{3}{2}\text{O}_2
\] (2.3)
Figure 2.4. Synthesis with mechanism of 50 nm Au NPs by seeded-growth method with H₂O₂ reduction.

2.4. Ultraviolet-Visible (UV-Vis) Characterization of Au Nanoparticles

Ultraviolet-Visible spectrophotometry (UV-Vis) is a branch of spectroscopy which detects the analyte based on the absorption or reflectance of light by a colored sample in the ultraviolet and visible spectrum range (approx. 200-700 nm). Many of the metal NPs in solution phase or while attached to the electrode surface show absorption at a specific wavelength that depends on the NPs size. Based on the wavelength of maximum absorption (λ\text{max}), the size of a metal NP can be ascertained. UV-Vis absorption spectroscopy can also be utilized to study the kinetics of reaction in a colored solution and other related parameters. This effect is also useful for the study of sintering/aggregation state of metal NPs as well as several sensing applications. In our work, UV-Vis was performed using a Varian instrument, Cary 50 Bio-spectrophotometer. We measured the UV-Vis spectra of different sized Au and Ag NPs. These NPs show localized surface plasmon resonance (LSPR) band that depends on the NPs size. Appearance of the size dependent LSPR band position of metal NPs is useful for NPs size characterization. We have carried out preliminary size characterization of Au and Ag NPs based on the position of λ\text{max} when the absorbance is measured from 800 nm to 300 nm. The peak position shifts to longer wavelengths with an
increase in NP size or when the NPs are aggregated. For example, 4 nm Au NPs show $\lambda_{\text{max}}$ at ~505 nm while 15 nm at ~518 nm. However, small Au clusters (particles < 2 nm in diameter) do not show a well-defined LSPR band for the lack of collective oscillation of conducting electrons upon excitation with electromagnetic radiation.

In this dissertation, UV-Vis was performed using a Varian Cary 50 Bio-spectrophotometer. UV-Vis spectra were obtained in aqueous solutions of different sized Au NPs from 350-850 nm at a fast scan rate of 80 nm/second using water as the blank.

### 2.5. Functionalization of Electrodes and Attachment of NPs

**Functionalization of Electrodes.** After cleaning as in section 2.2, the glass/ITO electrodes were immersed into a solution containing 100 $\mu$L of 3-Aminopropyl)triethoxysilane (APTES), 10 mL of 2-propanol, and a few drops of nanopure water and heated at 70 °C for 30 min. After heating, the electrodes were thoroughly rinsed with 2-propanol and dried under N$_2$. The electrodes were finally soaked in the appropriate as-prepared or diluted Au NP solution for few to several min, depending on the desired coverage, rinsed with nanopure water thoroughly, and dried with N$_2$. The negatively charged citrate-stabilized Au NPs attach to APTES by electrostatic attraction, while the interactions between THPC-stabilized Au NPs and glass/ITO/APTES are not well understood. Figure 2.5 shows the steps involved for the functionalization of glass/ITO electrodes. The soaking times led to Au NP coverages that resulted in Au anodic stripping charges ranging from $\sim 1.0 \times 10^{-6}$ to $1.0 \times 10^{-4}$ Coulombs, corresponding to $3.5 \times 10^{-12}$ to $3.5 \times 10^{-10}$ moles Au, assuming Au oxidation occurred by a 3-electron process.
Attachment of NPs to the Functionalized Electrodes. The glass/ITO/APTES electrodes were soaked into the appropriate solution of NPs, then rinsed with nanopure water thoroughly and dried with \(N_2\) before further experimental procedure or analysis. The glass/ITO electrodes were placed in NP solutions immediately after APTES functionalization, rinsed, and characterized electrochemically immediately after metal NP attachment in order to reduce surface contamination and improve reproducibility. Figure 2.6 illustrates the procedure for the attachment of NPs onto the electrode.

**Figure 2.5.** Functionalization of glass/ITO with 3-(Aminopropyl)triethoxysilane (APTES).

**Figure 2.6.** Attachment of metal NPs onto APTES functionalized glass/ITO electrode.
After attachment of NPs to the electrode surface, the size of Au NPs was determined separately by field emission scanning electron microscope (FESEM) and/or scanning transmission electron microscopy (STEM).

### 2.6. Thermal Treatment of Electrode Attached Au NPs

Thermal treatment of Au NPs attached to glass/ITO/APTES or glass/FTO/APTES electrode was carried out in a Barnstead Thermolyne furnace (Model No. FB1315M). The heating time and temperature were maintained as per the need of specific experiments. For heating the NPs above 400 °C, APTES functionalized fluorine doped tin oxide (FTO) electrodes were used.

### 2.7. Ozone Treatment of Electrode Attached Au NPs

After attachment of different sized Au NPs onto the glass/ITO/APTES surface, they were placed in a model no. 42 UVO ozone cleaner (Jelight Company, Inc) for 30 min to remove any organic impurities or citrate stabilizer from the Au or glass/ITO/APTES surface. However, 1.6 nm Au NPs were not subjected to ozone treatment due to their reported size increase within 2 min of ozone exposure.

### 2.8. Electrochemical Characterization and Instrumentations

Electrochemical techniques are a class of techniques in analytical chemistry, which study the electrical and chemical changes by measuring the potential and/or current in an electrochemical cell containing the analyte. Recently, electrochemical techniques have been extensively employed for study of stability and reactivity of materials, electro-
synthesis/fabrication, electrocatalysis, sensing, electroplating, and many more. In most cases, the electrochemical changes of the analyte in electroanalytical chemistry takes place via oxidation-reduction process taking place at the electrode-electrolyte interface. The three main categories of electroanalytical chemistry include: i) potentiometry (the difference in electrode potentials is measured as a function of change in the analyte concentration/composition), ii) coulometry (the cell charge is measured over time) and iii) voltammetry (the cell current is measured at varying cell potential). The mostly employed electrochemical technique in my dissertation work is voltammetry which applies a constant and/or varying potential at an electrode's surface and measures the resulting current in a three-electrode set up. This section of the dissertation will focus on the complete electrochemical set-up and different electrochemical techniques used for the electrochemical study of metal NPs.

**Electrochemical Cell.** An electrochemical cell is a device which generates electrical signal as a consequence of a chemical reaction, or a chemical reaction occurs at the expense of electrical energy. There are two types of electrochemical cells: galvanic (ones that spontaneously produce electrical energy) and electrolytic (ones that consume electrical energy). The main component of an electrochemical set up consists of: (i) a three-electrode cell containing a working, reference, and counter electrode, (ii) a container with proper electrolyte, (iii) a potentiostat and (iv) a computer/software for receiving/plotting the electrochemical signal. In our experiment we used a 50 mL beaker having three electrodes (working, reference and counter electrode) as an electrochemical cell.

**Working Electrode.** The working electrode is the electrode of an electrochemical system where the electrochemical reactions of interest take place. Under the condition of
a constant or varying potential, the current produced due to redox phenomenon is measured using a specially designed electrical system. The working electrode is often used in conjunction with a reference electrode and an auxiliary or counter electrode in a three-electrode system. In our experiment, we used glass/ITO, glass/ITO/NPs, glass/ITO/APTES, glass/ITO/APTES/NPs, and glass/FTO/APTES/NPs as working electrodes. The details of fabrication of the working electrode for this dissertation work is as discussed earlier in this section.

**Reference Electrode.** The reference electrode is an electrode having a stable and well-known potential useful to determine and control the potential of the working electrode. The commonly used reference electrodes are: normal hydrogen electrode (NHE), silver/silver chloride (Ag/AgCl), and standard calomel \((\text{Hg/Hg}_2\text{Cl}_2)\). In our experiment, we used Ag/AgCl (3M KCl) as a reference electrode due to its low cost, ease of simplicity and null hazardous nature. This electrode consists of a silver wire electrode coated with solid AgCl and immersed in a solution of 3 M KCl electrolyte solution. Sometimes, a quasi-reference electrode is also used depending upon the experimental needs. We used an Ag wire as a quasi-reference electrode in certain instances.

**Counter Electrode.** The counter electrode, also called auxiliary electrode, is an electrode used to close the current circuit in an electrochemical cell. It allows the charge to flow through it which ultimately balances the current flowing at the working electrode. The counter electrode is usually made of inert or noble materials such as platinum, gold, graphite or glassy carbon. In our work, we used a Pt wire as the counter electrode.
2.9. Electrochemical Analysis

2.9.1. Linear Sweep Voltammetry (LSV)

Linear sweep voltammetry is a voltammetric method where the current at a working electrode is measured while the potential between the working electrode and a reference electrode is swept linearly with time. The sweep or scan rate (V/s) in LSV depends on the experimental parameters and purpose of the research work. Oxidation or reduction of electroactive species on the electrode surface takes place with the potential change on the working electrode which is manifested as the current signal in the potentiostat. In this dissertation, LSV has been better termed as ‘anodic stripping voltammetry, ASV’ as the electrode attached analyte in our work undergoes oxidative dissolution/stripping in anodic direction. The current potential waveform obtained during the redox process in ASV is also referred to as a voltammogram. In the voltammogram, the potential on the working electrode is linearly increased with time and the current is produced due to the electrochemical reaction on the electrode-electrolyte interface. By integration of the area under the current-potential curve, it is possible to calculate the total charge involved in the electrochemical process which in turn is proportional to the total amount of metal (Au) present on the electrode surface (section 1.9). In this dissertation ASV was used for a) qualitative/quantitative size information, b) compositional information, and c) quantitation of analytes by ASV monitoring of the amount of Au deposited onto the electrode during EPD.
2.9.2. Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is an electroanalytical technique which measures the current developed in an electrochemical cell under the conditions where voltage is in excess of that predicted by the Nernst equation. It is a type of potentiodynamic electrochemical method and is similar to LSV. In CV, the electrochemical response of electroactive species is recorded as current with a constant sweeping of potential on the working electrode in the forward and reverse directions. The sweep rate or scan rate (V/s) depends on the experimental parameters of the research work. The resulting current is measured as a function of potential. The oxidation and reduction process of an electroactive species is possible to be monitored in CV due to the complete cycle of this technique. CV can be utilized to check for the reversibility of an electrochemical process, reaction kinetics, and reaction mechanism, estimation of diffusion coefficients and analyte concentration, and calculation of formal reduction potentials. Typically, the experiment begins at a potential where there is no oxidation or reduction reaction and moves to potentials where there is

Figure 2.7. Illustrating the variation in potential and corresponding redox process in a cyclic voltammetry (left) and typical cyclic voltammogram (right).
reduction or oxidation of the electroactive species. In the typical CV (Figure 2.8), $ipc$ is the cathodic peak current, $ipa$ is anodic peak current, $Ep,c$ is potential of the cathodic peak and $Ep,a$ is potential of the anodic peak. In our studies, we used CV to measure the electrochemical surface area (SA) of Au NPs and hence useful for controlling the coverage of NPs on the electrode. CV was also used to determine the size of metal NPs by measuring the SA/V ratios as discussed earlier in section 1.11. CV was also used to carry out deliberate ripening of electrode attached Au NPs under varieties of conditions and for ORR analysis.

2.9.3. Chronocoulometry (CC)

Chronocoulometry involves the measurement of variation in electrical charge with time once a potential step waveform is applied on the working electrode. Typically, a CC experiment starts at a certain potential at which no electrochemical change occurs. Then the potential is abruptly stepped to a preselected higher potential at which desired electrochemical change takes pace. CC offers several advantages over other potential step experiments such as enhancement of signal with time, high signal to noise ratio and easy overcoming of contributions from double layer charging and absorbed species. CC is used to study kinetics of chemical reactions, diffusion process and adsorption. We used single potential step experiment mode of CC in our dissertation work to monitor the relative stability of electrode attached different sized electrode-attached Au NPs coated with alkanethiol self-assembled monolayers (SAMs).

After electrochemical analysis, SEM/STEM were used as post treatment for size and compositional analysis to correlate with electrochemical analysis.
2.10. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a microscopic tool which produces an image of a sample by scanning the surface of the sample with a focused beam of electrons. The energetic and focused electron beam is scanned on the surface in a raster scan fashion and the position of the beam is combined with the intensity of the detected signal to produce an image. These images are useful for analyzing the size, shape, and morphology of nanomaterials. Figure 2.9 shows the results of the interactions of an electron beam with a sample. A typical SEM instrument consists of the energetic electron gun, electron beam scanning coil, electromagnetic lenses, apertures, a specimen stage, high-vacuum environment, signal detection, processing system, and image recording. As the energetic electrons are incident on a sample specimen, they produce a set of signals such as secondary electrons (SE), reflected or back-scattered electrons, and characteristic X-rays. Analysis of the different types of electrons produced on the sample is useful for imaging.

In our research work, SEM was used for size characterization of Au NPs attached on to the glass/ITO electrode surface in their as-prepared or after various chemical or electrochemical treatment conditions. We collected SEM images with a Carl Zeiss SMT AG SUPRA 35VP field emission scanning electron microscope (FESEM) operating at an accelerating voltage of 17.00 kV using an in-lens ion annular secondary electron detector.
In addition to SEM, scanning transmission electron microscopy (STEM, 200 kV FEI Tecnai F20) was also used for the size characterization of sub-2 nm diameter Au NPs which is not possible simply by SEM due to low resolution issue of the instrument.

**Figure 2.8.** General outline of interaction of electron beam with sample in SEM.
CHAPTER III

SIZE-DEPENDENT RIPENING OF GOLD NANOPARTICLES THROUGH REPETITIVE ELECTROCHEMICAL SURFACE OXIDATION-REDUCTION CYCLING

3.1. INTRODUCTION

Small sized metal nanoparticles (NPs) are extensively used for catalysis\textsuperscript{213-216} and sensing\textsuperscript{217-220} due to their high surface area-to-volume ratio (SA/V) and large number of surface active sites. The stability of the NPs, which is critical for their widespread applications, is mainly determined by the surface free energy, which is proportional to the exposed interfacial area.\textsuperscript{107} Thermodynamically, NPs tend to achieve stabilization by the reduction of interfacial area, which leads to the transformation in size and morphology of the NPs. It has been reported in the literature that metal NPs undergo size transformation when used in various catalytic applications, such as CO\textsubscript{2} reduction,\textsuperscript{87} CO oxidation,\textsuperscript{108} and the Hydrogen evolution reaction.\textsuperscript{109} This increase, also known as ripening, significantly reduces or alters the optical,\textsuperscript{110} catalytic,\textsuperscript{111} and electronic\textsuperscript{112} behavior of the metal NPs. The ripening processes have been broadly explained in term of Ostwald ripening and Smoluchowski ripening.\textsuperscript{11, 40, 108, 113} In Ostwald ripening, smaller-sized NPs in a size disperse sample oxidize and dissolve into solution and redeposit onto larger-sized NPs. The process is driven by a difference in the chemical potential, controlled by the surface free
energy of the different-sized NPs. In Smoluchowski ripening, two or more particles combine via particle movement and coalescence, producing bigger-sized particles.

The changes in electrochemical behavior of Au when subjected to oxidation-reduction cycling by cyclic voltammetry (CV) in various electrolyte solutions has long been studied by several researchers. For example, Nicol and coworkers observed the formation of reversible Au-AuOₓ on the Au surface as evidenced by fast scan CV of polycrystalline Au performed in HClO₄. During the electrochemical redox process, an unstable Au(OH) is first formed on the Au surface. By chemical disproportionation of Au(OH), a variety of Au species, such as AuOₓ, HAuO₃²⁻ and Au(OH)₃ were formed under different potential, pH and polarization conditions. The most common form is AuOₓ, which is reduced back to Au or converted to soluble Au(III) species during the redox process. The dissolution of Au was followed by redeposition onto the electrode surface in the reverse cycle as observed by Nicol et al. and Cherevko et al. The most common chemical or electrochemical changes taking place to form various Au oxide species such as AuOₓ and Au₂O₃ are represented by equations 3.1-3.3.

\[
\begin{align*}
\text{Au} + \text{H}_2\text{O} & \rightleftharpoons \text{Au(OH)}_{\text{x(ads)}} \quad (3.1) \\
\text{Au} + 3\text{H}_2\text{O} & \rightleftharpoons \text{Au(OH)}_3 + 3\text{H}^+ + 3\text{e} \quad (3.2) \\
2\text{Au(OH)}_3 & \rightleftharpoons \text{Au}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (3.3) \\
\text{Au}_2\text{O}_3 + 6\text{H}^+ + 6\text{e} & \rightleftharpoons \text{Au} + \text{H}_2\text{O} \quad (3.4)
\end{align*}
\]

Subsequent reduction of the Au oxide occurs on the reverse scan (equation 3.4). The existence of the above mentioned and several other intermediate species and their stability depends on the potential and pH. This electrochemistry was extensively studied by electrochemical scanning tunneling microscopy (ECSTM) on bulk Au(100) and Au(111).
surfaces in acidic solution,\textsuperscript{225-226} revealing the presence of surface roughening, corrosion, for Au-Ag alloys in HClO\textsubscript{4},\textsuperscript{227} and surface reconstruction, for example.\textsuperscript{228} Based on these observations, we were interested in what would occur for confined three-dimensional (3D) NP structures, which are quite different than long range bulk single crystal two-dimensional (2D) surfaces. 3D NP structures also have potential electrochemical applications in various fields as discussed earlier.

The change in the surface morphology of continuous Au films during electrochemical oxidation-reduction cycling in acidic solution was studied by ECSTM by several researchers.\textsuperscript{227-230} Trevor \textit{et al.} first carried out ECSTM studies of Au(111) during electrochemical oxidation-reduction in HClO\textsubscript{4} solution.\textsuperscript{229} They observed roughening and surface mobility of Au(111) terraces accompanied by formation of mono or multilayer Au oxide pits on the surface, which increased with the number of oxidation-reduction cycles. Based on the larger morphological changes occurring on the various low index faces of 2D extended films of Au during oxidation-reduction cycling in acid, we were interested to determine what would occur on 3D Au nanocrystals under similar conditions as a function of the nanocrystal (or NP) size.

\textit{In-situ} imaging studies of metal NPs under potential control can provide valuable information about NP stability and potential-controlled size transformation.\textsuperscript{120, 231-232} For example, Sagawara and coworkers found a rapid loss in electrochemically active surface area (EASA) of Pt NPs in parallel with NP agglomeration when subjected to electrochemical oxidation-reduction cycling from 0.0 to 1.4 V in acidic solution.\textsuperscript{120} Kang and coworkers studied the electrochemical size-dependent degradation mechanism of Pt NPs when employed in proton exchange membrane fuel cells.\textsuperscript{109} During the process,
smaller-sized Pt NPs with an average diameter of 2.2 and 3.5 nm exhibited significant size transformation while those above 5 nm remained mostly stable. Plowman and coworkers performed repetitive potential cycling of carboxylic acid stabilized Au nanospheres in acidic solution and observed a high level of surface defects due to AuO formation along with electrodissolution of Au. Steven et al. studied the electrochemical stability during the first 100 oxidation-reduction cycles in acid of Au NPs from 0.8 nm to 4.5 nm in diameter deposited with Vulcan carbon. They observed a size increase for all Au NPs but only a significant loss of EASA for the Au NPs below 4.5 nm. The size increase and loss of EASA required scanning to potentials into the Au oxide formation region and they suggested Ostwald ripening was the likely mechanism for the size increase. Rhieu et al. described a decrease in size for 4 nm and 20 nm Au NPs on glass/ITO by oxidation-reduction cycling in citrate buffer (pH 6) due to Au dissolution upon each cycle, but did not consider ripening as a possibility. Pattadar et al. studied the effect of size, coverage and size dispersity on the potential-controlled ripening behavior of Au NPs in halide containing electrolyte. Taken together, most of the literature shows a size transformation and decrease in EASA followed by performance degradation of metal NPs following electrochemical potential cycling.

Our group previously determined the size of citrate- and phosphine-stabilized Au\(^2^-\) and Ag\(^{71}\) NPs by ASV, where the oxidation peak potential (E\(_p\)) in KBr electrolyte was directly correlated to the size of the NPs as predicted theoretically by Pleith. The dependence of E\(_p\) on the size of small metal NPs provides a way to monitor size transformations that may occur during oxidation-reduction cycling. For example, we found the average E\(_p\) of 1.6 nm Au nanoclusters to be 0.46 V vs Ag/AgCl in Br\(^-\) containing...
electrolyte while it showed an $E_p$ of 0.72 V after one complete oxidation-reduction cycle in acid containing electrolyte.\(^3\) We alternatively reported the size determination of metal NPs by measuring their SA/V by a combination of CV and ASV, which showed excellent agreement with the size measured by scanning electron microscopy (SEM).\(^4,11,95\) The $E_p$ in ASV and SA/V is also sensitive to the aggregation state of Au NPs\(^15\) and the composition and atomic arrangement of bimetallic Au-Cu NPs.\(^123\) This shows the significance of ASV and electrochemical SA/V measurements to analyze electrode-attached metal NPs. Electrochemical techniques are low cost, simple, fast, and high throughput, allowing many variables to be quickly studied with meaningful statistics.\(^59,234\)

In comparison, monitoring the NP size by electron microscopy is much more expensive and tedious, with throughput that is often too low to be practical from a time and cost standpoint when the study involves many different samples and experimental conditions.

Here we describe the use of ASV and electrochemical SA/V measurements to measure size transformations of Au NPs ranging from 1.6 to 15.1 nm in diameter attached to glass/ITO electrodes as the result of surface oxidation-reduction cycling in acid. There are several important differences between our work and the previous studies mentioned. First, our Au NPs are not mixed with a Vulcan carbon support material. Carbon supports have been shown to alter the stability and EASA of Au NPs previously. Second, we perform our studies with a Ag quasireference electrode, which avoids potential contamination from Cl\(^-\) from a Ag/AgCl reference electrode. This can dramatically affect the results. Third, we examine the role of Au NP electrode coverage on the size transformation. Fourth, our size characterization is performed electrochemically for Au NPs attached directly to the electrode. This avoids potential issues with measuring particle
size and performing other types of analyses following removal of the Au NPs from the electrode. Finally, we determined the potentials that lead to the size transformation and measured the fraction of the Au dissolved from the surface during cycling. This study of weakly-stabilized Au NPs is important, as they are useful for electrocatalysis, electrochemical sensing, and other applications, but prone to undergo oxidation and size transformations during fairly mild electrochemical treatments.\(^3\) This type of study is also important because various ligand-stabilized NPs are often subjected to electrochemical oxidation-reduction cycling as a means to clean the metal surface from ligand stabilizers or chemical impurities before their application.\(^{235-236}\) It is important to know if the treatment leads to size instability as that would negatively affect their electrochemical properties.

### 3.2. RESULTS AND DISCUSSION

#### 3.2.1. General Overview of the Experiment. The goals of this study were to 1) better understand the size-dependent ripening of metal NPs undergoing electrochemical oxidation/reduction cycling and 2) demonstrate that electrochemical SA/V and ASV are useful methods for monitoring size-transformations that occur during various electrochemical treatments directly on electrode surfaces. Figure 3.1 illustrates the different steps of the experimental procedure carried out in this work. We first synthesized THPC-stabilized 1.6 nm diameter Au NPs, citrate-stabilized 4.1 nm diameter Au NPs, and citrate-stabilized 15.1 nm diameter Au NPs and then attached them to glass/ITO/APTES
electrodes as shown in steps 1 and 2, respectively. UV-vis spectroscopy (Figure 3.2) and transmission electron microscopy (TEM) analysis confirmed the successful synthesis while electrochemistry and scanning electron microscopy (SEM) confirmed their successful attachment to the electrode surface and NP size. The as-synthesized 4.1 and 15.1 nm diameter Au NPs displayed a localized surface plasmon resonance band (LSPR) in the UV-vis spectrum at 506 nm and 519 nm, respectively, while 1.6 nm Au NPs do not show a distinct LSPR band in this range.\textsuperscript{3,61} In step 3, we subjected the electrode-attached Au NPs to multiple oxidation-reduction cycles in 0.1 M HClO$_4$ electrolyte solution using cyclic voltammetry (CV). In step 4, we again characterized the resulting Au NPs by

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3_1.png}
\caption{General experimental procedure followed in this work.}
\end{figure}
electrochemical SA/V, ASV and SEM measurements (SA/V and ASV were measured after ozone treatment for the 4.1 nm and 15.1 nm Au NPs, but not 1.6 nm Au NPs).

![Graph showing UV-vis absorbance of THPC coated Au NPs](image)

**Figure 3.2.** UV-vis absorbance of THPC coated 1.6 nm (pink), citrate coated 4.1 nm (blue), and citrate coated 15.1 nm (red) Au NPs.

### 3.2.2. Oxidation-Reduction Cycling and Electrochemical Analysis of Au NPs

A CH Instrument model CHI 660E electrochemical work-station was used to perform all cyclic voltammetry (CV) and anodic stripping voltammetry (ASV) experiments. The 3-electrode electrochemical cell consisted of glass/ITO/APTES/Au NPs as the working electrode, Ag/AgCl (3 M KCl) as the reference electrode, and Pt wire as the counter electrode. CVs were performed between -0.2 to 1.6 V at a scan rate of 0.1 V/s in 0.1 M HClO₄ solution for the total surface area (SA) analysis while the ASVs were obtained from 0.0 V to 1.2 V at a scan rate of 0.01 V/s in 0.01 M KBr plus 0.1 M KClO₄ solution for the size and volume analysis. Oxidation-reduction cycling was performed by obtaining multiple consecutive CVs of a glass/ITO/APTES/Au NP working electrode with a Pt wire as counter electrode and a bare Ag wire as quasi-reference electrode to avoid Cl⁻
contamination from an Ag/AgCl reference electrode. The CVs were obtained at scan rates of 0.5 V/s or 0.1 V/s for 100, 200, 500 and 1000 consecutive cycles to determine the effect of cycling on the ripening of the different Au NPs.

We performed the different number of consecutive CVs between -0.2 and 1.6 V at a scan rate of 0.5 V/s in 0.1 M HClO₄ on the various Au NP-modified electrodes. Figure 3.3 shows cycles 1, 10, 50, 100, 500, and 1000 of glass/ITO/APTES coated with 4.1 nm diameter Au NPs. In cycle 1, the reduction peak appeared at 0.8 V vs. an Ag wire (blue plot) and in the 10th cycle, the peak area clearly decreased with a small positive shift (red plot). In the subsequent 50th, 100th, 500th, and 1000th cycles, the reduction peak area decreased significantly until it was barely noticeable at cycle 1000 (pink plot). Steven and coworkers studied the behavior of carbon-supported Au NPs when treated with up to 100 oxidation-reduction cycles in acidic solution, where they first observed an increase in the electrochemically active surface area (EASA) with the number of cycles (based on increased area of the reduction peak), which slightly decreased further with an increasing number of cycles. They didn’t observe a significant change in EASA for the carbon-supported 4.5 nm Au NPs, while our results show a large decrease in the Au oxide reduction current with an increase in the number of oxidation-reduction cycles for the citrate-coated 4.1 nm Au NPs with an average initial Au oxide reduction charge of 1.46 (± 0.31) x 10⁻⁵ Coulombs (n = 3) and charges of 7.28 (± 1.54) x 10⁻⁶, 2.94 (± 0.78) x 10⁻⁶, and 1.50 (± 0.56) x 10⁻⁶ Coulombs at 200, 500 and 1000 CV cycles, respectively. The decrease in the Au oxide reduction peak height and area is attributed to 1) the ripening of the Au NPs into
larger sizes, which lowers the total SA of the electrode-attached Au NPs and 2) dissolution of Au into solution. The Au oxide reduction peak is directly related to the total SA of all combined Au NPs on the surface, which is related to the NP size if we assume that V is not changing dramatically, but could also be related to loss of Au. We discuss these two possibilities more later. The different behavior in our study compared to Steven and co-workers could be due to the different electrolyte (HClO$_4$ vs H$_2$SO$_4$), higher potential in our work, or stability provided by Vulcan carbon in their work.\textsuperscript{88}

**Figure 3.3.** Cyclic voltammograms (CVs) of a glass/ITO/APTES electrode coated with citrate-stabilized 4.1 nm diameter Au NPs obtained in 0.1 M HClO$_4$ solution at a scan rate of 0.1 V/s. (vs. Ag wire quasireference electrode). The cycle number is indicated in the figure legend. The CVs were run at 0.5 V/s in between the CVs shown.
3.2.3. Effect of Oxidation-Reduction Cycling Measured by ASV. To further explore the decrease in the Au oxide reduction peak size with the number of oxidation-reduction cycles, we performed ASV of the different glass/ITO/APTES/Au NPs before and after 1000 CV cycles. Oxidative stripping of Au was carried out in the presence of 0.01 M KBr in 0.1 M KClO₄ taking place by the following reactions (equations 3.5-3.6).²

\[
\text{Au}^0 + 4\text{Br}^- \rightarrow \text{AuBr}_4^- + 3e^- \quad (E^0 = 0.85 \text{ V vs NHE}) \quad (3.5)
\]

\[
\text{Au}^0 + 2\text{Br}^- \rightarrow \text{AuBr}_2^- + e^- \quad (E^0 = 0.96 \text{ V vs NHE}) \quad (3.6)
\]

The peak oxidation potential \(E_p\) in ASV is indicative of the NP size and the integrated charge under the peak is indicative of the total number of Au NPs on the electrode surface. Figure 3.4 shows the ASVs of glass/ITO/APTES coated with 1.6, 4.1 and 15.1 nm average diameter Au NPs that were not cycled and were cycled 1000 times in 0.1 M HClO₄ at scan rate of 0.5 V/s. Since ASV is a destructive technique, the ASVs before and after cycling are from two different, but identically-prepared samples. We observed that the \(E_p\) of 1.6 nm Au NPs shifted from 0.47 V for non-cycled NPs to 0.72 V after 1000 cycles (Figure 3.4A). Based on the Plieth equation²³⁷ and our previous work using ASV for size analysis, the diameter increased to \(~4.4\) nm after the 1000 CV cycles. Similarly, the non-cycled 4.1 nm Au NPs displayed an \(E_p\) of 0.71 V compared to 0.82 V after 1000 cycles (Figure 3.4D), which corresponds to particle diameters of 4.2 nm and \(~7.2\) nm, respectively, from the Plieth equation. The 15.1 nm Au NPs displayed an \(E_p\) of 0.78 V for the non-cycled NPs and 0.85 V for those cycled 1000 times (Figure 3.4G), which corresponds to particle diameters of 7.2 nm and 39.6 nm, respectively. These results clearly indicate that all of the different-sized NPs increased significantly during the 1000 oxidation-reduction cycles, since the \(E_p\) is a good indicator of their size.³ The deviation of the measured 15.1 nm
diameter size by the Plieth equation for non-cycled NPs has been observed by our group previously and is not well-understood. Regardless, there is a clear size transformation during the oxidation-reduction cycling.

Figure 3.4. Anodic stripping voltammetry (ASV) in 0.01 M KBr plus 0.1 M KClO₄ of glass/ITO/APTES electrodes coated with THPC 1.6 nm (A), citrate 4.1 nm (D) and citrate 15.1 nm (G) Au NPs before (blue) and after 1000 oxidation-reduction CV cycles (red) at 0.5 V/s in 0.1 M HClO₄. STEM/SEM images of 1.6 nm Au NPs (B-C), 4.1 nm Au NPs (E-F), and 15.1 nm Au NPs (H-I) before and after 1000 CV cycles respectively.
Electron microscopy images of glass/ITO/APTES/Au NPs electrodes with 1.6, 4.1 and 15.1 nm Au NPs after 1000 CV cycles confirmed the NP size transformations determined by ASV (Figure 3.4B-I). After 1000 CV cycles, the 1.6 nm diameter NPs (Figure 3.4B) increased to 19.1 ± 4.8 nm (Figure 3.4C). Similarly, the size of 4.1 (Figure 3.4E) and 15.1 nm (Figure 3.4H) Au NPs increased to 26.6 ± 7.1 nm (Figure 3.4F) and 38.1 ± 9.6 nm (Figure 3.4I), respectively. The corresponding NPs size histograms is as shown in Figure 3.8. The size measured by SEM was fairly similar to the ASV determined size for the 15.1 nm Au NPs but much larger than predicted by ASV for the 1.6 nm and 4.1 nm diameter Au NPs. This is likely because ASV is most accurate for sizes in the 1-4 nm diameter range and 30-50 nm diameter range, while it is less accurate in the 10-30 nm diameter range.\textsuperscript{3,104} For this reason, we electrochemically measured the SA/V as a more accurate measure of the size.

3.2.4. Effect of Oxidation-Reduction Cycling Measured by SA/V. The diameter of the NPs after a different number of CV cycles was calculated by measuring the SA/V and using the relation of \( SA/V = 6/D \) (\( D \) = NP diameter) to determine the diameter, as reported by our group previously.\textsuperscript{4} The SA/V values for non-cycled 1.6, 4.1, and 15.1 nm Au NPs were found to be 2.32 ± 0.09, 0.75 ± 0.02, and 0.43 ± 0.03, respectively, and 0.31 ± 0.04, 0.20 ± 0.02, and 0.18 ± 0.01 after 1000 cycles, respectively (Table 3.1). Based on these SA/V ratios, the calculated non-cycled diameter was found to be 2.6 ± 0.1, 8.0 ± 0.1, and 14.0 ± 1.8 nm, respectively, and 19.5 ± 1.2 (19.1 nm SEM), 29.8 ± 3.6 (26.6 SEM), and 33.6 ± 3.7 nm (38.1 SEM) in diameter, respectively, after 1000 CV cycles. These calculated sizes are in much better agreement with the SEM determined sizes, especially for those after 1000 cycles. The SA/V is particularly accurate for Au NPs greater than 10
nm in diameter as long as ozone cleaning is performed. We similarly calculated the SA/V ratios of 1.6, 4.1 and 15.1 nm diameter Au NPs after 100, 200 and 500 CV cycles, which was found to decrease with an increase in the number of CV cycles (diameter increased). Table 3.1 summarizes the SA/V ratio and corresponding NP diameter of the different sized Au NPs after the different CV cycles. All of the integrated CV and ASV peak areas in term of charge (in Coulombs) for cycling at 0.5 V/s are provided in Table 3.2.

**Table 3.1.** SA/V ratios and calculated NPs diameter for 1.6, 4.1 and 15.1 nm diameter Au NPs as a function of the number of CV cycles at a scan rate of 0.5 V/s.

<table>
<thead>
<tr>
<th>No. of CV cycles</th>
<th>1.6 nm</th>
<th>4.1 nm</th>
<th>15.1 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SA/V</td>
<td>Diameter (nm)</td>
<td>SA/V</td>
</tr>
<tr>
<td>0</td>
<td>2.32 ± 0.09</td>
<td>2.6 ± 0.1</td>
<td>0.75 ± 0.02</td>
</tr>
<tr>
<td>100</td>
<td>0.63 ± 0.08</td>
<td>9.7 ± 1.2</td>
<td>0.42 ± 0.05</td>
</tr>
<tr>
<td>200</td>
<td>0.59 ± 0.04</td>
<td>10.1 ± 0.6</td>
<td>0.37 ± 0.06</td>
</tr>
<tr>
<td>500</td>
<td>0.48 ± 0.04</td>
<td>12.2 ± 0.9</td>
<td>0.29 ± 0.04</td>
</tr>
<tr>
<td>1000</td>
<td>0.31 ± 0.04</td>
<td>19.5 ± 1.2</td>
<td>0.20 ± 0.02</td>
</tr>
</tbody>
</table>
The ASV, SEM, and SA/V data all indicate a significant size increase, or ripening, for all Au NPs after oxidation-reduction cycling. Figure 3.5A shows a plot of the NP diameter as a function of the number of oxidation-reduction CV cycles for 1.6, 4.1 and 15.1 nm average diameter Au NPs as a function of CV cycles run in 0.1 M HClO₄ at a scan rate of 0.5 V/s. This data is for the lower ASV coverage (~20-35 µC) of Au NPs calculated from their Au oxide reductive charges in CV before cycling.

Table 3.2. Integrated charges (in Coulombs) obtained under the CV and ASV peaks of glass/ITO/APTES electrodes coated with 1.6, 4.1 and 15.1 nm average diameter Au NPs as a function of CV cycles run in 0.1 M HClO₄ at a scan rate of 0.5 V/s. This data is for the lower ASV coverage (~20-35 µC) of Au NPs calculated from their Au oxide reductive charges in CV before cycling.

<table>
<thead>
<tr>
<th>No of CV cycles</th>
<th>1.6 nm</th>
<th>4.1 nm</th>
<th>15.1 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CV (C)</td>
<td>ASV (C)</td>
<td>CV (C)</td>
</tr>
<tr>
<td>100</td>
<td>4.69 x 10⁻⁶</td>
<td>8.57 x 10⁻⁶</td>
<td>1.25 x 10⁻⁵</td>
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<td></td>
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<td>2.03 x 10⁻⁵</td>
<td>1.12 x 10⁻⁵</td>
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<td>1.06 x 10⁻⁵</td>
<td>1.83 x 10⁻⁵</td>
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<td>1.11 x 10⁻⁵</td>
<td>1.24 x 10⁻⁵</td>
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<td>1.88 x 10⁻⁶</td>
<td>3.82 x 10⁻⁶</td>
<td>3.97 x 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>2.15 x 10⁻⁶</td>
<td>4.68 x 10⁻⁵</td>
<td>2.58 x 10⁻⁶</td>
</tr>
<tr>
<td>1000</td>
<td>6.77 x 10⁻⁶</td>
<td>2.31 x 10⁻⁵</td>
<td>3.45 x 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>7.25 x 10⁻⁶</td>
<td>2.18 x 10⁻⁵</td>
<td>4.23 x 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>1.66 x 10⁻⁵</td>
<td>5.51 x 10⁻⁵</td>
<td>2.99 x 10⁻⁶</td>
</tr>
</tbody>
</table>
nm Au NPs in order to understand the effect of NP size on the extent of ripening. There is a significant increase in NP size with an increase in the number of CV cycles for all Au

![Image](image.png)

**Figure 3.5.** Plot of (A) NP diameter and (B) relative increase in diameter \(D_{\text{final}}/D_{\text{initial}}\) vs. the number of CV cycles in 0.1 M HClO₄ for 1.6 (blue plot), 4.1 (pink plot) and 15.1 (red plot) nm Au NPs. (C) Plot of nanoparticle diameter vs number of CV cycles at lower (~200 NPs/µm², blue plot) and higher (~2000 NPs/µm², red plot) coverages at a scan rate of 0.5 V/s for 4.1 nm Au NPs and (D) Plot of \(D_{\text{final}}/D_{\text{initial}}\) vs number of CV cycles for 4.1 nm Au NPs at the two coverages.

NPs. The absolute change in diameter was in the 15-25 nm range for all sizes, but the relative diameter increase \(D_{\text{final}}/D_{\text{initial}}\) was largest for the smallest sized 1.6 nm Au NPs. Figure 3.5B shows \(D_{\text{final}}/D_{\text{initial}}\) as a function of the number of cycles, which clearly increases as the initial NP size decreases. We observed that there is a significant NP size
transformation within the first 200 cycles with a 1.44%, 0.54%, and 0.43% diameter increase per cycle for 1.6, 4.1, and 15.1 nm Au NPs, respectively. After 200 cycles, the size is more stable until later cycles, where there is again a relatively larger increase in size, but still less than the first 200 cycles. The relative rate of size transformation between 200 to 1000 CV cycles was 0.11%, 0.099% and 0.036% diameter increase per cycle for 1.6, 4.1, and 15.1 nm Au NPs respectively, which is much slower than that within the first 200 cycles. This shows that the ripening process slows down as the Au NPs increase in size and become more thermodynamically stable. Overall, the NP size transformation is size-dependent and measurable directly on the electrode surface by SA/V measurements.

3.2.5. Effect of Au NP Coverage on Oxidation-Reduction Induced Ripening. Au NP coverage is usually an important factor that affects electrochemical ripening.\textsuperscript{11,238-239} As the coverage decreases, the rate of ripening generally decreases due to less communication between neighboring NPs, which is needed for both Ostwald and Smoluchowski ripening. We directly monitored the effect of NP coverage directly on the ripening of 4.1 nm Au NPs with a coverage of \(2.0 \times 10^{-4}\) Coulombs (\(~2000\) NPs/\(\mu m^2\)) and \(2.0 \times 10^{-5}\) Coulombs (\(~200\) NPs/\(\mu m^2\)) on glass/ITO/APTES. The surface coverage was maintained similar to our previous electrochemical Ostwald ripening studies in KBr solutions performed by Pattadar \textit{et al.},\textsuperscript{11} which was also monitored by measuring the SA/V ratio.\textsuperscript{4} Figure 3.5C shows the variation of NP diameter of 4.1 nm Au NPs with number of CV cycles performed in 0.1 M HClO\(_4\) at a scan rate of 0.5 V/s. We observed that the ripening is more significant for the higher Au coverage as compared to the lower coverage. Interestingly, the coverage did not play a significant role for ripening within the first 200 cycles but became more pronounced after 200 CV cycles (Figure 3.5C).
diameter increase ($D_{\text{final}}/D_{\text{initial}}$) as a function of CV cycles for the two coverages is shown in Figure 3.5D. From this plot, the rate of NP growth from the beginning to 1000 cycles was found to be 0.34% and 0.27% diameter increase per cycle for the coverage of 2000 NPs/µm$^2$ and 200 NPs/µm$^2$, respectively. Greater ripening at higher coverage is due to the greater number of interacting NPs per unit area on the electrode surface. Ripening involves mass transfer of Au from one NP to another, which is enabled by closer NP-NP distances at higher coverage. Table 3.3 shows the integrated CV and ASV peak areas in term of charge (in Coulombs) for cycling at 0.5 V/s at higher coverage.

3.2.6. Cycling Scan Rate Dependence on the Ripening Process. To gain more insight about the ripening process during oxidation-reduction cycling, we altered the scan rate of the CV cycles while keeping the total scanning time constant by reducing the total number of scans for the slower scan rates. Scanning faster allows the NPs to undergo a greater number of oxidation-reduction cycles in a constant amount of total time compared to scanning slow, which provides fewer oxidation-reduction cycles, but the same total time at each potential. We cycled glass/ITO/APTES coated with 4.1 nm diameter Au NPs from -0.2 V to 1.6 V at a scan rate of 0.5 V/s for 1000 CV cycles and at a scan rate of 0.1 V/s for 200 cycles, which amounts to 93.3 min total of potential cycling in both cases. The final diameter was 29.8 ± 3.6 nm at 0.5 V/s for 1000 cycles as compared to 20.6 ± 0.7 nm at 0.1 V/s for 200 cycles (Figure 3.6A). This indicates that ripening depends mainly on the number of full cycles rather than the total time spent at any particular potential. In another experiment, we performed 1000 CV cycles at the lower scan rate of 0.1 V/s, which amounts to a total cycling time of 465 min while maintaining the total number of CV cycles the same at both scan rates. The Au NPs increased to 34.4 ± 2.5 nm, which is not significantly
larger than the faster scan rate with 1000 CV cycles, confirming that the number of cycles dictates the extent of ripening as opposed to time spent at any potential (Figure 3.6A). Table 3.3 shows the integrated CV and ASV peak areas in term of charge (in Coulombs) for cycling at 0.1 V/s.

We also held the electrode-attached 4.1 and 15.1 nm Au NPs at a potential of 1.4 V for 93.3 min in 0.1 M HClO₄ and scanned back to -0.2 V once to compare to the 0.1 V/s and 0.5 V/s scan rates. At this potential, NPs were in the oxidized state throughout the same time as the cycled samples, but only reduced one time. After completing the potential hold, one complete oxidation-reduction cycle was performed from -0.2 to 1.6 V to analyze Au NP size by SA/V. Interestingly, we found that the NP size remained unchanged as revealed by CV and ASV (Figure 3.6B-C) along with the measured SA/V ratio and E₀ value (Table 3.4). From the two samples, whose CVs were first obtained without holding the potential to confirm a similar coverage (Figure 3.6B, blue and red plots), one sample was directly subjected to ASV analysis (Figure 3.6C, red) while the other was first held at 1.4 V for 93.3 min before SA/V analysis (Figure 3.6B and 3.6C, green plots). For 4.1 nm Au NPs, the average E₀ and SA/V after potential holding were found to be 0.728 V vs Ag/AgCl and 0.753, respectively, which are pretty close to the corresponding average values for no holding, as also measured in our previous work.⁴ This observation clearly indicates that electrochemical ripening of Au NPs requires numerous oxidation and reduction cycles as opposed to the oxidation only over a long time. This is likely due to the formation of a complete passivating mono or multilayer of Au oxide on the NPs surface as reported by Nicol et. al.⁸⁹ This would likely prevent active ripening, which requires Au
Table 3.3. Integrated charges (in Coulombs) obtained under the CV and ASV peaks of glass/ITO/APTES electrodes coated with 4.1 nm Au NPs as a function of CV cycles in 0.1 M HClO$_4$ run at a scan rate of 0.5 V/s and 0.1 V/s as mentioned. This data is for the higher (-60-210 µC) and lower (-20-35 µC) ASV coverage of Au NPs calculated from their Au oxide reductive charges in CV before cycling. SA/V is also provided.

<table>
<thead>
<tr>
<th>No of CV cycles</th>
<th>4.1 nm Au with higher coverage CV cycling scan rate = 0.5 V/s</th>
<th>4.1 nm Au with lower coverage CV cycling scan rate = 0.1 V/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CV (C) ASV (C) SA/V</td>
<td>CV (C) ASV (C) SA/V</td>
</tr>
<tr>
<td>200</td>
<td>3.85 x 10^{-5} 1.03 x 10^{-4} 0.374</td>
<td>6.61 x 10^{-6} 1.92 x 10^{-5} 0.344</td>
</tr>
<tr>
<td></td>
<td>3.51 x 10^{-5} 1.04 x 10^{-4} 0.338</td>
<td>1.08 x 10^{-5} 3.33 x 10^{-5} 0.324</td>
</tr>
<tr>
<td></td>
<td>5.62 x 10^{-5} 1.76 x 10^{-4} 0.319</td>
<td>8.19 x 10^{-6} 2.17 x 10^{-5} 0.377</td>
</tr>
<tr>
<td>500</td>
<td>2.56 x 10^{-5} 1.18 x 10^{-4} 0.217</td>
<td>7.55 x 10^{-6} 3.50 x 10^{-5} 0.216</td>
</tr>
<tr>
<td></td>
<td>1.82 x 10^{-5} 6.82 x 10^{-5} 0.267</td>
<td>4.95 x 10^{-6} 2.10 x 10^{-5} 0.236</td>
</tr>
<tr>
<td></td>
<td>1.98 x 10^{-5} 9.61 x 10^{-5} 0.206</td>
<td>1.80 x 10^{-6} 5.80 x 10^{-6} 0.310</td>
</tr>
<tr>
<td>1000</td>
<td>1.34 x 10^{-5} 7.08 x 10^{-5} 0.189</td>
<td>3.52 x 10^{-6} 2.04 x 10^{-5} 0.173</td>
</tr>
<tr>
<td></td>
<td>5.49 x 10^{-6} 3.34 x 10^{-5} 0.165</td>
<td>5.94 x 10^{-6} 3.30 x 10^{-5} 0.180</td>
</tr>
<tr>
<td></td>
<td>1.19 x 10^{-5} 7.42 x 10^{-5} 0.160</td>
<td>3.91 x 10^{-6} 2.54 x 10^{-5} 0.154</td>
</tr>
</tbody>
</table>

ions to be oxidized and reduced (Ostwald ripening) or NP movement and coalescence. The reduction of the Au oxide layer and dissolved Au ions in solution are clearly necessary steps in the ripening process.
Table 3.4. Integrated CV and ASV charge (in Coulombs) for glass/ITO/APTES coated with 4.1 and 15.1 nm diameter Au NPs before and after holding the potential at 1.4 V for 93.3 min in 0.1 M HClO$_4$. SA/V and $E_p$ after are also provided. This data is for the lower ASV coverage (~26 -50 µC for 4.1 nm and ~43-58 µC for 15.1 nm) of Au NPs calculated from their Au oxide reductive charges in CV before holding potential.

<table>
<thead>
<tr>
<th>NPs diameter</th>
<th>CV and ASV charge (in Coulombs) before and after holding the potential and CV/ASV, and peak oxidation potential in ASV ($E_p$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CV before (C)</td>
</tr>
<tr>
<td>4.1 nm</td>
<td>3.84 x 10$^{-5}$</td>
</tr>
<tr>
<td></td>
<td>3.52 x 10$^{-5}$</td>
</tr>
<tr>
<td></td>
<td>1.97 x 10$^{-5}$</td>
</tr>
<tr>
<td>15.1 nm</td>
<td>2.49 x 10$^{-5}$</td>
</tr>
<tr>
<td></td>
<td>1.87 x 10$^{-5}$</td>
</tr>
<tr>
<td></td>
<td>2.51 x 10$^{-5}$</td>
</tr>
</tbody>
</table>

3.2.7. Ripening Versus Gold Dissolution. We wanted to understand what fraction of Au ripens and what fraction permanently dissolves during cycling. The ASV peak area indicates the amount of Au on the electrode, which decreased after cycling as shown in Figure 3.4. Since we measured the ASV before and after cycling on two different samples, it was not possible to measure the amount of Au lost because the initial Au NP coverage could have been different on the two different samples to begin with. To get around this, we first obtained two samples with the same initial Au NP coverage as determined by the same Au oxide reduction peak area from a CV obtained in 0.1 M HClO$_4$. Then we
measured the ASV from one sample without any treatment and from the second sample after running 1000 CV cycles in 0.1 M HClO$_4$. This allowed comparison of the amount of Au from two samples that initially had an identical Au coverage. This was possible to do with the 4.1 and 15.1 nm diameter Au NPs, since they are size stable after one CV cycle in 0.1 M HClO$_4$, but it was not possible on the 1.6 nm diameter Au NPs due to size instability after one CV cycle.$^3,^{10}$ Instead, the approximate amount of Au lost for the 1.6 nm Au NPs was determined by soaking 8 different glass/ITO/APTES electrodes into the as prepared solution of 1.6 nm Au NPs for 3 min each and performing ASV on 4 samples that were not cycled and comparing that to 4 samples that were cycled 1000 times. The results show that 50.5 ± 11.6%, 39.1 ± 18.3%, and 31.4 ± 15.1% of Au were lost from the electrode surface for the 1.6, 4.1 and 15.1 nm diameter Au NPs, respectively (Table 3.5). The dissolution behavior is similar to that observed by Cherevko et al. for Au foils subjected to potential cycling and anodic polarization as measured by inductively-coupled plasma mass spectrometry (ICP-MS).$^{119}$ Our results show a greater amount of Au lost during oxidation-reduction cycling as the size of the Au NPs decreases. Presumably, the loss of Au is due to oxidative dissolution, but it is also possible that full in-tact Au NPs become removed from the electrode during the cycling without dissolution into Au ions. We do not have a way to conclusively determine if both possibilities exist at this time.
**Table 3.5.** Integrated charges (in Coulombs) obtained under the CV and ASV peaks for glass/ITO/APTES electrodes coated with 1.6, 4.1 and 15.1 nm Au NPs before and after 1000 CV cycles run in 0.1 M HClO₄ at a scan rate of 0.5 V/s.

<table>
<thead>
<tr>
<th>NPs diameter (nm)</th>
<th>CV₁ before cycling (C)</th>
<th>ASV before cycling (C)</th>
<th>Average ASV before cycling (C)</th>
<th>CV₂ before cycling (C)</th>
<th>ASV after cycling (C)</th>
<th>Average ASV after cycling (C)</th>
<th>% Au loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>N/A</td>
<td>2.30 x 10⁻⁵</td>
<td>2.87 (± 0.38) x 10⁻⁵</td>
<td>N/A</td>
<td>1.14 x 10⁻⁵</td>
<td>1.45 (± 0.14) x 10⁻⁵</td>
<td>50.5 ± 11.6</td>
</tr>
<tr>
<td></td>
<td>N/A</td>
<td>3.13 x 10⁻⁵</td>
<td></td>
<td>N/A</td>
<td>1.51 x 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N/A</td>
<td>2.98 x 10⁻⁵</td>
<td></td>
<td>N/A</td>
<td>1.34 x 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N/A</td>
<td>3.07 x 10⁻⁵</td>
<td></td>
<td>N/A</td>
<td>1.68 x 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>1.74 x 10⁻⁵</td>
<td>2.85 x 10⁻⁵</td>
<td>3.07 (± 0.23) x 10⁻⁵</td>
<td>1.89 x 10⁻⁵</td>
<td>2.11 x 10⁻⁵</td>
<td>1.20 (± 0.47) x 10⁻⁵</td>
<td>39.1 ± 18.3</td>
</tr>
<tr>
<td></td>
<td>1.89 x 10⁻⁵</td>
<td>3.31 x 10⁻⁵</td>
<td></td>
<td>2.18 x 10⁻⁵</td>
<td>1.63 x 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.15 x 10⁻⁵</td>
<td>3.06 x 10⁻⁵</td>
<td></td>
<td>2.08 x 10⁻⁵</td>
<td>1.87 x 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.1</td>
<td>1.13 x 10⁻⁵</td>
<td>2.67 x 10⁻⁵</td>
<td>2.58 (± 0.22) x 10⁻⁵</td>
<td>1.17 x 10⁻⁵</td>
<td>1.78 x 10⁻⁵</td>
<td>1.81 (± 0.32) x 10⁻⁵</td>
<td>31.4 ± 15.1</td>
</tr>
<tr>
<td></td>
<td>1.17 x 10⁻⁵</td>
<td>2.74 x 10⁻⁵</td>
<td></td>
<td>9.01 x 10⁻⁶</td>
<td>1.66 x 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.94 x 10⁻⁶</td>
<td>2.33 x 10⁻⁵</td>
<td></td>
<td>9.24 x 10⁻⁶</td>
<td>1.88 x 10⁻⁵</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.6. (A) Bar graph indicating the size transformation of 4.1 nm diameter Au NPs after 1000 CV cycles with different scan rate, coverage of NPs, and when holding the potential of the working electrode for the same time as scanning, (B) CV of 4.1 nm Au NPs without holding the potential (blue and red) and after 93.3 min of holding the potential at 1.4 V (dark green), (C) ASV of 4.1 nm Au NPs before (red) and after (dark green) holding the potential, (D) CV of 4.1 nm Au NPs before (dark green) and after (dotted dark green) 1000 CV cycles in 0.1 M HClO$_4$ solution and red CV represents a separate 4.1 nm Au NPs sample without CV cycles, and (E) ASV of 4.1 nm Au NPs after 1000 CV cycles (green) and without CV cycles (red).
Since the amount of ripening depends on Au NP coverage, we also measured the amount of dissolution at a very low coverage of 4.1 nm diameter Au NPs on the electrode surface. Figures 3.6D and 3.6E show the CVs and ASVs, respectively, for an initial CV coverage of \( \sim 1.60 \times 10^{-6} \) Coulombs, which is about 10 times lower than the earlier ripening studies. In this case, the reduction peak for Au in the CV completely disappeared after 1000 CV cycles in 0.1 M HClO\(_4\) at a scan rate of 0.5 V/s (Figure 3.6D, dotted dark green plot). Consistent with this, the oxidation peak for Au in the ASV of the same electrode in Br\(^-\) containing electrolyte disappeared (Figure 3.6E, dark green plot). To compare this finding, we performed the surface oxidation-reduction in 0.1 M HClO\(_4\) (Figure 3.6D, red plot) and ASV stripping of another sample having a similar Au coverage of \( 1.45 \times 10^{-6} \) Coulombs but with no cycling (Figure 3.6E, red plot). In this case, we observed a clear stripping peak for Au. This clearly indicates that 100% of the Au was lost at low NP coverages during potential cycling. The amount of Au lost compared to ripening during oxidation-reduction cycling clearly depends on the size and coverage of the Au NPs. A high or moderate coverage of smaller NPs allows them to stabilize through ripening, whereas a very low coverage leads to their complete dissolution.

We hypothesized that the Au NPs mainly dissolve as soluble ions during the multiple CV cycles as opposed to being removed as in-tact NPs, based on previous work carried out on 2D Au surfaces.\(^{119}\) To test this, we attached a high coverage (\( 3.6 \times 10^{-4} \) Coulombs) of 15.1 nm Au NPs on the glass/ITO/APTES surface and subjected them to 5000 CV cycles in 0.1 M HClO\(_4\) at a scan rate of 0.5 V/s. Then we carried out electrochemical deposition (ECD) at -0.2 V for 1000 seconds on a fresh glass/ITO surface using the same electrolyte used for the multiple CV cycles. ECD leads to the formation of
Au on the electrode surface from reduction of Au ions in the electrolyte. This was confirmed by the presence of a significant reduction peak in a CV in 0.1 M HClO₄ and oxidation peak in ASV in Br⁻ (Figure 3.7). The ECD of Au onto the electrode surface indicates the presence of soluble Au ions in the electrolyte solution following the multiple CV cycles. This does not completely rule out that in-tact Au NPs could also be removed as well though.

**Figure 3.7.** CV in 0.1 M HClO₄ at a scan rate of 0.1 V/s (A) and ASV in 10 mM KBr and 0.1 M KClO₄ at a scan rate of 0.01 V/s (B) of Au electrochemically deposited on a glass/ITO electrode at -0.2 V for 1000 seconds. Electrodeposition of Au was carried out using the electrolyte where a glass/ITO/APTES electrode coated with 15.1 nm diameter Au NPs (at a high coverage of 1.0 x 10⁻⁴ Coulombs of Au stripping charge) was subjected to 5000 CV cycles in 0.1 M HClO₄ at a scan rate of 0.5 V/s.

**3.2.8. Ripening Mechanism.** Figure 3.8 shows the size histogram of 350 Au NPs before and after 1000 oxidation-reduction cycles for 1.5 nm Au NPs in 0.1 M HClO₄. The average diameter was 15.1 ± 1.7 nm before and 38.1 ± 9.6 nm after cycling. The average size and dispersity increased, and some smaller NPs appeared in the size population that were not present prior to cycling. This is indicative of Ostwald ripening, as observed for
Au clusters during CO oxidation in the work of Hu et al.\textsuperscript{40} Since AuO\textsubscript{x} formation during cycling leads to the formation of dissolved ionic Au species, it is likely that the ionic Au comes from the smaller Au NPs and reduction causes those ions to deposit onto the larger, more stable Au NPs. Our data is most consistent with an Ostwald ripening mechanism during the multiple electrochemical oxidation-reduction cycles, where some ionic Au species diffuse away from the surface completely and do not redeposit. We cannot completely rule out that Smoluchowski ripening also occurs, but there is no direct evidence to support it at this point.
In summary, we measured the electrochemical ripening behavior of 1.6-15.1 nm diameter, weakly-stabilized Au NPs attached to glass/ITO/APTES electrodes during oxidation-reduction cycling in 0.1 M HClO₄ by our recently developed size-sensitive electrochemical ASV and SA/V measurements. We have drawn several conclusions and new insights from these studies. First, the relative ripening rate of the Au NPs is size-
dependent, with smaller-sized NPs ripening faster relative to their initial size compared to larger NPs under identical conditions. Second, the ripening rate for any particular size of Au NPs increases as the coverage of the Au NPs increases on the electrode surface. Third, ripening occurs as a result of the full oxidation-reduction cycle as opposed to just the oxidation step. The more cycles performed, the more ripening occurs, with the total time being less important than the number of cycles. Fourth, a significant amount of Au removal from the electrode surface occurs during oxidation-reduction cycling, ranging from 30-50% for relatively high NP coverages up to 100% for low coverages. The amount of removal increases as the NP size decreases and the presence of soluble Au ionic species in the electrolyte solution suggests that removal is due to Au oxidative dissolution during cycling. Our results on scan rate, Au dissolution, and SEM-based size distribution measurements for the 15.1 nm Au NPs after cycling are most consistent with size transformation by electrochemical Ostwald ripening. This does not necessarily rule out Smoluchowski ripening form also occurring and it is not clear what the dissolution products are during the oxidation process. Overall, this work provides new insight into the fundamental understanding of size-dependent ripening of Au NPs during electrochemical surface oxidation-reduction cycling in acid. This work demonstrates the usefulness of ASV and electrochemical SA/V measurements to monitor metal NP size transformations directly on surfaces in a fast, straightforward manner and the results will be of general interest to those exploring electrochemical applications for metal NPs, especially in electrocatalysis, sensors, and energy-related devices, where NP size stability at various potentials and in different electrolyte is crucial.
CHAPTER IV

MONITORING THE THERMAL SINTERING OF WEAKLY-STABILIZED SUB-4 nm GOLD NANOPARTICLES USING ANODIC STRIPPING VOLTAMMETRY

4.1. INTRODUCTION

In recent years, metal nanoparticles (NPs) and nanoclusters (NCs) have gained significant attention due to their unique size-dependent thermal, optical, and electrochemical reactivities that are different from their bulk counterparts. The unique size-dependent properties of NPs have been used for various catalytic, sensing, and nanoelectronic applications. In order to use NPs for applications, they are often treated with ozone in order to remove the stabilizing ligands and unwanted impurities. During some applications, such as catalysis or sensing, metal NPs are utilized at elevated temperature. Electrochemical environments often lead to electrochemical or photoelectrochemical annealing, leading to an increase in size. Various factors such as size, stabilizing ligands, and support material play a significant role in the thermal stability and catalytic activity of metal NPs. It is clearly important to have a thorough understanding of the thermal stability of metal NPs for them to be useful in applications.

The thermal stability of Au NPs has gained attention over the years since Au NPs are relatively inert, easy to synthesize, and have many possible applications.
analytical techniques such as optical,\textsuperscript{253} microscopic,\textsuperscript{254-255} spectroscopic,\textsuperscript{256} differential scanning calorimetry (DSC),\textsuperscript{250} and thermal gravimetric analysis (TGA)\textsuperscript{250} methods have been used to study the thermal stability of Au NPs. For example, Albrecht \textit{et al.} studied the impact of the electron beam from a transmission electron microscope (TEM) on the thermal stability of cetyltrimethylammonium bromide (CTAB)-coated Au nanorods (length = 64.5 nm, width = 18.6 nm).\textsuperscript{257} It was observed that the Au nanorods undergo sintering at temperatures as low as 100 °C indicating that the electron beam may cause the sintering. Shivhare \textit{et al.} monitored the thermal sintering of phenylethanthiolate- and hexanethiolate-coated Au\textsubscript{25} NCs by TEM and extended X-ray absorption fine structure (EXAFS) spectroscopy. They found that the NCs show mild sintering in the temperature range of 125-200 °C and rapid sintering occurred at 200 °C.\textsuperscript{255} Bevelry \textit{et al.} reported the sintering of Au NPs by using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and X-ray photoelectron spectroscopy (XPS) analysis.\textsuperscript{250} They observed that N,N,N-Trimethylammonium ethanethiol trifluoroacetate-stabilized 1.2 and 0.9 nm diameter Au NPs began ligand loss and sintering at 143 and 164 °C, respectively, whereas 2-mercaptoethanesulphonic acid-stabilized 1.5 and 1.0 nm diameter Au NPs began ligand loss and sintering at 242 and 245 °C, respectively. This work shows that both NP size and type of stabilizing ligand have a strong influence on the thermal sintering behavior of metal NPs.

In addition to sintering, there have been efforts to study the size-dependent melting behavior of metal NPs, which occurs during or after the sintering process.\textsuperscript{25,127} It is well known that the melting temperature of metal NPs decreases with decreasing size of the NPs.\textsuperscript{32,127,258} Various analytical approaches including DSC, nanometer scale calorimetry,
scanning transmission electron microscopy (STEM), optical, and in-situ TEM have been undertaken to determine the melting temperature of metal NPs.\textsuperscript{127, 258} For example, Schlexer \textit{et al.} monitored the melting temperature of Au NPs by in-situ TEM, finding that the melting point decreased significantly for NPs <10 nm in diameter.\textsuperscript{127} It was found that the crystalline lattice fringes of 2 nm diameter Au NPs on a SiN substrate disappeared at about 300 °C, which was further supported by molecular dynamics simulation. Foster \textit{et al.} employed high resolution STEM along with simulation methods to determine the melting point of 2-5 nm diameter Au NPs supported on carbon films, which showed a higher melting point for the core atoms as compared to the surface atoms.\textsuperscript{258}

Most sub-4 nm diameter Au NP/NCs have been synthesized with thiol stabilizers in organic media.\textsuperscript{259-261} The thiolate ligands are highly passivating due to the strong Au-S interaction.\textsuperscript{8} The thermal sintering and melting properties of the pure metal NPs is difficult to determine because of the influence of the strongly coordinated thiolate ligands, which provide thermal stability. Much less attention has been paid to unstabilized Au NPs or Au NPs coated with weakly-bound water-soluble ligands, such as phosphines, phosphoniums, or amines, despite the potential applications of water-soluble NPs/NCs in catalysis\textsuperscript{3} and biology.\textsuperscript{262} We hypothesized that the thermal reactivity of sub-4 nm diameter Au NPs coated with weak phosphine ligands would exhibit thermal properties more similar to bare Au, which would be very different from similar-sized Au NPs stabilized with strongly-bound thiolate ligands. A great advantage of the phosphine-stabilized Au NPs is that we can use anodic stripping voltammetry (ASV) to characterize their size before and after exposure to various temperatures.\textsuperscript{3, 10} This is not possible with thiolate-coated Au NPs,
which do not undergo size-dependent oxidation due to the highly passivating thiolate ligands.

The purpose of this work was to monitor the thermal sintering of weakly-coated, water-soluble 0.9, 1.6 and 4.1 nm diameter Au NPs/NCs by ASV and correlate the results to other melting point studies in the literature. Determining the size-dependent sintering and melting properties of Au NPs and ultrasmall Au NCs directly on electrode surfaces is uniquely suited to ASV analysis, since the method allows for the direct size determination after various temperature treatments. Our group previously used ASV for analyzing metal size, aggregation state, composition, and atomic arrangement, and size stability under various conditions. Applying our electrochemical approach for studying thermal stability is of special interest because it allows for fast, low cost size analysis of surface-attached metal NPs at different temperatures. In contrast, electron microscopy is much more expensive and tedious. While microscopy techniques allow for real time imaging as a function of temperature, it does not allow sintering studies directly on traditional electrode surfaces. These electrochemical measurements are highly sensitive and relatively fast and cheap, allowing high sample throughput and statistical analysis.

4.2. RESULTS AND DISCUSSION

In this work, we synthesized the different sized Au NPs (0.9 ± 0.2, 1.6 ± 0.4 and 4.1 ± 0.7 nm average diameter) following the protocols described in Chapter 2. Figure 4.1 shows the general experimental procedure involved in ASV analysis of thermal sintering behavior of different sized Au NPs. First, the NPs were freshly synthesized with citrate or phosphonium/phosphine stabilizers in aqueous solutions (Step 1). Next, we attached the
NPs to a glass/ITO/APTES electrode by electrostatic interactions (Step 2). Next, the NPs were thermally treated at different temperatures and times (Step 3). Finally, we analyzed the relative size of the electrode-confined Au NPs size by ASV (Step 4). It is very clear in the ASV if a particular size Au NPs becomes larger following thermal treatment. Our analysis assumes that the weak stabilizers used in this work do not significantly alter the sintering temperature of the Au NPs. This means that the Au NP/NC size is most responsible for the thermal behavior and that we are practically probing bare Au NPs. Since we are working with a monolayer or sub-monolayer coverage of Au NPs on the electrode surface, we assume that there is a negligible effect of the NPs coverage on the thermal sintering behavior.

We monitored the thermal stability of 0.9, 1.6, and 4.1 nm Au NPs/NCs by obtaining ASVs of the NPs/NCs attached to glass/ITO or glass/FTO electrodes after exposing them to different temperatures. Figure 4.2 shows the ASVs after 30 min at 25, 80, 100, 130, 150, and 200 °C for 0.9 nm and 1.6 nm Au NCs, and up to 500 °C for 4.1 nm

Figure 4.1. General experimental procedure involved in this work.
Au NPs. The ASVs of 0.9 nm Au NCs showed a single peak with a peak potential \( (E_p) \) of \( 0.22 \) V at \( 25 \) °C. The appearance of a small second peak at \( 0.63 \) V occurred after heating at \( 80 \) °C for 30 min. Based on theoretical work by Plieth and our previous experimental studies,\(^\text{30}\) the peak at \( 0.63 \) V correlates to \( \sim 3.6 \) nm diameter Au NPs, indicating that some of the 0.9 nm Au NCs transformed into larger size NPs. The peak current increased at \( 0.63 \) V and decreased at \( 0.22 \) V upon further heating up to \( 100 \) °C (Figure 4.2A). The peak at \( 0.22 \) V completely disappeared after heating to \( 130 \) °C or higher, leaving only one peak in the ASV near \( 0.63 \) V. This indicates full transformation of all Au NCs from 0.9 nm to 3.5 – 4.0 nm diameter.

We observed similar behavior for 1.6 nm Au NCs when heated from room temperature to \( 200 \) °C. At \( 25 \) °C, the ASV of 1.6 nm Au NCs showed one peak at \( 0.47 \) V

![Figure 4.2](image.png)

**Figure 4.2.** ASVs of 0.9 nm (A), 1.6 nm (B), and 4.1 nm (C) average diameter Au NPs attached to glass/ITO/APTES electrodes at room temperature (25 °C) and after heating for 30 min to different temperatures as indicated. ASVs were obtained in 10 mM KBr plus 0.1 M KClO\(_4\) solution at a scan rate of 0.01 V/s.
(Figure 4.2B). As the NCs were heated to 80 °C, a small shoulder peak appeared at 0.66 V, indicative of an increased size in the Au NPs due to thermal sintering. The peak current at 0.66 V gradually increased while that at 0.47 V gradually decreased with increasing temperature, similar to the case of 0.9 nm Au NCs (Figure 4.2 B). At 130 °C, a small peak remained at 0.47 V. At 150 °C, one single peak appeared at 0.66 V concomitant with complete disappearance of the original peak at 0.47 V. As discussed earlier, this is indicative of the complete size transformation of 1.6 nm Au NCs to ~4 nm Au NPs. Upon further heating up to 200 °C for 30 min (Figure 4.3), the $E_p$ does not increase further, indicating that the NPs reached a size that is thermally stable up to 200 °C.

In contrast to 0.9 nm and 1.6 nm Au NCs, the ASV of 4.1 nm diameter Au NPs showed one single peak with $E_p$ at 0.71 V even after 30 min of heating up to 400 °C (Figure 4.2C), which is consistent with our previously published work. This is due to the greater temperature stability of larger Au NPs compared to smaller Au NCs. Upon further heating at 500 °C for 30 min using glass/FTO as a substrate, 4.1 nm Au NPs showed an increase in peak width at half maximum indicating that some of the NPs transformed to larger sizes through thermal sintering (or ripening). After heating up to 500 °C, the $E_p$ appeared at 0.81 V while the current at 0.71 V almost completely disappeared (Figure 4.2C, black plot). This indicates that 4.1 nm Au NPs started showing sintering at ~500 °C and transformed to $>4$ nm NPs (10-20 nm diameter). The $E_p$ continued to increase to almost 0.9 V upon heating up to 600 °C, which is approaching the bulk Au oxidation potential. This is consistent with sizes of 30 nm and larger. We could not heat the Au NPs above 600 °C due to the thermal instability of fluorine-doped tin oxide (FTO) beyond 600 °C.
Next, we studied the effect of thermal treatment on 1.6 nm Au NCs as a function of heating time at constant temperature by ASV. We heated the surface-attached 1.6 nm diameter Au NCs to 70 °C for up to 60 min, where a minor shoulder peak appeared at -0.65 V. This is consistent with a size increase due to some thermal instability at this temperature and time (Figure 4.3A, blue plot). After 10 min of heating at 80 °C, a shoulder peak at 0.65 V began to emerge. After 30 min, the shoulder peak emerged into a well-defined peak at -0.70 V (Figure 4.3 B, pink graph). The peak at -0.70 V along with the original peak at 0.47 V indicates that some of the 1.6 nm diameter Au NCs have sintered into larger NPs of ~4 nm diameter, while others have not transformed in size. The peak current at 0.70 V relative to that at 0.47 V increased after 60 min of heating, indicating that more NCs transformed into bigger-sized Au NPs with time (Figure 4.3B, black graph). Figure 4.3C shows ASVs following the heating of glass/ITO/APTES/Au NPs (1.6 nm) at 100 °C for 10, 30, and 60 min. For 10 and 30 min of heating, we observed both peaks at 0.47 and 0.70V (blue and pink plots). After 60 min of heating, the peak at 0.70 V became dominant.
Figure 4.3. (A) ASV overlay of glass/ITO/APTES attached 1.6 nm diameter Au NPs before and after 60 min of heating at 70 °C. (B-E) ASV overlay of glass/ITO attached 1.6 nm diameter Au NSs before and after 10, 30 and 60 min of heating at temperature 80, 100, 130 and 150 °C. (F) ASV overlay of glass/ITO attached 1.6 nm diameter Au NSs before and after 60 min of heating at 200, 300, and 400 °C. ASVs was taken in 10 mM KBr plus 0.1 M KClO₄ electrolyte solution with glass/ITO/APTES attached Au NPs as a working electrode and Ag/AgCl as a reference electrode with a scan rate of 0.01 V/s.

but not all Au NPs transformed in size as evidenced by the visible peak at 0.47 V (black
plot). Heating at 130 °C led to an even larger decrease in the peak current at 0.47 V while the peak at 0.70 V became even more dominant (Figure 4.3D). The trend continued at 150 °C, where the peak at 0.47 V was effectively absent after 30 and 60 min of thermal treatment (Figure 4.3E), indicating that a complete size transformation of 1.6 nm Au NCs took place. Figure 4.3F shows ASVs of 1.6 nm Au NPs attached to glass/ITO following heat treatment for 60 minutes at temperatures up to 400 °C. Complete size transformation occurred at 200 °C and very small changes in the range of 200-400 °C. There is some broadening of the peak in the ASV at 400 °C with only a minor positive shift in $E_p$. The ripening that occurred at 200-300 °C led to larger sized NPs that were fairly stable up to at least 400 °C.

Previous work on the thermal treatment of 1-2 nm diameter Au NCs showed that the onset of sintering began at 125-250 °C, depending on the stabilizing ligands. There are many thermogravimetric analysis (TGA) studies that reveal when ligands start to become removed from NPs/NCs, but TGA does not provide size information. Usually, NP sintering coincides with ligand loss, however. Our ASV results show that 1.6 nm diameter Au NCs start sintering as early as 70-80 °C. This indicates that the NC size may change before loss of the ligand stabilizer, which is consistent with the work of Beverly and coworkers. Alternatively, there may have been some ligand loss during the assembly and rinsing of the 1.6 nm THPC-stabilized Au NPs on the glass/ITO/APTES electrode. Previous studies showed that < 5% ligand loss from Au NPs (< 2 nm diameter) can be enough for sintering to occur.

We next used the ASV data to quantitatively determine the transition temperature for sintering for the different sized Au NPs as they transform from their original size to a
more stable size upon heating. This can be determined from ASV since the $E_p$ starts at one value, indicative of the NP/NC size, and then shifts to a more positive value upon heating due to size transformation to a larger size. Accordingly, we plotted the ratio of the current from the original peak to the current from the final transformed peak ($I_{E,\text{final}}/I_{E,\text{orig}}$) as a function of temperature for the different sized Au NPs/NCs (Table 4.1 and 4.2). For example, the $E_p$ shifts from 0.26 V to 0.63 V for the 0.9 nm diameter Au NCs, which correlates to a size transformation from 0.9 nm diameter to ~3.6 nm diameter NPs. A plot of $I_{0.63V}/I_{0.26V}$ as a function of temperature produced a sigmoidal curve, where the transition temperature is defined as the inflection point, similar to the endpoint of a titration curve. The same plot was generated for 1.6 nm Au NPs and 4.1 nm Au NPs using the ratio of $I_{0.66V}/I_{0.47V}$ and $I_{0.80V}/I_{0.72V}$, respectively, versus temperature as shown in Figure 4.4A. The transition size is from 1.6 nm to 3.5-4.0 nm and 4.1 nm to 15-20 nm diameter, respectively. We fit the sigmoidal plots for 0.9, 1.6 and 4.1 nm Au NPs in Figure 4.4A to the Boltzmann function and took a normalized first derivative as shown in Figure 4.4B. The sintering transition temperature is defined as the peak temperature in the first derivative plot as shown for 0.9 nm (red plot), 1.6 nm (black plot), and 4.1 nm (blue plot) NPs. The sintering transition temperatures ($T_{\text{sint}}$) are 109, 132, and 509 °C for 0.9 nm, 1.6 nm, and 4.1 nm Au NPs/NCs, respectively.

The size-dependent melting properties of Au NPs have been extensively studied theoretically and experimentally. Experimental studies are limited by the effect of stabilizers, especially when measuring the melting temperature of ultrasmall Au NCs below 2 nm in diameter. There are only few cases of experimental data measuring the melting point of bare Au NPs below 2 nm to our knowledge (Table 4.4). There are
Table 4.1. Peak current and peak current ratios at two potentials from ASV before and after 30 min heating of 0.9 nm and 1.6 nm Au NPs at different temperatures.

<table>
<thead>
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<th>Temp (°C)</th>
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<th></th>
<th>1.6 nm</th>
<th></th>
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<td></td>
<td>Peak current at 0.26 V</td>
<td>Peak current at 0.63 V</td>
<td>Peak current ratio (i_{0.63}/i_{0.26})</td>
<td>Peak current at 0.47 V</td>
<td>Peak current at 0.66 V</td>
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theoretical equations derived from a model as well as theoretical equations derived from experimental data of melting point measurements for larger sized Au NPs.

Figure 4.4. Plot of ratio of peak current at higher potential to lower potential for 0.9 ($i_{0.63V}/i_{0.26V}$), 1.6 nm ($i_{0.66V}/i_{0.47V}$) and 4.1 nm ($i_{0.80V}/i_{0.72V}$) Au NSs heated for 30 min at different temperatures (A), plot of first order derivative of normalized peak current ratios from A as a function temperature against temperature (B), plot of $T_{\text{Trans}}$ of Au NPs as taken from plot B (blue plot) and the m.pt. of Au NPs taken from LNG model (red plot) against the reciprocal of NPs diameter (C).
For example, Schlexer et al. derived the equation:

\[ f(x) = \frac{-1509}{d} + 1338 \]  

(4.1)

where \( f(x) \) = the melting temperature and \( d \) = the diameter of the NP (assuming a sphere shape), using the liquid nucleation and growth (LNG) model.\(^{127}\) That model predicts while this model doesn’t work for 0.9 nm Au NPs as the melting temperature in this case is found to be -611 °C. The melting point from LNG model and sintering temperature of 1.6 nm Au NPs show pretty close agreement to each other while there is small deviation between those for 4.1 nm Au NPs. Table 4.4 provides data for comparison of transition temperature \( T_{\text{trans}} \) determined from our ASV method with the different theoretical models melting temperatures of 122 and 687 °C for 1.6 and 4.1 nm Au NCs/NPs, respectively and experimental studies for prediction of melting of different-sized Au NPs (Figure 4.4C). We observed that in the majority of cases (except few cases in LNG model), the \( T_{\text{trans}} \) of the NPs is found to be lower than that the melting point indicating that sintering of NPs occurs during or prior to their melting.

We obtained scanning electron microscopy (SEM) images of the Au NPs before and after 30 and 60 min of heating at 200 and 400 °C to correlate the use of microscopy to also probe Au sintering. Figure 4.5 shows SEM images before and after thermal treatment. The 1.6 nm Au NCs were not visible by SEM before heating (Figure 4.5A) because this size is below the resolution of the SEM. After thermal treatment, the NPs became visible by SEM (Figure 4.5B) and the size was found to be 5.7 ± 0.9 nm in diameter when heated at 400 °C for 60 min (Figure 4.5C). This is consistent with the size transformation of 1.6 nm to ~4.0 nm determined by ASV, except that the SEM-determined size may be larger due to the higher temperature employed (400 °C vs 200 °C). The SEM images of citrate-
coated 4.1 nm Au NPs before (Figure 4.5D) and after thermal treatment (Figure 4.5E-F) at 200 and 400 °C respectively for 60 min showed no significant change in size upon heating. This is also generally consistent with the ASV, although ASV showed a small shift and broadening of the peak. The ASV may be potentially more sensitive than SEM at this size range.

![SEM images of THPC coated 1.6 nm Au NPs attached to glass/ITO/APTES without thermal treatment (A) and after 30 min (B) and 60 min (C) of thermal treatment at 200 and 400 °C respectively. SEM images of citrate-coated 4.1 nm Au NPs attached to glass/ITO before thermal treatment (D) and after 30 min (E) and 60 min (F) of thermal treatment at 200 and 400 °C.]

**Figure 4.5.** SEM images of THPC coated 1.6 nm Au NPs attached to glass/ITO/APTES without thermal treatment (A) and after 30 min (B) and 60 min (C) of thermal treatment at 200 and 400 °C respectively. SEM images of citrate-coated 4.1 nm Au NPs attached to glass/ITO before thermal treatment (D) and after 30 min (E) and 60 min (F) of thermal treatment at 200 and 400 °C.
We monitored the thermal sintering of 1.6 nm Au NPs attached to glass/ITO by UV-Vis spectroscopy. Figure 4.6 shows a featureless spectrum for the 1.6 nm Au NPs before heating, with maximum extinction at 400 nm that decreases exponentially with increasing wavelength. The spectra are characteristic of light scattering by the sub-2 nm diameter Au NPs, where there is no presence of a localized surface plasmon resonance (LSPR) absorbance peak. After heating at 100 °C up to 400 °C, a peak begins to develop in the 500-550 nm region, which is due to a LSPR band. The LSPR band appears for NPs greater than 2 nm in diameter. The peak increases and red shifts as the temperature increases, indicative of larger size particles and possibly aggregates forming due to thermally-induced sintering/ripening. The spectra are consistent with ASV and SEM data.
One potential problem with our size-dependent thermal studies is that the 4.1 nm diameter NPs are stabilized by citrate while the 0.9 nm and 1.6 nm diameter Au NCs are stabilized by THPC and TPPS, respectively. The different thermal properties could be due to the different stabilizing ligands as opposed to the NP/NC size. To rule this out, we compared ASV and SA/V data at different temperatures for citrate-stabilized 4.1 nm diameter Au NPs to THPC-stabilized 4.1 nm diameter Au NPs following the work of Sharma et al.\textsuperscript{4} (Figure 4.7 and Table 4.4). The THPC-stabilized 4.1 nm Au NPs were slightly broader and had a small positive shift in $E_p$ compared to the citrate-stabilized 4.1 nm Au NPs along with negligible change in SA/V ratios (Table 4.3), but the differences were not significant enough to explain the large differences between 0.9 nm/1.6 nm Au

Figure 4.6. UV-Vis spectra of 1.6 nm diameter Au NPs attached to glass/ITO/APTES before and after 60 min of thermal treatment at different temperatures of 100, 200, 300, and 400 °C.
NPs and the 4.1 nm Au NPs. Exploring the role of different ligands on size-dependent thermal sintering/ripening will be the focus of a future study.

**Figure 4.7.** ASV overlay 4.1 nm diameter Au NPs attached to glass/ITO/APTES stabilized with citrate (A) and THPC (B) before and after 60 min of heating at 100, 200, 300, and 400 °C. ASV was performed in 10 mM KBr plus 0.1 M KClO₄ solution with glass/ITO attached Au NPs as a working electrode and Ag/AgCl as a reference electrode with a scan rate of 0.01 V/s (data for SA/V is provided in Table 4.3).
Table 4.2. Peak current and peak current ratios at two potentials from ASV before and after 30 min heating of 4.1 nm Au NPs at different temperatures.

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<td>400 °C</td>
<td>6.31 x 10^-6</td>
<td>1.64 x 10^-6</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>4.21 x 10^-6</td>
<td>4.65 x 10^-6</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>7.65 x 10^-6</td>
<td>2.79 x 10^-6</td>
<td>0.37</td>
</tr>
<tr>
<td>500 °C</td>
<td>5.21 x 10^-6</td>
<td>7.74 x 10^-6</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td>2.85 x 10^-6</td>
<td>7.24 x 10^-6</td>
<td>2.54</td>
</tr>
<tr>
<td></td>
<td>3.22 x 10^-6</td>
<td>7.10 x 10^-6</td>
<td>2.20</td>
</tr>
<tr>
<td>550 °C</td>
<td>2.09 x 10^-6</td>
<td>1.11 x 10^-5</td>
<td>5.31</td>
</tr>
<tr>
<td></td>
<td>2.20 x 10^-6</td>
<td>1.08 x 10^-5</td>
<td>4.90</td>
</tr>
<tr>
<td></td>
<td>2.45 x 10^-6</td>
<td>9.84 x 10^-6</td>
<td>4.02</td>
</tr>
<tr>
<td>600 °C</td>
<td>2.67 x 10^-6</td>
<td>1.09 x 10^-5</td>
<td>4.08</td>
</tr>
<tr>
<td></td>
<td>4.09 x 10^-6</td>
<td>1.76 x 10^-5</td>
<td>4.30</td>
</tr>
<tr>
<td></td>
<td>3.23 x 10^-6</td>
<td>1.82 x 10^-5</td>
<td>5.63</td>
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</table>
Table 4.3. Integrated charge under CV and ASV peaks for THPC-stabilized 4.1 nm Au NPs heated at different temperature and time, surface area-to-volume ratio (SA/V) and calculated NPs diameter.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>CV measured surface area (Coulombs)</th>
<th>ASV measured volume (Coulombs)</th>
<th>SA/V</th>
<th>Calculated diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>60</td>
<td>2.53 x 10^{-5}</td>
<td>2.20 x 10^{-5}</td>
<td>1.15</td>
<td>5.14 ± 0.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.87 x 10^{-5}</td>
<td>1.66 x 10^{-5}</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.79 x 10^{-5}</td>
<td>1.46 x 10^{-5}</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>100°C</td>
<td>60</td>
<td>7.24 x 10^{-5}</td>
<td>6.72 x 10^{-5}</td>
<td>1.08</td>
<td>5.81 ± 0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.22 x 10^{-5}</td>
<td>9.44 x 10^{-5}</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.51 x 10^{-4}</td>
<td>1.44 x 10^{-4}</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>200°C</td>
<td>60</td>
<td>1.98 x 10^{-4}</td>
<td>1.78 x 10^{-5}</td>
<td>1.11</td>
<td>5.67 ± 0.24</td>
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<tr>
<td></td>
<td></td>
<td>4.76 x 10^{-5}</td>
<td>5.19 x 10^{-5}</td>
<td>0.92</td>
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<tr>
<td></td>
<td></td>
<td>4.54 x 10^{-5}</td>
<td>4.36 x 10^{-5}</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>300°C</td>
<td>60</td>
<td>1.89 x 10^{-5}</td>
<td>1.69 x 10^{-5}</td>
<td>1.11</td>
<td>5.40 ± 0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.85 x 10^{-5}</td>
<td>1.93 x 10^{-5}</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.62 x 10^{-5}</td>
<td>4.27 x 10^{-5}</td>
<td>1.08</td>
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</tr>
<tr>
<td>400°C</td>
<td>60</td>
<td>1.07 x 10^{-4}</td>
<td>1.14 x 10^{-5}</td>
<td>0.94</td>
<td>6.25 ± 0.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.85 x 10^{-5}</td>
<td>3.04 x 10^{-5}</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.82 x 10^{-5}</td>
<td>6.76 x 10^{-5}</td>
<td>1.01</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.4. Size-dependent melting point of Au NPs based on literature with different models (LNG = liquid nucleation and growth, LSM = liquid skin melting, HMM = homogeneous melting hypothesis, HR-TEM = high resolution transmission electron microscopy) and transition temperature of sintering ($T_{\text{Trans}}$) from our ASV data.

<table>
<thead>
<tr>
<th>Model</th>
<th>Approx. NPs diameter (nm)</th>
<th>Approx. m. pt. ($^\circ$C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qi Model</td>
<td>0.9</td>
<td>-</td>
<td>Qi et al.\textsuperscript{266}</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>342</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>782</td>
<td></td>
</tr>
<tr>
<td>Guenther Model</td>
<td>0.9</td>
<td>247</td>
<td>Guenther et al.\textsuperscript{263}</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>387</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>767</td>
<td></td>
</tr>
<tr>
<td>HMM Model</td>
<td>2</td>
<td>697</td>
<td>Nanda et al.\textsuperscript{32}</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>837</td>
<td></td>
</tr>
<tr>
<td>LSM Model</td>
<td>2</td>
<td>355</td>
<td>Nanda et al.\textsuperscript{32}</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>797</td>
<td></td>
</tr>
<tr>
<td>HR-TEM (Experimental)</td>
<td>2</td>
<td>320</td>
<td>Schlexer et al.\textsuperscript{127}</td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td>360</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>540</td>
<td></td>
</tr>
<tr>
<td>LNG Model</td>
<td>0.9</td>
<td>-611</td>
<td>Nanda et al.\textsuperscript{32}</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>121</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>687</td>
<td></td>
</tr>
<tr>
<td>ASV $T_{\text{Trans}}$</td>
<td>0.9</td>
<td>109</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.1</td>
<td>509</td>
<td></td>
</tr>
</tbody>
</table>

4.3. CONCLUSIONS

We characterized the thermal sintering behavior of 0.9 nm, 1.6 nm, and 4.1 nm diameter Au NCs/NPs using ASV. As shown previously in theoretical and experimental size-dependent Au NP melting point studies, the thermal stability decreases with decreasing Au NC/NP size. The use of relatively weak phosphine, phosphonium, and citrate stabilizers allowed for ASV analysis, since these weak stabilizers do not effectively
passivate the Au from electrochemical oxidation (stripping). These weak stabilizers importantly do not seem to strongly alter the size-dependent thermal properties of the Au, allowing an assessment of the properties of the metal. More work is needed to determine the role of various ligands in the future, however. ASV size analysis shows that TPPS-stabilized 0.9 nm Au NCs begin to sinter at ~70 °C and completely transform in size to 3-4 nm diameter at ~130 °C for 30 min heating. Similarly, THPC-stabilized 1.6 nm diameter Au NCs begin to sintering at 70-80 °C and completely transform to 4-5 nm diameter Au NSs at ~150 °C in 30 min. The ASV data is consistent with the appearance of a LSPR band in the UV-Vis spectrum for 1.6 nm Au NCs after heating at 100 °C or higher. Citrate-stabilized 4.1 nm diameter Au NPs begin to sinter at around 400 °C and undergo complete size transformation in the 500-600 °C range. Our defined sintering transition is 109, 132, and 509 °C for 0.9 nm, 1.6 nm, and 4.1 nm diameter Au NCs/NPs, respectively. The trend is consistent, but the absolute values deviate from the melting point values of 122, and 687 °C for 1.6 and 4.1 nm diameter, respectively, predicted by the LNG model. It is not surprising that sintering would occur at temperatures lower than the melting point as shown for 4.1 nm Au NPs (509 °C vs. 687 °C). It is surprising that the sintering temperature is higher than the melting point for 1.6 nm Au NCs, however. This could be due to ligand effects, substrate effects, and limitations of the model. More work will be needed to improve theoretical models, but ASV can find great use to determine the experimental temperature for size transformation as a function of NP/NC size, support surface, ligand stabilizers, and metallic composition. ASV size analysis for characterization of thermal sintering behavior of sub-4 nm metal NPs is potentially faster, lower in cost, and more sensitive compared to microscopy, spectroscopy or calorimetry methods. It is also
applicable to metal nanostructures supported on electrode surfaces operating in their native environment and is therefore not affected by vacuum conditions or electron beam effects that are potential issues in electron microscopy studies.
CHAPTER V

REVERSE SIZE-DEPENDENT ELECTROOXIDATION OF GOLD NANOPARTICLES COATED WITH ALKANETHIOL SELF-ASSEMBLED MONOLAYERS

5.1. INTRODUCTION

In recent years, metal nanoparticles (NPs) have drawn increasing interest due to their potential applications in the fields of catalysis, sensing, plasmonics, nanoelectronics, and photothermal therapy, as some examples. The benefits and performance of the NPs in these applications depends on various factors, such as NP stability, cytotoxicity, and biocompatibility. Among them, stability of the NPs is a key factor that is usually determined by the type of ligand or surfactant stabilizer used in the synthesis. One common way to increase the stability is by direct adsorption of protecting ligands on the NP surfaces, which are referred to as self-assembled monolayers (SAMs). Customarily, SAMs are comprised of ordered organic molecules adsorbed onto solid metal surfaces from the solution or gas phase. The order and orientation of these molecular assemblies, acting as thin film coatings, play an important role in NP stability, surface functionality, assembly and physical properties. In spite of the presence of stabilizing agents, there are many examples where NPs cannot be used as intended due to their inadequate stability.
The oxidative dissolution of metal NPs is one type of chemical instability. Several researchers previously studied the size-dependent electrochemical dissolution of metal NPs, showing that smaller-sized metal NPs oxidize (dissolve) at lower potentials compared to larger ones for sizes below about 40 nm in diameter.\textsuperscript{10, 71, 97, 99} Larger NPs are also typically more stable against ripening compared to smaller NPs, as demonstrated in recent constant potential measurements in halide solutions\textsuperscript{11} and electrochemical oxidation/reduction cycling studies of different-sized Au NPs.\textsuperscript{1, 88} Based on electrochemical scanning tunneling microscopy (ECSTM), Tang et al. examined the electrochemical dissolution of different sized Pt-black NPs (particle radius of 0.58, 0.62, 0.83, and 1.43 nm) in acidic solution as a function of potential, where the dissolution potential decreased with a decrease in NP size.\textsuperscript{277} Our group recently studied the size-dependent electro-dissolution of Ag and Au NPs, where smaller NPs oxidized at lower potentials compared to larger sizes.\textsuperscript{2-3, 10} This is generally consistent with the theory developed by Plieth, which predicts a negative shift in the standard potential of metal NPs proportional to $1/$radius.\textsuperscript{30}

The lack of proper stability of metal NPs can be an issue for many electrocatalytic applications of the NPs, such as in fuel cells.\textsuperscript{140} For example, Trindell \textit{et al.} reported that 2 nm diameter Au NPs stabilized by citrate and sixth generation hydroxy-terminated polyamidoamine (G6-OH) dendrimers rapidly grew into bigger sizes when used for electrocatalytic CO$_2$ reduction.\textsuperscript{87} Such instability made it impossible to correlate the electrocatalytic behavior with the NP size. Several other reports have shown that metal NPs <10 nm exhibit superior catalytic performance over bigger sizes under a variety of conditions.\textsuperscript{3, 141-145} As an example, Tang \textit{et al.} reported a 2.5-fold increase in kinetic current
towards the oxygen reduction reaction in alkaline medium when the average size of polystyrene-block-poly(2-vinylpyridine)-stabilized Au NPs decreased from 7 nm to 3 nm in diameter.\textsuperscript{142} Success for these applications requires strategies to enhance the stability of smaller-sized metal NPs without negatively affecting their catalytic properties. This is challenging because smaller NPs contain a larger proportion of edge and corner atoms, which are often the sites where catalytic reactions take place, but these same sites are usually less electrochemically stable. Ligand stabilizers are needed to stabilize the NPs without poisoning their catalytic properties.

Enhancing the stability of a metal, such as Au, via the assembly of organomercuricaptan self-assembled monolayers (SAMs) has long been practiced by several researchers.\textsuperscript{146-148} The assembly of alkanethiols with different chain lengths onto bulk two-dimensional (2D) Au surfaces, as described in the work of Porter \textit{et al.}, showed that longer chain alkanethiols form more ordered and densely-packed SAMs compared to shorter ones.\textsuperscript{146} This was accompanied by the enhancement in surface coverage, increased packing density, and capacity to block electron transfer with longer carbon chain alkanethiols. Zamborini and Crooks studied the effect of chain length and end group of alkanethiolate SAMs on the corrosion passivation of Au in KBr solution.\textsuperscript{278} It was observed that thiols terminated with the more hydrophilic -COOH and -OH end groups were better passivating agents against corrosion than the hydrophobic -CH\textsubscript{3} end groups, considering the same SAM thickness. Further, the passivation was more pronounced with SAMs having the same end group but longer carbon chain lengths due to the better organization with longer carbon chains.

We were interested in studying the barrier properties of various chain length alkanethiol SAMs assembled on 3D Au NPs against oxidative dissolution similar to the
already studied 2D Au films.\textsuperscript{150-151} Thiol ligand stabilizers are well-known for providing stability against aggregation, ripening, and oxidation (corrosion), especially for Au NPs, due to the high strength of the Au-thiolate bond.\textsuperscript{8-9} Accordingly, different researchers have been able to develop synthetic strategies for preparing thiolate-coated Au clusters, termed monolayer-protected clusters (MPCs), ranging from 1 nm to about 5 nm in diameter.\textsuperscript{153} MPCs 1.6 nm and below are commonly termed atomically-precise Au nanoclusters (APNCs).\textsuperscript{152, 154-159} The \textit{Au}_{25}(SR)_{18} (SR = organothiolate) is an example of an APNC, which incorporates 6 \textit{Au}_2S_3 staple motifs around a \textit{Au}_{13} cluster core.\textsuperscript{154} Additionally, Kwak \textit{et al.} recently reported \textit{Au}_{25}(SR)_{18}, \textit{Au}_{38}(SR)_{24}, and \textit{Au}_{102}(SR)_{44} APNCs.\textsuperscript{154} Negishi \textit{et al.} found that the growth of Au clusters during their synthesis can be suppressed by passivation with thiolates, indicating improved stability of small Au clusters with thiolates.\textsuperscript{160} Different groups have observed the enhancement in stability of Au NPs coated with thiols.\textsuperscript{279-281} Studies also show the replacement of citrate with thiols on citrate-stabilized Au NPs, forming mixed citrate/thiol layers due to the stronger Au-thiolate interaction compared to the Au-citrate interaction.\textsuperscript{67}

It is not directly clear what the effect of Au NP size will be on the oxidation of thiolate-coated Au NPs in the presence of an etchant, such as Br\textsuperscript{−}, due to a few different factors. Two potential factors predict greater oxidation with decreasing size, while two other factors predict hindered oxidation with decreasing size. For the former, it is well-known from the Plieth equation,\textsuperscript{30} Gibbs–Thomson relation,\textsuperscript{282} and recent experimental results that the oxidation potential for metal NPs decreases as the size of the NP decreases.\textsuperscript{10, 193} This effect is based on the surface free energy related to the exposed surface area of a sphere, taking into account the geometry only and not potential size-dependent
differences in Au–thiolate adsorbate binding. Also, as the Au NP size decreases, the increased NP curvature results in alkanethiolate monolayers with high density near the Au surface, but lower density away from the surface. The alkane chains exhibit the general all-trans zigzag structure but have greater mobility, chain folding, and a greater number of gauche defects at distances farther from the Au core.\textsuperscript{283} The geometry-based size relation and increase in alkane chain defects with decreasing Au NP size could lead to greater amounts of oxidation with decreasing NP size. On the other hand, there are two reasons to predict a decrease in oxidation with decreasing NP size. First, the curvature and number of Au atom defects (edge and corner sites) increases with decreasing Au NP size, leading to a much higher alkanethiolate ligand coverage for monolayers on small Au NPs as compared to those on larger Au NPs or 2D Au films (>50% coverage as compared to \(\sim 33\%\) on 2D films).\textsuperscript{283–284} The increasing alkanethiolate coverage with decreasing size could lead to a decrease in oxidation. Second, studies have shown greater alkanethiolate monolayer electrochemical stability on NPs and highly curved surfaces compared to 2D planar surfaces.\textsuperscript{285} This is due to a shorter and stronger thiolate bond on the high energy surfaces of the smaller Au NPs, which contain a larger number of atomic defects.\textsuperscript{284, 286} Au NPs accordingly exhibit a contraction in the Au–Au lattice with decreasing size, especially below \(\sim 4\) nm, which is relaxed upon strong binding with alkanethiolate monolayers to reduce the overall surface stress.\textsuperscript{284} It is therefore possible that stronger alkanethiolate bonding to smaller Au NPs would lead to a lower surface energy and less oxidation compared to larger Au NPs with the same alkanethiolates.

Clearly there are two possible factors leading to increased oxidation with decreasing Au NP size (geometric surface area and alkane chain defects) and two reasons
to expect decreased oxidation with decreasing Au NP size (ligand density and reduced surface energy due to stronger thiolate bonding), making this an important topic to explore. It is also important to consider that some of the effects would alter the thermodynamics of oxidation, such as those involving changes in surface free energy (geometry and thiolate binding), while others would more likely alter the oxidation kinetics, such as ligand density and chain defect density. Different amounts of ligand density and chain defects could sterically alter access of the etchant to the Au surface. Accordingly, we here describe the electrochemical oxidation of electrode-attached, citrate-stabilized 4.1, 15.1, and 50.3 nm diameter Au NPs (1) as-prepared and (2) following modification with butanethiolate (C4S), decanethiolate (C10S), or hexadecanethiolate (C16S) SAMs. We compare the oxidative dissolution of citrate- and alkanethiolate-modified Au NPs as a function of size in acidic Br− electrolyte by cyclic voltammetry (CV), chronocoulometry (CC), and UV−Vis spectroelectrochemistry.
5.2. RESULTS AND DISCUSSION

5.2.1. General Experimental Set-up. In this study, we synthesized three different sized citrate-coated Au NPs with average diameters of 4.1, 15.1 and 50.3 nm as described by our group previously. As shown in Figure 5.1, the citrate-coated Au NPs were first synthesized (Step 1) and then electrostatically attached to glass/ITO/APTES electrodes by simply soaking the electrodes into the aqueous solutions of the Au NPs (Step 2). Next, the glass/ITO/APTES/Au NPs were coated with different alkanethiol self-assembled monolayer (SAMs), where presumably a large portion of the citrate ligands become replaced by thiolates (Step 3). Finally, we characterized the relative oxidation behavior of the different-sized thiol-coated Au NPs by cyclic voltammetry (CV),

![Figure 5.1. General experimental procedure in this work](image)
chronocoulometry (CC), and UV-Vis spectroelectrochemistry (Step 4) and compared the results to those of citrate-coated Au NPs.

5.2.2. Characterization of Au NPs. The synthesized Au NPs were characterized by UV-vis spectroscopy in solution and by scanning electron microscopy (SEM) after attachment to glass/ITO/APTES electrodes which is fully consistent with these same sized Au NPs synthesized and characterized by our group previously.\textsuperscript{4, 11}

5.2.3. Constant Coverage of Au NPs. In order to compare the stability of the different-sized, electrode-attached citrate and thiol-coated Au NPs towards oxidative dissolution, it is important to keep the total coverage (in terms of Au atoms) constant on the electrode surface. In order to do this, we first subjected the electrode-attached Au NPs to cyclic voltammetry (CV) in 0.1 M HClO\textsubscript{4} from 0 V to 1.6 V vs Ag/AgCl. This provides information about the oxidation-reduction behavior of the surface Au atoms. In the first positive scan, Au becomes oxidized to AuO\textsubscript{x}, possibly as Au\textsubscript{2}O\textsubscript{3}, while in the negative scan of the cycle, Au\textsubscript{2}O\textsubscript{3} is reduced back to metallic Au (Equation 5.1) at around 0.80 V for all Au NPs in this study. The integrated charge obtained from the Au oxide reduction peak at 0.80 V is proportional to the total surface area (SA) of the Au NPs since it only involves oxide formation of the surface Au atoms. By knowing the total SA experimentally and using the previously measured SA/V ratio for the different sized Au NPs,\textsuperscript{4} we were able to determine the total V of Au for the different sized Au NPs on glass/ITO/APTES. The total V is directly proportional to the coverage in terms of Au atoms (equations 5.2-5.3). Based on our previous work, the average SA/V ratio is 0.64, 0.23 and 0.060 for 4.1, 15.1, and 50.3 nm Au NPs, respectively (not cleaned with ozone).\textsuperscript{4} From this value, we were able to calculate the expected total V of Au (target of 5.70 x 10\textsuperscript{-5} C) by dividing the
electrochemically-measured SA by the previously reported SA/V,\textsuperscript{4} which gave target SA values of 3.4 x 10\textsuperscript{-5} C, 1.3 x 10\textsuperscript{-5} C, and 3.6 x 10\textsuperscript{-6} C for 4.1 nm, 15.1 nm, and 50.3 nm diameter Au NPs, respectively. Figure 5.2A-B show an example of 3 samples, where the SA values were 3.30 x 10\textsuperscript{-5}, 1.29 x 10\textsuperscript{-5} and 3.48 x 10\textsuperscript{-6} Coulombs of integrated charge for the reduction peak at 0.80 V, which resulted in ASV coverages (or V) obtained in 0.01 M KBr plus 0.1 M KClO\textsubscript{4} of 5.55 x 10\textsuperscript{-5}, 5.63 x 10\textsuperscript{-5}, and 5.76 x 10\textsuperscript{-5} Coulombs for 4.1, 15.1, and 50.3 nm Au NPs, respectively. Table 5.1 shows the integrated charge (in Coulombs) of glass/ITO/APTES/Au NP electrodes obtained from the Au oxide reduction peak in 0.1 M HClO\textsubscript{4} and the oxidative charge from the 1\textsuperscript{st} scan of the ASV in 0.01 M KBr plus 0.1 M KClO\textsubscript{4}. Likewise, Table 5.2 shows the experimentally-measured integrated SA coverages of the different-sized Au NPs and the corresponding calculated V of all the samples used (using the SA/V from our previous work)\textsuperscript{4} for the CV and CC experiments in this work.

\begin{align*}
\text{Au}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- & \rightleftharpoons 2\text{Au} + 3\text{H}_2\text{O} \quad (5.1) \\
\text{Au}^0 + 4\text{Br}^- & \rightarrow \text{AuBr}_4^- + 3\text{e}^- \quad (E^0 = 0.85 \text{ V vs NHE}) \quad (5.2) \\
\text{Au}^0 + 2\text{Br}^- & \rightarrow \text{AuBr}_2^- + \text{e}^- \quad (E^0 = 0.96 \text{ V vs NHE}) \quad (5.3)
\end{align*}

\textbf{5.2.4. Deposition of Alkanethiol SAMs on Au Nanoparticles}

The different sized Au NPs were first attached on the APTES functionalized glass/ITO surface by directly soaking the substrate in the aqueous solution for different time depending on the coverage needed. Care was taken to maintain the same total amount of Au on the electrode surface for the different-sized Au NPs by soaking them for different times and having different concentrations of Au NPs through dilution (4 nm: 2-3 min in 3 times dilute solution, 15 nm: 6-8 min in direct solution, 50 nm: 25-30 min in direct
solution). This was ensured by taking the ratio of SA/V of the Au NPs as discussed earlier. After soaking the glass/ITO/APTES in an Au NP solution the electrodes were rinsed thoroughly with nanopure water, dried under N₂, and then the Au coverage was determined by electrochemically measuring the surface area (SA) from the Au oxide reduction peak in a cyclic voltammogram (CV) obtained in 0.1 M HClO₄ electrolyte and determining the volume (V) from the known SA/V ratio for each size Au NPs. The total V of Au NPs measured in this way is directly proportional to the total amount of Au attached to the glass/ITO/APTES electrode. If the V did not reach a specific pre-determined value, the electrode was rinsed with nanopure water, dried under N₂, and placed back into the Au NP solution for more time. The process was repeated until the desired coverage. Once reached, the samples were rinsed with nanopure water, dried under N₂ and then either analyzed directly or functionalized with the alkanethiol of interest. Electrodes that did not fall into the pre-determined Au coverage range were discarded and not included in the statistics. It was then cleaned by nanopore water and dried under N₂. Each of the substrate was then overnight soaked in 200 proof ethanolic solution of 2 mM n-butanethiol (C₄S), n-decanethiol (C₁₀S) and n-hexadecanethiol (C₁₆S), cleaned with ethanol, and dried whereby SAMs was deposited on the Au NPs surface.
Table 5.1. Integrated charges (Coulombs) of citrate-coated 4.1 ± 0.7, 15.1 ± 1.3 and 50.3 ± 1.7 nm Au NPs attached to glass/ITO/APTES electrodes obtained from the Au oxide reduction peak by cyclic voltammetry (CV) in 0.1 M HClO₄ at a scan rate of 0.1 V/s before performing CV in Figure 5.2. The oxidation stripping and reduction charge and their averages for the 3 sizes of Au NPs were also obtained from the 1st CV scan in 0.01 M KBr plus 0.1 M HClO₄ at a scan rate of 0.1 V/s.

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Table 5.2. Integrated charges (Coulombs) of Au NPs attached to glass/ITO/APTES electrodes obtained from the Au oxide reduction peak by CV in 0.1 M HClO₄ for the different samples of 4.1 ± 0.7, 15.1 ± 1.3 and 50.3 ± 1.7 nm Au NPs. The measured charge is proportional to total surface area (SA), which allowed a calculation of total volume (V) based on the known SA/V ratio of 0.64, 0.23 and 0.060 for 4.1 ± 0.7, 15.1 ± 1.3 and 50.3 ± 1.7 nm Au NPs, respectively (no ozone treatment).

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Figure 5.2. CVs of (A) citrate-coated 4.1 ± 0.7 nm (blue), 15.1 ± 1.3 nm (green), and 50.3 ± 1.7 nm (red) diameter Au NPs attached to glass/ITO/APTES electrodes obtained in 0.1 M HClO₄ at a scan rate of 0.1 V/s and (B) ASVs of the same samples in (A) obtained in 0.01 M KBr plus 0.1 M KClO₄ at a scan rate of 0.01 V/s. This shows the three different sized Au NPs on glass/ITO/APTES with a similar total amount of Au (B) obtained by soaking in the Au NP solution of interest and monitoring the SA as in (A) until the SA reaches the desired level. CVs of 4.1 ± 0.7 nm (blue), 15.1 ± 1.3 nm (green) and 50.3 ± 1.7nm (red) citrate-coated Au NPs attached to glass/ITO/APTES obtained in 0.01 M KBr plus 0.1 M HClO₄ at a scan rate of 0.1 V/s. C - 1st scan, D - 5th scan, E - 50th scan.
5.2.5. Stability Against Oxidation as Measured by CV. To analyze the stability of citrate- and alkanethiolate-coated Au NPs, we performed CV experiments in the presence of 0.01 M KBr plus 0.1 M HClO₄, where Br⁻ was used to oxidize Au from the electrode surface, forming soluble AuBr₄⁻ and AuBr₂⁻ complexes as shown in reactions 5.2 and 5.3. Figure 5.2C shows CVs of citrate-coated 4.1 nm, 15.1 nm, and 50.3 nm Au NPs having similar volume on the electrode surface taken in 0.01 M Br⁻ plus 0.1 M HClO₄ solution at a scan rate of 0.1 V/s. The oxidation peak potential (Eₚ,ox) appears at 0.96 V, 0.86 V, and 0.80 V for the 50.3 nm, 15.1 nm, and 4.1 nm diameter Au NPs, respectively, which agrees with the well-known decrease in peak oxidation potential with decreasing size described by us and others in the literature.²⁻⁹⁷ Next, we determined the stability of the different sized alkanethiolate-coated Au NPs by monitoring their trend of oxidation in the Br⁻-containing acidic electrolyte. The relative stability of Au NPs coated with alkanethiolate SAMs was studied by comparing the current observed for the reduction of AuBr₄⁻/AuBr₂⁻ during the reverse negative scan of the CV (Figure 5.3) rather than the oxidation peak, since Br⁻ oxidation to Br₂ can occur near the Au oxidation peak. On the 1st CV scan, there was a significant amount of reduction current for 4.1 nm, 15.1 nm, and 50.3 nm C4S-coated Au NPs (Figure 5.3A). C4S-coated 4.1 nm Au NPs showed the least amount of current while the 15.1 nm was intermediate and 50.3 nm Au NPs showed the most current. This suggests that more Au dissolved from the 50.3 nm Au NPs, indicating that the C4S passivated them the least. We continued scanning up to 50 CV cycles. On the 5th scan (Figure 5.3B), there was still slightly more reduction current for the 50.3 nm Au NPs compared to the 15.1 nm and 4.1 nm Au NPs. The peak current for Au reduction gradually decreased and was significantly low by the 50th scan (Figure 5.3C) for all sizes.
The close to disappearance of the reduction peak is due to the eventual complete oxidative dissolution of all Au NPs, where the Au fully dissolved (except the tiny peak for 50.3 nm) and diffused away from the electrode surface, where it could no longer be re-reduced. The overall behavior indicates that C4S-coated 4.1 nm Au NPs are more resistive to dissolution by Br\textsuperscript{-} than the bigger-sized C4S-coated 15.1 nm and 50.3 nm Au NPs. This trend is opposite of what occurred for citrate-coated 4.1 nm, 15.1 nm, and 50.3 nm Au NPs, where $E_{p,ox}$ increased with increasing size on the first scan (Figure 5.2C), while the stripping charge was similar (Table 5.1). The re-reduction charge was 40%, 46%, and 30% of the oxidation charge for the 50.3, 15.1, and 4.1 nm Au NPs, respectively, as shown in Table 5.1 (reduction peak charge divided by oxidation peak charge). The smaller re-reduction charge for 4.1 nm Au NPs in this case is not due to greater stability. The reduction charge is somewhat complicated by higher mass transport away from the smaller Au NPs, longer time for AuBr\textsubscript{4}/AuBr\textsubscript{2}\textsuperscript{-} ions to diffuse away for smaller Au NPs due to lower $E_{p,ox}$, and earlier times for re-reduction of AuBr\textsubscript{4}/AuBr\textsubscript{2}\textsuperscript{-} due to higher overpotentials for reduction on larger Au NPs (more negative reduction potential on 50.3 nm Au NPs). Nevertheless, by the 50\textsuperscript{th} CV scan (Figure 5.2C), all the Au clearly dissolved and diffused away for 4.1 nm and 15.1 nm, while there remained a small amount of undissolved Au for 50.3 nm NPs, showing greater stability for the largest size Au NPs.

We next performed similar measurements with the same three Au NPs but coated with C10S (Figure 5.3D-F) and C16S (Figure 5.3G-I) SAMs, where again the smallest size 4.1 nm diameter Au NPs showed the smallest reduction peak current (blue plot) while the largest 50.3 nm Au NPs showed the largest reduction peak current (red plot). The 5\textsuperscript{th} scan showed the same trend while very low reduction peak current appeared for all Au NPs on
the 50th scan, indicating very little Au dissolution occurring at that point. This data again shows that the 4.1 nm Au NPs are more passivated by alkanethiolates than the 15.1 nm and 50.3 nm Au NPs. Figure 5.3G shows the 1st CV scan of the different sized Au NPs coated with the longest C16S thiolate SAMs. Unlike C4S and C10S SAMs, the reduction peak

Figure 5.3. Cyclic voltammograms (CVs) of 4.1 nm (blue), 15.1 nm (green) and 50.3 nm (red) Au NPs attached to glass/ITO/APTES and coated with C4S (1st column, A-C), C10S (2nd column, D-F) and C16S (3rd column, G-I) alkanethiol SAMs. Rows 1, 2 and 3 represent the 1st, 5th and 50th CV scans respectively. Frames C, F and I having low oxidation-reduction current level are blown up 10 times as included in the inset for more visibility of the current. CVs were taken from 0.0 to 1.2 V in 0.01 M KBr and 0.1 M HClO₄.
current in this case is negligible for all the Au NP sizes on the 1st scan, indicating very little Au dissolution for any of them. Upon continued CV scanning, the reduction peak current remained negligible on the 5th scan (Figure 5.3H) and very small on the 50th scan as well (Figure 5.3I), although there are very small peaks observed for 50.3 nm and 15.1 nm Au NPs on the 50th scan as shown in the inset with the current scale blown up 10 times. This is again consistent with less passivation for the larger Au NPs. This data also indicates stronger passivation against dissolution for all sized Au NPs as the alkanethiolate chain length increases from C4S to C16S, which is consistent with what has been observed previously on 2D Au electrodes.278-279, 287 The CVs in Figure 5.4 clearly show the significant effect of chain length of the alkanethiolates on the oxidation behavior of the different-sized Au NPs on the 1st CV scan.
5.2.6. Stability Against Oxidation Measured by CC. As mentioned, the reduction current in the CVs can be complicated by diffusion of soluble species away from the surface upon dissolution as well as different times between oxidation and reduction potentials. Also, it is not clear that a lack of a reduction peak is indicative of passivation or complete dissolution of Au on later scans. In order to resolve this confusion, we used chronocoulometry (CC) to further confirm the relative stability of different-sized Au NPs coated with alkanethiolate SAMs. CC of alkanethiolate-coated Au NPs was performed by holding the potential of the working electrode at 1.0 V for 1000 sec in 0.01 M KBr plus 0.1 M HClO₄.
0.1 M HClO₄. As shown in the CC plots of citrate-coated 4.1 nm, 15.1 nm, and 50.3 nm Au NPs (Figure 3A), this potential oxidizes more than 90% of the Au for all Au NP sizes within 500 sec and we successfully maintained a similar amount of Au for each size on the electrode based on the final charge of 600-750 µC for the citrate-coated Au NPs (Figure 5.5A). Figure 5.5B-D show the CCs of 4.1 nm, 15.1 nm, and 50.3 nm Au NPs coated with C4S, C10S, and C16S SAMs, respectively. In all cases, the total stripping charge is lowest for the 4.1 nm diameter Au NPs compared to the 15.1 nm and 50.3 nm Au NPs, consistent with the strongest passivation of the smallest Au NPs. The C4S SAMs passivated the 15.1 nm Au NPs more effectively compared to 50.3 nm Au NPs, while C10S and C16S were similar for 15.1 nm and 50.3 nm Au NPs. Figure 5.6 summarizes the CC data, where the average stripping charge was not significantly different for citrate coated Au NPs of all sizes (520-620 µC). They also were not significantly different for C16S coated Au NPs (all <100 µC), since all 3 sizes were well passivated. For C4S-coated Au NPs, the 4.1 nm Au NPs showed a significantly lower stripping charge (~100 µC) followed by 15.1 nm Au NPs (~200 µC) and finally 50.3 nm Au NPs (~350 µC). For C10S-coated Au NPs, only the 4.1 nm Au NPs showed significantly lower stripping charge (~50 µC) compared to the 15.1 nm and 50.3 nm Au NPs (~100 µC).

One possible reason for the different stripping charge for the different sized Au NPs in the CC plots could be that the thiols dissolve some of the Au NPs during assembly. If they dissolve the 4.1 nm Au NPs more readily during assembly, then this could explain the reason for the lower stripping charge for the 4.1 nm Au NPs. To rule this possibility out,
we attached a similar amount of different sized Au NPs on to the electrode surface and formed SAMs of C10S as already described. We then treated all of the samples with ozone for 30 min, which removes the thiolate ligands from the Au NP surfaces as reported previously. We then performed CC, with the results shown in Figure 5.5C (dashed plots)
and Figure 5.6. Since the charge is statistically the same as the citrate coated Au NPs, this conclusively shows that the thiol self-assembly does not dissolve any Au significantly and does not itself alter the amount of Au on the surface. This confirms that the thiol SAMs do passivate the smaller Au NPs more effectively than the larger Au NPs. The CC results in Figures 5.5 and 5.6 agree well with the CV results in Figures 5.3 and 5.4 but are more conclusive.

**Figure 5.6.** Bar plot showing the average of charges along with standard deviation obtained in CC for 4.1 nm (blue), 15.1 nm (dark green) and 50.3 nm (red) citrate coated Au NPs and those after treatment with C4S, C10S and C16S alkanethiol SAMs. Far right side of the plot diagram represents the average of CC charges of Au NPs in C10S thiol SAMs followed by 30 min of ozone treatment.
To further explore the passivating ability of SAMs as a function of Au NP size, we soaked glass/ITO/APTES/Au NP electrodes, having the same total amount of Au but different size Au NPs, in C4S to form the SAM coatings. Next, we performed CC by stepping from 0.0 V to 1.0 V in 0.01 M KBr plus 0.1 M HClO₄ for 400 s. As shown in Figure 5.7A, the charge due to Au oxidation decreased as the size of the Au NPs decreased, similar to the results in Figure 5.5B and Figure 5.6. Following the CC, we removed the electrodes from the electrochemical cell, rinsed with nanopure water, and dried under nitrogen. Then we treated the samples with ozone for 30 min to remove any C4S remaining on the Au NPs. Finally, we performed ASV in 0.01 M KBr plus 0.1 M KClO₄ to determine how much Au was left on each of the electrodes. As shown in Figure 5.7B, we observed that the Au oxidation peak size followed the order of 4.1 nm > 15.1 nm > 50.3 nm Au NPs. The average integrated ASV charge was 29.0 ± 3.1 μC, 15.7 ± 2.6 μC, and 9.7 ± 0.1 μC for the 4.1 nm, 15.1 nm, and 50.3 nm Au NPs, respectively (n=3). The larger Au oxidation peak shows that there was less Au dissolution during the CC experiment for 400 s at 1.0 V. This confirms that the C4S passivated the smaller 4.1 nm diameter Au NPs the most effectively.
Figure 5.7. (A) Chronocoulometry (CC) measurements obtained by stepping from 0.0 V to 1.0 V and monitoring the charge as a function of time for 400 s in 0.01 M KBr plus 0.1 M HClO₄ of glass/ITO/APTES electrodes coated with 4.1 ± 0.7 nm (blue), 15.1 ± 1.3 nm (green), and 50.3 ± 1.7 nm (red) Au NPs functionalized with C4S SAMs. (B) Anodic stripping voltammetry (ASV) obtained from 0.0 V to 1.2 V in 0.01 M KBr plus 0.1 M HClO₄ of the different sized Au NPs on glass/ITO/APTES electrodes following the CC treatment in (A) and 30 min of ozone treatment. The ASV stripping charge in Coulombs (C) is provided in Frame B corresponding to the different size Au NPs. The larger peak for Au oxidation of 4.1 ± 0.7 nm Au NPs compared to the 15.1 ± 1.3 nm and 50.3 ± 1.7 nm Au NPs proves that the C4S protected the smallest Au NPs the most from oxidative dissolution by Br⁻.

### 5.2.7. Spectroelectrochemical Characterization

The size-dependent oxidative stripping of citrate-stabilized and thiolate-coated Au NPs was monitored by measuring the decrease in absorbance of the Au localized surface plasmon resonance (LSPR) extinction
band in the UV-Vis region in a spectroelectrochemical set up. The absorbance was measured of the glass/ITO/APTES/Au NPs electrodes against a glass/ITO/APTES blank at 1.0 V vs. Ag/AgCl in 0.01 M KBr plus 0.1 M HClO$_4$ at various times. Strong optical absorbance requires a high coverage of all sized Au NPs on the electrode surface which we obtained by soaking functionalized glass/ITO/APTES into the as-prepared solution of Au NPs for different time (4.1 nm – 2 hr, 15.1 nm – 3 hr, 50.3 nm – 5 hr) so that the color of the Au NPs attached onto the electrode was visible. Under high coverage, Au NPs were clearly showing the LSPR band at different positions than that expected for solution-phase NPs (Figure 5.8). We assume that the partial aggregation of Au NPs due to high coverage, the dielectric properties of glass/ITO/APTES, or the combination of them could cause a shift in the LSPR band position. Figure 5.8C shows a plot of the normalized absorbance of the LSPR peak ($\lambda_{\text{max}}$) for citrate-coated 4.1 nm, 15.1 nm, and 50.3 nm Au NPs during CC in 0.01 M KBr plus 0.1 M HClO$_4$ solution at 1.0 V vs Ag/AgCl. We observed that the normalized absorbance decreased relatively fast for all sized Au NPs indicating that these NPs have low stability against oxidation in Br$^-$ at 1.0 V. The 4.1 nm and 15.1 nm Au NPs dissolved faster compared to the 50.3 nm Au NPs, showing a decrease in normalized absorbance from 1.0 to 0.0 within 500 s for the former as compared to 700 s for the latter. This is consistent with the greater stability of larger-sized citrate-stabilized Au NPs.$^{2-3}$ Figure 5.8D shows the decrease in normalized absorbance at ~540 nm for C4S-coated Au NPs as a function of time. In this case, the absorbance decreased faster for the 50.3 nm Au NPs than the smaller sized 15.1 nm and 4.1 nm Au NPs. Consistent with the CV and CC results, this trend is opposite to the trend exhibited by citrate-coated Au NPs, showing again that the smaller-sized 4.1 nm Au NPs are significantly more stable when coated with C4S.
SAMs than the 15.1 nm or 50.3 nm Au NPs. Similar behavior was observed for Au NPs coated with C10S thiols (Figure 5.8E) and C16S thiols (Figure 5.8F). In order to confirm whether all the Au on the electrode was oxidized or not when coated with the longer chain alkanethiolate SAMs (C10S and C16S), we switched the CC potential to 1.2 V beyond 1000 s. We found that the absorbance value decreased significantly for the 4.1 nm Au NPs when we continued at 1.2 V for an additional 400 s, confirming that more Au existed on the electrode surface after the first 1000 s (Figures 5.8E and 5.8F). In contrast, the normalized absorbance did not decrease further for C10S-coated 15.1 nm and C10S-coated or C16S-coated 50.3 nm Au NPs, confirming that those Au NPs had already fully dissolved in the first 1000 s. The C16S-coated 15.1 nm Au NPs did not completely dissolve within 1000 s, so we continued oxidizing them for another 400 sec at 1.2 V. We observed that at 1300 s total, the normalized absorbance decreased significantly (Figure 5.8F). The spectroelectrochemical data clearly support our conclusion of a reverse size-dependent stability of alkanethiolate-stabilized Au NPs compared to citrate-stabilized Au NPs.
Figure 5.8. UV-Vis absorbance of 4.1 nm (A) and 50.3 nm (B) Au NPs attached to glass/ITO/APTES and coated with C4S measured at different chronocoulometry. Plot of normalized absorbance of 4.1 nm (blue), 15.1 nm (green) and 50.3 nm (red) Au NPs in 0.01 M KBr and 0.1 M HClO₄ at 1.0 V taken up to 1400 s from chronocoulometry experiments for C) bare Au NPs, D) Au NPs coated in C4S, E) Au NPs coated in C10S, F) Au NPs coated in C16S alkanethiolate SAMs. The CC operating potential was set at 1.0 V up to 1000 s and at 1.2 V between 1000 to 1400 s.
5.3. CONCLUSIONS

CV, CC, and spectroelectrochemical experiments all reveal the trend in size-
dependent oxidation of Au NPs coated with alkanethiolates, where oxidation is surprisingly
more pronounced on larger-sized Au NPs. This is opposite of the behavior of Au NPs
stabilized with more weakly-bound citrate ligands, which show more pronounced
oxidation on smaller-sized Au NPs in agreement with the thermodynamic prediction by
Plieth. While the reasons are not conclusively known, we believe the higher defect, lower
coordination Au atoms on the surface of smaller Au NPs promotes stronger binding to
alkanethiolates, which results in stronger passivation against oxidative dissolution in Br⁻,
which would require binding of Br⁻ to the Au NP surface. This effect appears to be more
important than the lower ordering of the alkane chains when assembled on high curvature
smaller 3D Au nanocrystals and more important than the lower thermodynamic stability of
small Au NPs due to their high surface area-to-volume ratio (SA/V). The stronger Au-S
binding evens things out thermodynamically and actually provides higher stability for
smaller Au NPs relative to larger Au NPs. Future studies will explore sub-4 nm diameter
Au NPs and different types of ligand stabilizers. Optimization of NP stabilizers to provide
the NPs with high metal stability but also strong reactivity in terms of catalysis or sensing
is crucial. Our methods are useful for better understanding metal NP oxidative stability as
a function of size and stabilizer to render them useful for future applications.
CHAPTER VI

ANTI-GALVANIC EXCHANGE OF SUB-2 nm GOLD NANOPARTICLES WITH COPPER AND SILVER: ATOMIC LEVEL DOPING AND EFFECT ON OXYGEN ELECTROREDUCTION

6.1. INTRODUCTION

Metal nanoparticles (NPs) have been used in many important areas of modern science including catalysis,\textsuperscript{87} \textsuperscript{288} sensing,\textsuperscript{217} photovoltaics,\textsuperscript{289} optoelectronics,\textsuperscript{290} spectroscopy,\textsuperscript{291} and biomedicals.\textsuperscript{292} The properties and applications of the NPs can be varied in a number of ways such as by change in NPs size and morphology, composition and stabilizing ligands.\textsuperscript{141, 293} Galvanic replacement reactions (GRR) in metal NPs, where atom/s from a metal nanoparticle undergo exchange with more noble metal ions is a common thermodynamically favored process of forming bimetallic or multimetallic nanostructures.\textsuperscript{167-168} When the replacement occurs in the opposite direction of what is predicted thermodynamically, then that is called anti-galvanic replacement (AGR). It is not thermodynamically favored for bulk sizes, but as the nanoparticle size becomes smaller than about 4 nm for Au NPs, the AGR process becomes spontaneous.\textsuperscript{7, 170} The study of AGR reaction has been poorly carried out in the literature as it is weakly favored from kinetic and thermodynamic aspects. AGR or GRR is a mild and facile way of engineering
a variety of metal nanostructures, including hollow nanocubes\textsuperscript{171} and nanocages\textsuperscript{172} whereby their desirable properties can be tuned.\textsuperscript{173-174}

Different researchers have extensively studied AGR behavior with metal NPs.\textsuperscript{170} \textsuperscript{294-295} AGR between thiolate stabilized Au\textsubscript{25} nanoclusters and Ag\textsuperscript{+} and Cu\textsuperscript{2+} ions was first carried out by Choi and coworkers.\textsuperscript{294} They observed an addition of Ag\textsuperscript{+} ions onto the thiolate coated Au\textsubscript{25} nanoclusters (NCs), which was explained to occur by reduction of Ag\textsuperscript{+} ions by negatively charged thiolate ligands. Wu \textit{et al.} carried out the AGR of thiolate protected \textless 3 nm Au and Ag NCs with Cu\textsuperscript{2+} ions as evidenced by mass spectrometry (MS), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) data.\textsuperscript{170} Their work excluded the possible reducing ability of negatively-charged Au\textsubscript{25}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{18} by experiment carried on similar neutral species with Ag\textsuperscript{+} ions. Such a reaction was found to occur due to increasing reducing ability of metal NPs with decreasing NPs size. Wang and coworkers observed GRR of atomically precise Au\textsubscript{25}(SR)\textsubscript{18} clusters with thiol complexed with Cu(II), Ag(I), Cd(II), and Hg(II) forming alloyed NCs such as Cu\textsubscript{x}Au\textsubscript{25-x}(SR)\textsubscript{18}, Ag\textsubscript{x}Au\textsubscript{25-x}(SR)\textsubscript{18}, Cd\textsubscript{1}Au\textsubscript{24}(SR)\textsubscript{18}, and Hg\textsubscript{1}Au\textsubscript{24}(SR)\textsubscript{18}.\textsuperscript{295} (SR=alkanethiol). Tian and coworkers performed AGR of Au\textsubscript{25}(PET)\textsubscript{18}, (PET=polyethylene terephthalate) with Ag\textsuperscript{+} by playing with variable ion-precursor and ion-doze with atomically precise control in composition, structure, and properties in the resultant nanostructures.\textsuperscript{178} Besides composition, significant changes in the electrocatalytic behavior of metal hetero nanostructures also occurs once metal NPs are subjected to GRR. For example, Young \textit{et al.} reported that AuAg NCs after galvanic exchange of Au with Ag showed significantly improved electrocatalytic oxygen reduction reaction in alkaline media as compared to Au-Ag alloys prepared by other methods.\textsuperscript{167}
AGR of thiol stabilized Au NCs was further explained by several researchers such as replacement with Ag\(^+\) by Xia\(^{175}\) and replacement of selenate stabilized Au\(_{25}\) clusters with Cu\(^{2+}\) by Kurashige\(^{176}\) as some examples.

Besides controlled doping of Au NCs via GRR, several researchers carried out the stability study of the doped nanostructure and its relation to geometric and electronic structures\(^{13,14,177-178,296-300}\) such as doping of Au\(_{25}\) clusters with Cu by Negishi\(^{13}\), doping and electrocatalytic property of Au\(_{25}\) with Ag by Yao\(^{178}\) and doping and stability study of different sized Au NCs by Ghosh\(^{177}\). Murray et al. observed a relatively less stable nature of Pd\(_1\)Au\(_{24}\)(SC\(_2\)H)\(_{18}\) by co-reduction (besides GRR) of Au(III) and Pd(II) salts using a suitable ligand as compared to Pt doped Au NCs\(^{14}\). They observed that doping by co-reduction of precursor metal ions can’t often produce NCs with controlled atomic level doping. Unlike the cases of Pt and Pd, Negishi et al. showed that doping by Ag incorporates a variable number of Ag atoms (ranging from 1 to 11) into the Au\(_{25}\)(SR)\(_{18}\) NCs\(^6\) due to differences in atomic size of the dopant elements and Au as well as position and energy gap of the dopant in the NCs. This is true even for Cu doping as reported by Gittlie\(^{301}\) and Ackerman\(^{302}\), where the number of incorporated Cu atoms could go up to 5 per Au\(_{25}\)(SR)\(_{18}\) cluster. In addition to extensive doping studies on Au\(_{25}\)(SR)\(_{18}\) and Au\(_{38}\)(SR)\(_{24}\) NCs, Kumara et al. performed alloying of Au\(_{144}\)(SR)\(_{60}\) by AGR with Ag and observed a distribution of Ag\(_x\)Au\(_{144-x}\)(SR)\(_{60}\) species using electrospray ionization (ESI)-MS\(^{303}\). Unlike the case of Ag\(_x\)Au\(_{38-x}\)(SR)\(_{24}\) in which stability decreased with increasing Ag composition, the stability of Ag\(_x\)Au\(_{144-x}\)(SR)\(_{60}\) became more pronounced. In spite of this, co-reduction generates a complex mixture of undoped and doped NCs with variable composition and one needs to use complicated techniques such as size-exclusion
The relatively lower stability of Cu and Ag doped Au NCs as compared to those doped by Pt and Pd via co-reduction of metal ion precursors necessitates the development of an alternative doping strategy. Further, a facile way of characterizing the NCs and studying the stability of these doped NCs is equally formidable.

Silver based nanomaterials are promising candidates for oxygen reduction reaction (ORR) and so act as a rational substitute for Pt due to its similar reaction mechanism and kinetics with Pt, cost effectiveness, and highly conductive nature.\textsuperscript{304} The activity towards ORR of Ag based nanomaterials is determined by several factors such as selection of electrode material, size, and morphology of Ag nanostructures,\textsuperscript{39, 305} and composition of Ag in bimetallic or multimetallic nanostructures.\textsuperscript{166} Regarding the size effect of Ag NPs, 15 nm diameter citrate-stabilized Ag NPs, as example, are found to be better catalyst for ORR as compared to 95 nm Ag NPs.\textsuperscript{305} Yang et al. reported that Ag nanoclusters with 2-5 atoms display better ORR activity than Pt itself indicating the high impact of NPs size on the electroreduction of oxygen.\textsuperscript{306} The best composition of Ag in the electrode material or alloyed nanostructures exhibiting highest electroreduction of oxygen in term of onset potential and current density is still under debate.\textsuperscript{166, 307} For example, Coutanceaus et al. reported 20 wt % of Ag as the best composition in Ag/C while Fazil and Chetty found 40 wt % Ag in Ag/carbon nanotube (CNT) is the optimum Ag loading for best ORR activity.\textsuperscript{166} Wang et al. reported the introduction of single atom catalysts (SACs) of Pt onto the cathode of proton exchange membrane fuel cell causing comparable ORR activity as produced by commercial Pt.\textsuperscript{308} SACs possess the highest metal utilization and excellent activity because of the minimum size of metal and unique
coordination structure and thus provide a potential alternative to Pt-based materials for ORR. These instances direct the need of further works to introduce concept of single atom/s and to determine the best Ag composition in AuAg nanostructures for best electrocatalytic activity. Literature is also lacking to explore what the effect on ORR would be caused by atomic level percentage of Ag doped into Au NCs via AGR.

Most of the literature works involving synthesis and GRR with other metals are usually carried out for thiolate-stabilized metal NCs.\textsuperscript{5, 309-310} Thiolate ligands provide a strong barrier against the electrooxidation and electrocatalysis of metal NCs by blocking the free access to the core metal atoms for electron transfer.\textsuperscript{10} The weakly-stabilized Au NPs/NCs are the good substitutes for many of these applications as compared to those coated with thiols.\textsuperscript{311} For example, Liao and coworkers used differential pulse anodic stripping voltammetry (ASV) for predicting stability of the doped nanostructure based on HOMO-LUMO energies of Au\textsubscript{24}Hg\textsubscript{1}(PET)\textsubscript{18} obtained by doping of Au\textsubscript{25}(PET)\textsubscript{18} with Hg.\textsuperscript{312} Hutchinson and coworkers reported the effect on ORR with AuAg nanostructures obtained by selective doping of Ag into 1.6 nm thiolate-stabilized Au NPs via AGR.\textsuperscript{167} It was reported that deposition of Ag onto 1.6 nm Au NPs forming Au/Ag core/shell structure favors ORR to undergo a 4-electron pathway with certain AuAg composition (~40-70 % Ag). However, to the best of our knowledge, an absolute electrochemical study of controlled atomic percentage doping of Ag onto weakly coated Au NPs/NCs via AGR and electroreduction of oxygen has not been reported so far.

Our method of electrochemical study of AGR of Au NPs/NCs and ORR activity is advantageous for several reasons. First, we are dealing with Au NPs stabilized by weak phosphine ligands. An electrochemical study on weakly coated metal nanostructures is of
special importance due to their ease of electrooxidation by ASV.\textsuperscript{3, 10} Based on the peak oxidation potential ($E_p$) of metal NPs in ASV and the peak intensity, an absolute identification of a metal and its composition, together with its size/stability can be determined.\textsuperscript{2, 23, 59, 123} Previously, our group successfully studied the size dependent oxidation of Au, Ag and Cu and bimetallic NPs by using $E_p$ in ASV.\textsuperscript{2, 4, 23, 46} A positive shift in $E_p$ during AGR indicates that NPs are unstable as a result of size transformation or aggregation while no shift in $E_p$ demonstrates their stable nature. Second, the AGR and subsequent analysis of metal NPs can be carried out directly on the electrode surface. Third, precise control of doping of Au NPs can be performed by varying the soaking time of electrode attached Au NPs in the aqueous solution of Cu$^{2+}$/Ag$^+$ with varying concentration. Our electrochemical method of studying AGR is simple, cheap, fast, and sensitive as compared to existing sophisticated high vacuum spectroscopic and microscopic techniques.

**6.2. RESULTS AND DISCUSSION**

The experimental workflow in this study is as mentioned in the different steps of Figure 6.1. First, 1.6 nm and 4.1 nm Au NPs were chemically synthesized by following the protocols in Chapter 2. After successful synthesis of the Au NPs, glass/ITO/APTES electrodes were soaked into as prepared or diluted solution of the Au NPs, cleaned thoroughly with nanopure water, and dried under a stream of N$_2$ (step 2). The electrode attached Au NPs were then soaked into the appropriate aqueous solution of Cu$^{2+}$ and Ag$^+$ to carry out the AGR reaction (step 3). The soaking time and concentration of metal ions was optimized to obtain the desired composition of Au, Cu, and/or Ag in the alloyed
nanostructures. After soaking Au NPs into the appropriate aqueous solution of Cu$^{2+}$ and Ag$^{+}$ for a prefixed time, the alloyed AuAg nanostructure with variable Ag composition was used for electroreduction of oxygen in basic medium and the results were compared with the non-alloyed Au NPs (step 4). Depending upon the type of metal and the NPs size, the peaks for electrooxidation of the different metal NPs are obtained at different potentials with stripping charges proportional to the quantity of the metal atoms in the alloyed nanostructure (step 5). This information will be useful to analyze the composition and stability of the resultant nanostructures after AGR followed by ORR.

![Workflow of experiments in this work](image)

**Figure 6.1.** Workflow of experiments in this work

### 6.2.1. Galvanic Exchange of Au NPs with Cu and Ag and ASV Analysis

For galvanic replacement, Au NPs were first attached onto the glass/ITO/APTES by direct soaking. The electrode was then cleaned with nanopure water, dried under N$_2$, and soaked into the aqueous solution of CuSO$_4$ and AgNO$_3$ with different concentration for different
time. The electrode was again cleaned with water, dried with stream of nitrogen, and subjected to ASV analysis. ASV of electrode soaked with Cu\(^{2+}\) was taken in 10 mM KCl plus 0.1 M HClO\(_4\) between 0.0 to 1.2 V at a scan rate of 0.01 V/s while ASV of electrode soaked in Ag\(^+\) was first taken in 0.1 M HClO\(_4\) to quantitatively strip all Ag followed by stripping of Au in 10 mM KCl plus 0.1 M HClO\(_4\). Thus, single ASV run was enough for ASV analysis of Au and Cu in AuCu, whereas two ASV scans were required for the analysis of Au and Ag in AuAg. Stripping of Ag by Cl\(^-\) forms an insoluble AgCl which partially blocks the electron transfer process on the electrode surface and makes it susceptible for accurate compositional analysis of Au and Ag. The compositional analysis of the alloyed nanostructures was carried out by integrating the area under the corresponding peaks in the ASV voltammograms by considering 3-, 2-, and 1- electron electrooxidation process of Au, Cu, and Ag respectively.

6.2.2. Controlled Doping. Figure 6.2 shows the ASV signature of individual 1.6 nm Au NPs as well as Au NPs alloyed with Cu and Ag via GRR. ASV was performed in the presence of 10 mM KCl plus 0.1 M HClO\(_4\) in the case of AuCu nanostructures while ASV of Ag was obtained in 0.1 M HClO\(_4\). A single ASV run is thus enough for stripping of Au and Cu from AuCu nanostructures while ASV in 0.1 M HClO\(_4\) followed by ASV in the Cl\(^-\) containing electrolyte is required for stripping of individual Au and Ag from AuAg nanostructures, as otherwise stripping of Ag by Cl\(^-\) will form a precipitate of AgCl on the electrode surface which might hinder further stripping process. Figure 6.2A (dark green plot) represents the ASV of 1.6 nm Au NPs attached to glass/ITO/APTES which shows a single oxidation peak with peak potential \((E_p)\) of \(~0.70\) V vs Ag/AgCl. Since ASV is a
destructive process, we used the separate samples of electrode attached Au NPs for galvanic replacement with Cu^{2+} and Ag^{+} in all the cases discussed subsequently in this work. The appearance of two distinct peaks at \(-0.2\) V and \(-0.7\) V (Figure 6.2A, black plot) after 15 min soaking of the electrode attached 1.6 nm Au NPs in 100 µM aqueous Cu^{2+} solution indicates the successful galvanic replacement of Au with Cu^{2+}. Following the work of Pattadar et al., the integrated charges under the individual Cu and Au peaks were then utilized to calculate the atomic percentage of Cu in the AuCu nanostructures with 20.1 ± 3.6 % of Cu (n=3) under the conditions mentioned earlier. For further confirmation of Cu replacement with Au NPs, we performed ASV of bare Cu NPs (\(~5\) nm in diameter) in Cl\(^{-}\) containing electrolyte and observed a stripping peak at \(-0.18\) V (Figure 6.2A, blue plot), close to the potential at which Cu was stripped from AuCu nanostructures. This observation concludes that 1.6 nm Au NPs should have undergone AGR with Cu^{2+}. We also tested
Figure 6.2. Anodic stripping voltammetry (ASV) of 1.6 and 4.1 nm Au NPs before and after galvanic replacement with Cu$^{2+}$ and Ag$^{+}$. A) 1.6 nm Au and Cu NPs, B) 1.6 nm and 4.1 nm Au with Cu$^{2+}$ replacement, C) 1.6 nm Au before and after replacement with Ag$^{+}$ D) 1.6 and 4.1 nm Au with Ag$^{+}$ replacement. In all cases, ASV of Au and Au alloyed with Cu was performed in 10 mM KCl plus 0.1 M HClO$_4$, ASV of Ag was performed in 0.1 M HClO$_4$. ASV of Au alloyed with Ag was performed only after Ag stripping between 0 to 0.5 V.

whether the extent of galvanic replacement with Cu$^{2+}$ is dependent on the size of Au NPs, for which we performed ASV of 4.1 nm Au NPs after attempted replacement with Cu$^{2+}$ under identical conditions. Unlike the case of 1.6 nm Au NPs, we could not observe any distinct stripping peak for Cu presumed to be appearing at -0.2 V while we observed a sharp
Au stripping peak at ~0.9 V (Figure 6.2B, black plot), a usual stripping peak for 4.1 nm Au in Cl\(^-\) containing electrolyte. This observation clearly demonstrates that galvanic replacement of Au NPs with Cu\(^{2+}\) is a function of size of Au NPs, with smaller NPs undergoing remarkable exchange. This observation is consistent with the previous work of Pattadar and Zamborini, and Wu et al. where the replacement is favored more for decreasing size of Au NPs.\(^7,\)\(^{170}\)

In addition to galvanic replacement with Cu\(^{2+}\), we performed the galvanic replacement of 1.6 nm Au NPs attached to glass/ITO/APTES with Ag\(^+\). We soaked the electrode attached Au NPs into 10 µM aq. Ag\(^+\) for 15 mins, rinsed and dried the electrode, and performed ASV in 0.1 M HClO\(_4\) between 0 to 0.5 V followed by ASV in 10 mM KCl and 0.1 M HClO\(_4\) between 0.0 to 1.2 V. In this case, we observed a distinct stripping peak at ~0.3 V, potential at which ~9 nm citrate-coated Ag NPs is stripped,\(^{46}\) when the ASV was performed in 0.1 M HClO\(_4\) solution (Figure 6.2C, blue plot). After scanning for the stripping of Ag, the sample was scanned again between 0 to 1.2 V in Cl\(^-\) containing HClO\(_4\) solution. In this case, a separate Au peak at ~0.7 V was obtained (Figure 6.2C, black plot), potential at which bare 1.6 nm Au NPs is stripped in Cl\(^-\) containing electrolyte (Figure 6.2C, dark green plot). This demonstrates the successful galvanic replacement of 1.6 nm Au with Ag\(^+\). Similarly, we also tested the galvanic exchange behavior of 4.1 nm Au NPs with Ag\(^+\) under identical conditions. We could hardly observe a distinct Ag peak after the attempted galvanic replacement (Figure 6.2D, blue plot), unlike the case of 1.6 nm Au NPs where the galvanic exchange was obvious (Figure 6.2D, red plot). This indicates that the galvanic replacement of Au NPs with Ag\(^+\) is a size-dependent phenomenon, similar to the case with Cu\(^{2+}\) exchange as discussed earlier and reported in the literature.\(^7\)
The electrochemical method of study of AGR of 1.6 nm Au NPs was used to predict the atomic level doping of Au with Cu\(^{2+}\) and Ag\(^{+}\). Atomic level doping of Au NPs with heterometal atom is of special importance to study the alteration in various electrocatalytic properties and applications as in the literature reported alloyed nanostructures.\(^{168, 174}\) This was optimized by changing the concentration of Cu\(^{2+}\) and Ag\(^{+}\) in the solution and soaking time. We observed that 5 min soaking of electrode attached 1.6 nm Au in 10 µM Cu\(^{2+}\) could furnish a distinct Cu peak with low intensity. Figure 6.3A (blue plot) shows the ASV peak of Cu at -0.2 V with its expanded view is as shown in Figure 6.3B. After calculation,

**Figure 6.3.** ASV of 1.6 nm Au before and after galvanic exchange with A) Cu\(^{2+}\) taken in 10 mM KCl and 0.1 M HClO\(_4\) B) Expanded from of A between 0.0 to 0.35 V C) Au only from AuAg taken in10 mM KCl plus 0.1 M HClO\(_4\) D) Stripping of Ag from AuAg in 0.1 M HClO\(_4\).
The atomic % of Cu in the AuCu alloy is found to be $1.4 \pm 0.3$ (n=3) which represents about 3 atoms of Cu per Au$_{144}$ nanocrystal for 1.6 nm Au. Below 10 µM Cu$^{2+}$ concentration with 5 min exchange, we were not able to observe any distinct Cu peak in ASV (not shown in figure). Similarly, we optimized the condition of minimum Ag doping into the 1.6 nm Au NPs, where we observed a distinct Ag peak when 1.6 nm Au NPs was soaked into 1 µM Ag$^+$ for 5 min. Figure 6.3C (blue plot) shows a distinct Au peak at -0.7 V in Cl$^-$ containing electrolyte while a distinct Ag peak was observed at -0.3 V in 0.1 M HClO$_4$ containing electrolyte for the same electrode as in Figure 6.3D, blue plot (stripping of Au was done after Ag stripped). The atomic % of Ag in this case was calculated to be $2.7 \pm 0.9$ (n=3) which is estimated to be 4-5 Ag atoms per Au$_{144}$ nanocrystal.

6.2.3. Stability Study. Further we were interested in what the stability of the individual Au, Cu, and Ag nanostructures would be in the resultant nanostructure due to AGR. The stability study of doped metal nanostructures is mostly carried out by single crystal X-ray diffraction (XRD), ESI or MALDI-MS and XPS. Here, we monitored the stability of the doped nanostructures by ASV owing to the fact that ASV not only shows size dependent oxidation behavior of metal NPs but also can tell if it is aggregated or not. So ASV could be utilized to predict the stability of the nanocrystals before and after galvanic replacement based on $E_p$. First, we checked the stability of the NPs after 5 min soaking of Au$_{144}$ NPs in 100 µM Cu$^{2+}$. We observed that $E_p$ for electrooxidation of Au NPs remains the same before and after Cu doping which is similar to the case discussed in earlier sections.
For another similar set of experiment, ASV was first performed just to strip Cu with potential scanned between 0.0 to 0.35 V leaving behind the Au on the electrode surface. After complete stripping of Cu by three subsequent ASV scans, the same electrode was again soaked back in to the Cu$^{2+}$ solution for the same time, and ASV for stripping of Cu was again performed. We continued this process for 5 times. In the 5th stage, we stripped Cu first followed by stripping of Au between 0.0 to 1.2 V (Figure 6.4A-B). Interestingly, we observed that the $E_p$ for electrooxidation of Au was found to remain the same as before the galvanic exchange (Figure 6.4A, blue and red plot). We performed similar experiment with Ag exchange by 5 min soaking of Au NPs in 10 µM Ag$^{+}$. In this case, stripping of Ag was first performed between 0.0 to 0.45 V in 0.1 M HClO$_4$ followed by Au stripping. In case of Ag exchange also, the $E_p$ for electrooxidation of 1.6 nm Au in ASV remained unchanged (Figure 6.4C, blue plot). This clearly indicates that the NCs tend to maintain their size stability during the AGR process even when performed multiple times. More importantly, we were also able to monitor the stability of Cu and Ag in the AuCu and AuAg nanostructures by ASV based on constant $E_p$ for electrooxidation of these metals in ASV in the multiple galvanic exchanges. Unfortunately, we were not able to achieve similar Cu and Ag composition in the doped nanostructures in these experiments as we observed a noticeable variation in the intensity of Cu and Ag stripping peaks among the different multiple galvanic exchanges (Figure 6.4B, 6.4D).
Figure 6.4. ASV of 1.6 nm Au before and after multiple galvanic exchange with Cu (A, B) and Ag(C, D). A) ASV of 1.6 nm Au before (red) and after (blue) 5th galvanic exchange with Cu. B) Expanded view showing stripping of Cu only between 0.0 to 0.35 V. C) ASV of 1.6 nm Au before (red) and after (blue) 5th galvanic replacement with Ag. D) Expanded view showing stripping of Ag only between 0.0 to 0.35 V for 5 times of performing galvanic replacement.
6.2.4. ORR Activity. We studied the activity of 1.6 nm Au NPs towards oxygen reduction reaction (ORR) in basic medium before and after galvanic exchange with Ag. As mentioned before, ASV is useful for the quantitation of the constituent elements in the AuAg nanostructure and allows correlation to the ORR activity. Figure 6.5A (green plot) shows the cyclic voltammogram for ORR of 1.6 nm Au NPs attached to glass/ITO/APTES in O₂ saturated 0.1 M KOH scanned from +0.1 V to -0.6 V at a scan rate of 0.01 V/s. The peak current (i_p) in the CV for ORR in this case was ~20 µA. After the CV scan is complete, the same electrode was immersed into an aqueous solution of 10 µM AgNO₃ solution for 5 min whereby Ag was doped into 1.6 nm Au NPs forming AuAg nanostructure with Ag % of 45.6 as calculated from the integrated charges of oxidation of Au and Ag from ASV (Figure 6.5B, blue and red plot). We then performed CV for ORR of the AuAg nanostructure under similar conditions as above. Figure 6.5A (blue plot) shows the cyclic voltammogram with i_p of 180 µA and ORR onset potential of -0.35 V vs Ag/AgCl, (~-0.75 V vs RHE) considering the current at onset potential is 5% of i_p with the onset potential comparable with literature reported value. The nearly 9-fold increase in i_p of 1.6 nm Au NPs after exchange with Ag clearly indicates that doping of 1.6 nm Au with Ag has remarkable effect on ORR. This behavior of 1.6 nm Au doped with Ag via AGR was found to be similar with that produced by citrate-stabilized ~9 nm average diameter Ag NPs having similar amount of total Ag atoms as that obtained from AuAg nanostructure (Figure 6.5A, pink plot and Figure 6.5B, blue and pink plot). This similar ORR activity in the two cases illustrates that Ag NPs are as good as 1.6 nm Au NPs alloyed with Ag via AGR in term of i_p and onset potential during the very first CV scan for ORR. The differences between
We also studied the effect of Ag percentage in the AuAg nanostructure towards ORR and found that the ORR activity remains nearly the same for the Ag % ranging from ~15 to 70 % showing that variation in Ag composition has a negligible effect on ORR (Figure 6.5C). This observation is in line with the study carried out previously.\textsuperscript{166}
Maintaining the stability of AuAg nanostructure towards ORR for a large number of cycles is an important factor to be considered. Accordingly, we compared the catalytic activity of 1.6 nm Au alloyed with Ag via AGR forming AuAg nanostructure with that produced by citrate-stabilized ~9 nm Ag NPs. In both cases, we performed CV in O\textsubscript{2} saturated 0.1 M KOH at a scan rate of 0.1 V/s. Figure 6.6A shows the CVs of AuAg (% Ag

**Figure 6.6.** CV for ORR of 1.6 nm Au after AGR with Ag for 1\textsuperscript{st}, 2\textsuperscript{nd}, 5\textsuperscript{th} and 20\textsuperscript{th} scan in O\textsubscript{2} saturated 0.1 M KOH at scan rate of 0.1 V/s (A) and CV for ORR of 9 nm Ag NPs under similar conditions as in A (B). ORR activity of 1.6 nm Au after galvanic exchange with atomic level % of Ag and stability up to 20\textsuperscript{th} scan during CV in O\textsubscript{2} saturated 0.1 M KOH (C), ASV of Ag from AuAg after 20 consecutive CV scans from C in 0.1 M HClO\textsubscript{4} (D). ASV of Au from AuAg after 20 consecutive CV scans from C is shown in plot D (red) with scale narrowed.
towards ORR run up to 20 scans. We observed that the CV signature and hence the ORR activity in this case remains the same indicating that AuAg nanostructure shows the stable ORR up to 20 CV cycles. Contrary to this, the ORR activity of citrate-stabilized ~9 nm Ag NPs gradually degraded with an increase in the number of CV cycles (Figure 6.6B). This demonstrates the stable nature of AuAg nanostructure towards ORR showing its preference over Ag NPs alone. Further, we tested the ORR stability of AuAg nanostructure having very low Ag composition (1.1 % Ag based on ASV in Figure 6.6D). As shown in Figure 6.6C, the ORR activity in this case also remains the same up to 20 CV cycles. We further examined the ORR stability of AuAg nanostructure (Ag % = 1.9 ) up to 100 CV cycles by potential scanned between +0.1 V to -1.0 V where the ORR activity remained the same even at the more -ve potential scan range (Figure 6.7). The similar ORR activity and stability of atomic level % of Ag in the AuAg nanostructure fabricated via GRR of 1.6 nm Au with Ag indicates that there is a unique AuAg coordination at low Ag content that tends to maintain such a high activity and stability towards ORR. This suggests that a very specific site exists at 1% doping level which enables such ORR activity; though we do not have a direct evidence to support it at this point.
We further continued to observe the ORR activity of AuAg nanostructure formed by GRR of 1.6 nm Au with Ag under the condition of relatively higher Ag content. We then deliberately removed Ag from AuAg nanostructure by ASV stripping of Ag in 0.1 M HClO₄. Stripping of Ag and subsequent monitoring of ORR activity of AuAg was carried out up to 3 subsequent scans of Ag stripping. Figure 6.8A shows the CV for ORR of AuAg before and during the intermittent Ag stripping from AuAg nanostructure (initial Ag % = 56.7). Interestingly, we observed that the $i_p$ for ORR slightly increases with stripping of Ag up to 3rd time of stripping with the onset potential remaining nearly constant (Figure 6.8B). We observed similar ORR behavior while taking the AuAg nanostructure with initial Ag %
Figure 6.8. CV of 1.6 nm Au after AGR with Ag with 56.9 % Ag in O₂ saturated 0.1 M KOH before three subsequent stripping scans of Ag in 0.1 M HClO₄ (A). ASV of Ag from AuAg after ORR in A (B). ASV of Au after 3rd scan of Ag stripping in 0.01 M KCl plus 0.1 M KClO₄ is given in inset of plot B with scale narrowed in frame B. CV under similar condition as in frame A but with Ag % of 1.5 (C) and corresponding ASV of Au and Ag from frame C (D). CV of 1.6 nm Au after AGR with Ag with similar Ag composition as in C after holding the potential at 0.6 V and 1.2 V for 5 min in 0.1 M HClO₄ (E), and ASV of 1.6 nm Au after potential holding and CV from frame E (F).
of 1.5 followed by stripping of Ag (Figure 6.8D). This shows that the atomic level % of Ag in the AuAg nanostructure has a unique structure-property correlation which synergistically produce the comparable or even higher ORR activity as produced by high % of Ag content (56.7 %).

One possible reason behind maintaining the high ORR activity of AuAg nanostructure even after ASV stripping of Ag could be related to the presence of a few Ag atoms in the AuAg nanostructure after stripping. We suspected that there could be a few Ag atoms still buried in the interior of the AuAg nanostructure (or Ag strongly bonded to Au making it hard to strip) even after several ASV attempts to strip Ag. We expected that the residual Ag in the AuAg nanostructure could be completely removed by holding the electrode at certain higher potential for longer time. For this, we held the potential of the electrode at 0.6 V in 0.1 M HClO₄ for 10 min after AGR of 1.6 nm Au NPs with Ag. With the results shown in Figure 6.8E (red and blue plot), we observed that the iₚ for ORR remains similar as before the potential hold. We further hold the potential at 1.2 V for 10 min in a separate 0.1 M HClO₄ solution. Under this condition, interestingly we observed a remarkable degradation in ORR activity of the AuAg nanostructure where the iₚ was found to dwindle by ~64 % along with a negative shift in ORR onset potential of ~50 mV as compared with the case before holding of potential (Figure 6.8E, pink plot). This clearly indicates that the number of Ag atoms per Au₁₄₄ nanocrystal should have decreased down a certain level or possibly completely removed due to stripping of Ag by potential holding at 1.2 V leading to a significant degradation in ORR activity. Further, as a consequence of holding of AuAg nanostructure at 1.2 V, Au NPs were found to undergo partial aggregation as indicated by electrooxidation of Au NPs appearing at several Eₚ values as shown in Figure
6.8F. We believe that the partial aggregation of Au NPs could lead to an alteration in geometric and electronic structure of the nanostructure. This alone or in combination with the additional stripping of Ag due to potential hold could lead to a substantial degradation in ORR activity.

6.3. CONCLUSIONS

In conclusion, we have employed a facile electrochemical ASV method for study of galvanic replacement in weakly-stabilized 1.6 nm Au NPs with Cu and Ag down to atomic % doping, which is poorly studied in the literature. We also observed that Au NPs maintain good size stability after multiple AGR with Cu and Ag based on the peak oxidation potential of Au, Cu, and/or Ag in ASV in the doped nanostructures. Our electrochemical study on the weakly coated Au NPs has key advantages as: i) galvanic exchanges can take place directly on the electrode surface, ii) control of doping can be easily maintained by simply changing the metal ions concentration and time, iii) possibility of direct electrooxidation of the electrode attached nanostructures, and iv) weakly-stabilized Au NPs can furnish good catalytic, sensing and many other applications due to easy access to Au core for redox processes on the electrode surfaces. The AuAg nanostructure after GRR of Au with Ag demonstrates high catalytic activity towards ORR with Ag composition ranging from ~70% down to ~1 %. More interestingly, the AuAg nanostructures maintain similar ORR activity and demonstrate high stability up to 100 cycles of the reduction process at all the Ag compositions studied, unlike the case of Ag NPs alone, where the ORR activity degrades significantly along with the number of cycles. In future, our alloying strategy can be extended to achieve controlled doping, stability study, and electrocatalytic activity of Au
NPs with many other hetero atoms (Pd, Co, Ni) besides AuAg. As an instance, the AuCu nanostructure with atomic % of Cu could be useful for study of hydrogen evolution reaction and CO$_2$ reduction reaction with advanced electrocatalytic activity.
CHAPTER VII

CHEMICAL DETECTION BY ANALYTE-INDUCED ALTERATION IN ELECTROPHORETIC DEPOSITION OF GOLD NANOPARTICLES

7.1. INTRODUCTION

Chromium is widely used in electroplating, dyestuff, leather tanning, metallurgy, and catalysis. As a consequence, chromium is released to the environment, causing a serious threat to human health. Cr(VI) is biotoxic, while Cr(III) is important in the activation of glucose and metabolism of proteins and lipids. However, excess Cr(III) intake induces oxidation of cellular components, such as DNA, proteins and lipids, leading to an increased risk of cardiovascular diseases, diabetes and cancer. Studies also show that Cr(III) is highly bioaccumulative and bioconvertible in nature, which causes considerable cell and tissue damage. Interconversion of the two ionic forms of Cr is common via simple oxidation-reduction processes. For these reasons, the detection of Cr(III) is necessary for environmental monitoring, including water and food safety.

Melamine (C₃H₆N₆) has applications as water-reducing agents, fire retardants, plastics, laminates, paints, and fertilizer mixtures. Some food processing companies deliberately use melamine as a food additive to enhance the protein content. However, since melamine is biotoxic in nature, it can cause many food borne diseases.
associated with the urinary tract and renal failure. For example, melamine is able to form an insoluble complex with cyanuric acid, which is associated with kidney malfunction. The recommended melamine concentration level in food is 2.5 mg/kg (2.5 ppm), with the daily melamine intake not exceeding 0.2 ppm of human body weight. Therefore, there is an increasing demand for feasible, reliable and sensitive methods to detect the melamine concentration in food and the environment.

The determination of Cr and melamine has been achieved previously by spectroscopic, chromatographic, colorimetric and electrochemical methods. Spectroscopic and mass spectrometry methods such as inductively-coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS) involve sophisticated instrumentation, complex sample preparation, time consumption, and high cost. Several researchers have employed Au NPs for the selective and sensitive detection of Cr and melamine by colorimetric methods. This is possible due to the plasmonic properties of Au NPs, which provides them with a high extinction coefficient. Detection is based on variation in absorbance and shift in the localized surface plasmon resonance (LSPR) band due to analyte-induced Au NP-Au NP interactions or aggregation. For example, Chen and coworkers selectively detected Cr(III) and Cr(VI) by using gallic acid-capped Au NPs in the presence of citrate, thiosulphate and ethylene diamine tetraacetic acid (EDTA) as masking agents. They observed little or no optical response to other types of ions. Similarly, Shuang and coworkers used sodium hyaluronate-capped Au NPs for the detection of Cr(III) based on the absorbance ratio of two LSPR peaks at two different wavelengths (A650/A525) obtained after analyte-induced aggregation. Dengying et al. applied colorimetric determination of Cr(III) by synergistic aggregation of Au NPs
in the presence of thiourea.\textsuperscript{199} Elavarasi and coworkers demonstrated individual and simultaneous detection of Cr(VI) and Cr(III) based on fluorescence quenching of Au NPs caused by aggregation in the presence of Cr(III).\textsuperscript{331} Once aggregated, the close proximity of the Au NPs results in a gradual decrease in fluorescence intensity with increasing Cr(III) concentration. The reduction of Cr(VI) to Cr(III) by NaBH\textsubscript{4} prior to analysis made it possible to detect both forms of Cr simultaneously. Colorimetric and fluorometric methods may suffer from matrix interference and they require highly selective complexing agents to cause analyte-induced aggregation of the Au NPs.\textsuperscript{333}

Both colorimetric and electrochemical methods involve simple instrumentation, high speed, and low cost along with high accuracy in spite of their relatively lower sensitivity compared to spectroscopic and mass spectrometry techniques.\textsuperscript{199, 327, 334} The detection of Cr and melamine by electrochemical methods are of interest due to these potential benefits.\textsuperscript{59, 326, 334-337} As an example, Lee et al. fabricated an electrochemical ion sensor based on the electrocatalytic reaction between Cr(VI) and methylene blue (MB).\textsuperscript{334} The surface immobilized MB was reduced to leucomethylene blue (LMB) on the electrode surface, whose charge was then monitored by reduction of Cr(VI) to Cr(III) as LMB became oxidized back to MB. Wyantuti et al. performed voltammetric detection of Cr(VI) by using a glassy carbon electrode (GCE) modified with Au NPs.\textsuperscript{337} Taher and coworkers developed an electrochemical sensing platform using a nano-structured Cr(III) imprinted polymer-modified carbon-composite electrode.\textsuperscript{324} They monitored the oxidation of Cr(III) adsorbed into the film by differential pulse voltammetry. Trisna et al. detected Cr(VI) in river water by cyclic voltammetry (CV) and AC impedance using a graphene/Au NP-modified GCE.\textsuperscript{338}
In addition to Cr(III), there are several reports of detection of melamine by electrochemical methods. Guo et al. reported an electrochemical sensor for detection of melamine by forming a copper-melamine complex using an ordered mesoporous carbon-modified GCE with a limit of detection (LOD) down to ~2 nM.\textsuperscript{339} Rovina et al. reported an electrochemical sensor for rapid determination of melamine using ionic liquid/zinc oxide NPs/chitosan/Au electrode with ~0.01 pM LOD.\textsuperscript{340} The fabrication and characterization of the sensor was, however, tedious and complicated for routine analysis. Peng et al. utilized Au NPs deposited onto graphene-doped carbon paste electrodes for the selective and sensitive detection of melamine.\textsuperscript{341} Strong interactions between Au and melamine led to a decrease in the peak current for the reduction of Au NPs with increasing melamine concentration. The signal was enhanced by differential pulse voltammetry (DPV) with a LOD of ~20 pM. Daizy et al. detected melamine at a reduced graphene oxide-copper nanoflowers modified GCE using ascorbic acid (AA) as an active recognition element with a LOD ranging from 10 nM to 90 nM.\textsuperscript{336} H-bonding between AA and melamine made it possible to correlate the electrochemical signal from AA to the melamine concentration.

Inspired by previous reports on Au NP aggregation-based colorimetric detection of Cr and melamine and our recent demonstration that the peak potential in the anodic stripping voltammetry (ASV) of citrate-stabilized Au NPs (cit-Au NPs) shifts dramatically positive upon aggregation,\textsuperscript{15} we set out to detect Cr\textsuperscript{3+} and melamine by ASV-based detection of analyte-induced Au NP aggregation. Our idea is similar to the recently published work of Zahran and co-workers, who detected 20 ppb atrazine indirectly from the fact that it increased the electrooxidation current in the ASV by aggregation of cit-Ag
Our method involves interactions between Cr\(^{3+}\)/melamine and cit-Au NPs followed by fast electrophoretic deposition (EPD) of the Au NPs, and finally ASV to determine the analyte concentration based on the peak current or peak oxidation potential. The partial charge neutralization and/or aggregation effect of Au NPs due to the presence of Cr\(^{3+}\) (having chelating nature) and melamine (having H-bonding ability) in colloidal Au NPs makes the detection possible. EPD is a unique aspect of this detection scheme compared to Zahran and co-workers and other previous works.\(^{86, 192}\) EPD quickly concentrates the Au NPs on the electrode surface, where interactions between the cit-Au NPs and analyte can alter the electrophoretic mobility of the Au NPs. This in turn alters the ASV peak potential and/or peak current. In either detection mode (potential or current), EPD is a critical component that has not been exploited previously.

### 7.2. RESULTS AND DISCUSSION

#### 7.2.1. Detection Strategy

The main goal of this work was to develop a simple, cheap, and sensitive electrochemical method that combines selective interactions between analyte and ligand-stabilized metal NPs with electrophoretic deposition (EPD) and anodic stripping voltammetry (ASV) analysis. Figure 7.1 shows the general analysis strategy. Step 1 involves the synthesis of ligand-stabilized Au nanoparticles (NPs) and step 2 requires mixing of the Au NPs with the analyte of interest, where there is some selective affinity between the analyte and ligand stabilizer. In this work, citrate-stabilized Au NPs (cit-Au NPs) selectively bind to Cr\(^{3+}\) ions or melamine as the analyte.\(^{332, 336}\) In step 3, we perform EPD of the cit-Au NPs in the absence and presence of various analyte
concentrations under defined EPD conditions (constant potential and time) using the method of Allen et al., who recently described the EPD of cit-Au NPs on to the glass/ITO surface in the presence of hydroquinone (HQ). The number of cit-Au NPs deposited will depend on the electrophoretic mobility, which depends on the charge/size ratio of the cit-Au NPs. The negative charge can be decreased by neutralizing the carboxylate groups of citrate with Cr$^{3+}$ and melamine (NH$_3^+$ groups) and the size can potentially be increased by Cr$^{3+}$- or melamine-induced aggregation of the Au NPs. Both processes would lead to reduced electrophoretic mobility, leading to a lower amount of deposited cit-Au NPs onto the glass/ITO electrode surface. Finally, in step 4 we use ASV to determine the amount of cit-Au NPs deposited by EPD by integrating the charge under the peak corresponding to Au oxidation by Br$^-$ according to equations 7.1-7.2.

$$\text{Au}^0 + 4\text{Br}^- \rightarrow \text{AuBr}_4^- + 3e^- (E^0 = 0.85 \text{ V vs NHE})$$ (7.1)
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\[ \text{Au}^0 + 2\text{Br}^- \rightarrow \text{AuBr}_2^- + e^- \quad (E^0 = 0.96 \text{ V vs NHE}) \]  

(7.2)

Based on the proposed mechanism, the integrated charge of the Au oxidation peak in ASV should decrease as the analyte concentration increases. The analytical signal, change in peak charge (\( \Delta Q_{\text{peak}} = Q_{\text{blank}} - Q_{\text{analyte}} \), is plotted versus the analyte concentration. The peak oxidation potential (\( E_p \)) could also shift to higher potentials if the analyte induces significant aggregation of Au NPs, according to our previous work\textsuperscript{15} and recent report by Zahran \textit{et al.}\textsuperscript{192}

### 7.2.2. Electrophoretic Deposition (EPD) of Au NPs

After the successful synthesis of different sized Au NPs, 50 µL of five different concentrations (0.010, 0.050, 0.10, 0.20 and 0.30 mM) of Cr\textsuperscript{3+} were added to 5 mL of as-synthesized 4.1 and 15.1 nm Au NPs so that the final Cr\textsuperscript{3+} concentrations were 5, 25, 50, 100, and 150 ppb, respectively. After addition of Cr\textsuperscript{3+} solution to the Au NPs, the resulting solution sat for 1 hr. A blank sample for both Au NPs was prepared by just adding 50 µL of nanopure water into the 5 mL of as prepared solution of Au NPs. A solution mixture for EPD was then prepared by mixing 2 mL of the Cr\textsuperscript{3+}/Au NP solution, 23 mL of nanopure water, and 5 mL of 0.1 M HQ. Next, EPD was performed for 5 min using a CH Instruments (Austin, TX) model CHI660E electrochemical workstation with a 3-electrode set-up, including the cleaned glass/ITO as the working electrode (dimension = 1.2 cm x 0.7 cm), a Pt wire as the counter electrode, and Ag/AgCl as reference electrode. For 15.1 nm Au NPs, the EPD potential was set at 1.2 V vs Ag/AgCl while it was 1.0 V for 4.1 nm Au NPs. After EPD, the glass/ITO electrode was thoroughly rinsed with nanopure water and dried with N\textsubscript{2}. For melamine, five different aqueous solutions of melamine with concentrations of 0.0080, 0.020, 0.040,
0.080 and 0.12 mM were prepared. Then, 50 µL of each was added to 5 mL of nanopure water to obtain final concentrations of 10, 25, 50, 100, and 150 ppb, respectively. Melamine binds strongly to citrate-coated Au NPs due to the presence of three -NH₂ groups resulting in partial surface charge neutralization and/or aggregation of the Au NPs. Experiments for EPD of Au-melamine were performed under similar conditions as in the case of Au-Cr³⁺ where the EPD solution consisted of 2 mL of the melamine/Au NPs solution, 23 mL of nanopure water, and 5 mL of 0.1 M HQ. EPD was performed at the same potential and time as for Cr³⁺ detection.

7.2.3. Cr³⁺ Detection. Figure 7.2A shows ASVs of 15.1 nm cit-Au NPs obtained after exposure to different concentrations of Cr³⁺ for 1 hr followed by EPD at 1.2 V (vs. Ag/AgCl) for 5 min as described above. The peak oxidation potential (Eₚ) at 0.78 V is due to Au oxidative dissolution by Br⁻. The peak current and integrated charge under the peak clearly decreases as the concentration of Cr³⁺ increases as expected based on the potential mechanisms already described. The average charge under the peak for 0 ppb Cr³⁺ was 47.8 ± 1.4 µC while that with 5, 25, 50, 100, and 150 ppb Cr³⁺ was 43.1 ± 3.2, 36.5 ± 1.8, 32.4 ± 2.6, 25.9 ± 2.2, and 17.9 ± 2.0 µC, respectively. We believe the signal is dominated by Cr³⁺ neutralization of citrate as opposed to Cr³⁺-induced aggregation since the Eₚ does not change dramatically. Alternatively, the cit-Au NPs may aggregate with spacing between the Au NPs, where the surface area-to-volume ratio (SA/V) of the Au NPs does not change significantly. The binding event occurs due to the chelating nature of Cr³⁺, where a pair of Au NPs can be cross linked by a single Cr³⁺ ion via the negatively-charged carboxylate and hydroxyl group. The chelating behavior of Cr³⁺ is highly specific over other positively-charged ions, such as Cu²⁺, Pb²⁺, Fe³⁺, and Al³⁺.
Under identical conditions, we used 4.1 nm cit-Au NPs for the detection of Cr\(^{3+}\). We also found a decrease in peak current and Au oxidative charge with increasing Cr\(^{3+}\) concentration (Figure 7.2B). The oxidative charge was 33.1 ± 1.0, 28.0 ± 1.7, 24.4 ± 2.8, 21.1 ± 1.6, 13.7 ± 2.5 and 7.0 ± 1.5 µC, for 0, 5, 25, 50, and 150 ppb Cr\(^{3+}\), respectively. The response is due to the same mechanism described for 15.1 nm cit-Au NPs.

Table 7.1 displays the individual and average of Au electrooxidation charges obtained from ASV peak integration for 15.1 nm and 4.1 nm diameter cit-Au NPs after EPD in the presence of different concentrations of Cr\(^{3+}\). Figure 7.2C shows the calibration curves plotting the average $\Delta Q_{\text{peak}}$ as a function of Cr\(^{3+}\) concentration using both Au NP sizes. We found a linear dependence with a positive slope, where the $\Delta Q_{\text{peak}}$ increases with increasing Cr\(^{3+}\) concentration with an $R^2$ value of 0.947 and 0.966 for 15.1 and 4.1 nm cit-Au NPs, respectively. The sensitivity, as determined by the slope of the calibration curve,
is 0.19 µC/ppb and 0.17 µC/ppb for 15.1 and 4.1 nm Au NPs, respectively, which are not significantly different. The LOD was estimated by 3s/m, where s is the standard deviation

**Table 7.1.** Integrated charges and peak oxidation potential (E<sub>p</sub>) obtained by the electrooxidation of citrate-coated Au NPs treated with different concentrations of Cr<sup>3+</sup> and melamine followed by EPD on glass/ITO (n=3). Electrooxidation of Au NPs was performed by ASV in 0.01 M KBr plus 0.1 M KClO<sub>4</sub> at a scan rate of 0.01 V/s from 0.0 to 1.2 V vs Ag/AgCl.

<table>
<thead>
<tr>
<th>Cr&lt;sup&gt;3+&lt;/sup&gt; (ppb)</th>
<th>4.1 nm</th>
<th>15.1 nm</th>
<th>Melamine</th>
<th>4.1 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au charge (µC)</td>
<td>Av ± S.D. (µC)</td>
<td>E&lt;sub&gt;p&lt;/sub&gt; (V)</td>
<td>Au charge (µC)</td>
</tr>
<tr>
<td>0</td>
<td>34.2</td>
<td>33.1 ± 1.0</td>
<td>0.72</td>
<td>48.1</td>
</tr>
<tr>
<td>5</td>
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<td>28.0 ± 1.7</td>
<td>0.71</td>
<td>43.1</td>
</tr>
<tr>
<td>25</td>
<td>21.2</td>
<td>24.4 ± 2.8</td>
<td>0.69</td>
<td>37.7</td>
</tr>
<tr>
<td>50</td>
<td>20.5</td>
<td>21.1 ± 1.6</td>
<td>0.71</td>
<td>34.8</td>
</tr>
<tr>
<td>100</td>
<td>14.8</td>
<td>13.6 ± 2.5</td>
<td>0.73</td>
<td>28.1</td>
</tr>
<tr>
<td>150</td>
<td>7.09</td>
<td>7.0 ± 1.5</td>
<td>0.73</td>
<td>15.9</td>
</tr>
</tbody>
</table>
of the blank sample and \( m \) is the slope of the line of best fit. The limit of detection (LOD) was found to be 21.1 ppb for 15.1 nm Au NPs and 16.0 ppb for 4.1 nm Au NPs, which are also very similar. The EPA recommended level of total Cr in drinking water must be below 100 ppb in order to be safe, showing that this method is capable of detection below that limit.\(^{344}\)

We compared the EPD-ASV method to UV-Vis spectroscopy for \( \text{Cr}^{3+} \) detection by monitoring the change in the wavelength of maximum absorbance of the LSPR peak of the Au NPs in the presence of different concentrations of \( \text{Cr}^{3+} \). For 15.1 nm Au NPs (Figure 7.3A), we observed a variation in peak absorbance at \( \sim 518 \) nm for different \( \text{Cr}^{3+} \) concentration (details in Table 7.2). The absorbance was 0.499 ± 0.016, 0.482 ± 0.053, and 0.493 ± 0.023 for 0, 100, and 150 ppb of \( \text{Cr}^{3+} \), respectively. This very small change in absorbance was not statistically significant for analysis considering the variability. However, a small shoulder peak on the UV-Vis spectra was observed with an increase in \( \text{Cr}^{3+} \) concentration in the wavelength range from 550 nm to 900 nm. We therefore constructed a calibration curve of peak absorbance at 650 nm versus \( \text{Cr}^{3+} \) concentrations (Figure 7.3D, blue plot), which gave a sensitivity of 0.00069 a.u./ppb and LOD of 22.2 ppb for the 15.1 nm Au NPs. We also monitored the UV-Vis spectra of 4.1 nm Au NPs with varying \( \text{Cr}^{3+} \) concentration (Figure 7.3). A small decrease in peak absorbance occurred at 505 nm with increasing \( \text{Cr}^{3+} \) concentration, which was insignificant as in the case of 15.1 nm Au NPs. Figure 7.3C shows a calibration curve of \( \Delta A_{505} \) as a function of \( \text{Cr}^{3+} \) concentration, which had a sensitivity of \( \sim 0.00058 \) a.u./ppb and calculated LOD of 39.3 ppb. Similarly, we plotted the peak absorbance at 650 nm for 4.1 nm Au NPs as a function of \( \text{Cr}^{3+} \) concentration (Figure 7.3D, red plot), which showed a sensitivity of 0.00048
a.u./ppb and LOD of 29.4 ppb. The sensitivity and LOD for the EPD-ASV measurement was slightly better, but comparable with the UV-Vis methods.  

Table 7.2. UV-Vis absorbance (Abs, a.u.) of citrate-coated 4.1 and 15.1 nm Au NPs at different wavelength treated with different concentrations of Cr$^{3+}$ (n=3). Averages (Av) with standard deviations (S.D.) are provided in each case.

| Cr$^{3+}$ Conc. (ppb) | 4.1 nm | | | 15.1 nm | | |
|---|---|---|---|---|---|
| | At 505 nm | At 650 nm | At 505 nm | At 650 nm | At 505 nm | At 650 nm |
| | Abs | Av Abs ± S.D. | Abs | Av Abs ± S.D. | Abs | Av Abs ± S.D. | Abs | Av Abs ± S.D. |
| 0 | 0.321 | 0.329 ± 0.00 | 0.050 | 0.046 ± 0.00 | 0.517 | 0.499 ± 0.016 | 0.049 | 0.046 ± 0.005 |
| 5 | 0.322 | 0.322 ± 0.00 | 0.050 | 0.053 ± 0.00 | 0.478 | 0.484 ± 0.007 | 0.045 | 0.045 ± 0.003 |
| 25 | 0.313 | 0.308 ± 0.009 | 0.077 | 0.073 ± 0.003 | 0.483 | 0.470 ± 0.012 | 0.064 | 0.066 ± 0.002 |
| 50 | 0.286 | 0.278 ± 0.007 | 0.094 | 0.092 ± 0.004 | 0.476 | 0.482 ± 0.005 | 0.095 | 0.090 ± 0.005 |
| 100 | 0.283 | 0.271 ± 0.011 | 0.172 | 0.169 ± 0.004 | 0.466 | 0.469 ± 0.009 | 0.112 | 0.117 ± 0.004 |
| 150 | 0.253 | 0.245 ± 0.011 | 0.189 | 0.178 ± 0.009 | 0.495 | 0.493 ± 0.023 | 0.151 | 0.146 ± 0.004 |
**Figure 7.3.** UV-Vis of 15.1 nm (A) and 4.1 nm (B) Au NPs treated with different Cr\(^{3+}\) concentration. Calibration curve of deviation in UV-Vis absorbance at 505 nm of 4.1 nm Au NPs with different Cr\(^{3+}\) concentration compared to sample with no Cr\(^{3+}\) (ΔA) versus Cr\(^{3+}\) concentration (C) and calibration curve of deviation in UV-Vis absorbance at 650 nm of 15.1 nm (blue) and 4.1 nm (red) Au NPs at different Cr\(^{3+}\) concentration compared to sample with no Cr\(^{3+}\) versus Cr\(^{3+}\) concentration (D).
7.2.4. **Melamine Detection.** We next applied the EPD-ASV method to the detection of melamine, a biologically-relevant molecule, using 4.1 nm diameter cit-Au NPs. We observed that the area under the ASV peak decreased with increasing melamine concentration (Figure 7.4A) as it did with Cr\(^{3+}\). Interestingly, the peak oxidation potential also increased to some extent with increasing melamine concentration beyond 50 ppb (Figure 7.4A), suggesting that there was small aggregation of the cit-Au NPs in the presence of melamine. This leads to a positive shift in the oxidation potential due to a reduced surface area-to-volume ratio (SA/V) of the cit-Au NPs after aggregation.\(^4\), \(^15\) Binding with Cr\(^{3+}\), on the other hand, does not seem to alter the SA/V of the Au NPs since the peak potential did not change significantly. The three NH\(_2\) groups in melamine interact with the cit-Au NPs, causing the dissociation of citrate ions from the surface of Au NPs, leading to aggregation with close Au-Au NP contacts.\(^3\)\(^4\)\(^5\) The extent of aggregation and citrate charge neutralization depends on the concentration of melamine, leading to a decrease in the amount of Au NPs deposited by EPD with increasing analyte concentration as determined by ASV. Figure 7.4B shows a calibration curve of \(\Delta Q_{\text{peak}}\) as a function of melamine concentration, which has a \(R^2\) value of 0.976 and LOD of 45.7 ppb melamine. This is significantly lower than the EPA recommended lower limit of melamine (2.5 ppm) required for safe food and water.\(^206\)

We next monitored the variation in UV-Vis absorbance of 4.1 nm Au NPs with varying melamine concentration (Figure 7.4C). We observed a change in peak absorbance decrease at 505 nm and absorbance increase at 650 nm (details of the absorbance values in Table 7.3). A plot of \(\Delta A_{650}\) of 4.1 nm Au NPs against melamine concentration is shown in Figure 7.4D. Based on the curve, we calculated a sensitivity of 0.00096 a.u./ppb and
LOD of 40.6 ppb. The LOD of melamine is comparable to both the EPD-ASV and UV-vis methods.

Figure 7.4. ASV signature of 4.1 nm Au NPs treated with different melamine concentration followed by EPD (A) and calibration curve of deviation in Au stripping charges from sample with no melamine using ASV of 4.1 nm Au NPs ($\Delta Q$) versus melamine concentration (B). UV-Vis of 4.1 nm Au NPs treated with different melamine concentration (C) and calibration curve of deviation in UV-Vis absorbance of 4.1 nm Au NPs at 650 nm compared to sample with no melamine ($\Delta A$) versus melamine concentration (D).
Table 7.3. UV-Vis absorbance (Abs, a.u.) of citrate-coated 4.1 nm Au NPs at different wavelengths treated with different concentrations of melamine (n=3). Averages (Av) with standard deviations (S.D.) are provided in each case.

<table>
<thead>
<tr>
<th>Melamine Conc. (ppb)</th>
<th>4.1 nm</th>
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<tr>
<td></td>
<td>At 505 nm</td>
<td>Av Abs ± S.D.</td>
<td>At 650 nm</td>
<td>Av Abs ± S.D.</td>
<td>At 505 nm</td>
<td>Av Abs ± S.D.</td>
<td>At 650 nm</td>
<td>Av Abs ± S.D.</td>
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<tr>
<td>0</td>
<td>0.462 ± 0.016</td>
<td>0.071 ± 0.0021</td>
<td>0.466 ± 0.016</td>
<td>0.072 ± 0.0021</td>
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<tr>
<td>10</td>
<td>0.426 ± 0.005</td>
<td>0.078 ± 0.001</td>
<td>0.418 ± 0.005</td>
<td>0.078 ± 0.001</td>
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<tr>
<td>25</td>
<td>0.422 ± 0.006</td>
<td>0.079 ± 0.001</td>
<td>0.411 ± 0.006</td>
<td>0.079 ± 0.001</td>
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<tr>
<td>50</td>
<td>0.480 ± 0.023</td>
<td>0.089 ± 0.014</td>
<td>0.432 ± 0.023</td>
<td>0.112 ± 0.014</td>
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<tr>
<td>100</td>
<td>0.521 ± 0.046</td>
<td>0.129 ± 0.007</td>
<td>0.429 ± 0.046</td>
<td>0.123 ± 0.007</td>
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<tr>
<td>150</td>
<td>0.437 ± 0.004</td>
<td>0.217 ± 0.006</td>
<td>0.440 ± 0.004</td>
<td>0.212 ± 0.006</td>
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7.2.5. Increasing Limit of Detection (LOD) of the Method. Finally, we further increased the limit of detection of Cr$^{3+}$ by first 10-fold diluting the as-prepared 4.1 nm Au NPs followed by addition of 50 µL of 0.002 mM Cr$^{3+}$ (resulting 1 ppb Cr$^{3+}$ concentration in the resulting solution) and subsequent 5 min EPD and ASV. This way, we increased the Cr/Au ratio in the solution 10 times with 1 ppb of Cr$^{3+}$. Under identical conditions, the charges of Au obtained from ASV in presence of 1 ppb of Cr$^{3+}$ was found to be 25.4 ± 1.4 µC while that without Cr$^{3+}$ was 31.1 ± 1.3 µC, which are statistically different. Our result shows that detection of Cr$^{3+}$ even down to 1 ppb level is possible by this approach which is nearly 10-fold less than the one discussed earlier. This demonstrates the success of enhancement in detection limit in our method by simply increasing the Cr/Au ratio. Lowering the concentration of Au NPs relative to the Cr$^{3+}$ promotes greater interaction of Cr$^{3+}$ with Au NPs at lower Cr$^{3+}$ concentration. The detection limit could be further increased by optimization of the experimental conditions such as further alteration of Cr/Au ratio, Au NPs-analyte binding time and/or EPD time.

7.3. CONCLUSIONS

We described a unique electrochemical method for the detection of Cr$^{3+}$ and melamine by selective binding of analyte to cit-Au NPs followed by EPD of the cit-Au NPs and stripping of the Au by ASV. The ASV peak charge decreases linearly with increasing concentration based on reduced cit-Au NP electrophoretic mobility upon analyte binding due to reduced charge of the NPs or increased size caused by analyte-induced aggregation. A third possible mechanism is that analyte binding lowers the catalytic activity of the Au NPs towards oxidation of HQ which in turn decreases the extent of Au
deposited on the electrode during EPD. The ASV peak potential may also increase upon analyte-induced binding and aggregation, as observed slightly for melamine, but this is not extensive enough to be used as the analytical signal. Importantly, the citrate ligands show high selectivity for Cr\textsuperscript{3+} ions, the EPD is reproducible, and the change in peak charge with concentration is highly sensitive. The limit of detection is in the 10-50 ppb range for both Cr\textsuperscript{3+} and melamine, which is sufficient for environmental applications. The analysis takes about 1 h to complete with similar analytical merits as UV-Vis or fluorescence-based detection utilizing Au and Ag NPs. Our method has the potential advantage of being useful for non-plasmonic metal NPs and metal NPs of 2 nm and below, which do not exhibit a LSPR band. Further optimization is also possible to improve the LOD, which could include longer times for analyte binding and EPD.
CHAPTER VIII

SUMMARY, CONCLUSIONS, AND FUTURE DIRECTIONS

8.1. SUMMARY AND CONCLUSIONS

8.1.1. Stability Studies. This dissertation describes research focused on 1) the use of ASV and CV for the size-dependent ripening and stability of Au, AuAg, and AuCu NPs under a range of electrochemical, thermal, and electrocatalytic conditions. It also describes the use of voltammetry, coulometry, and spectroelectrochemistry to study the size-dependent stability against electrooxidation for Au NPs stabilized with alkanethiolate self-assembled monolayers as compared to weaker citrate, phosphine, and phosphonium stabilizers.

One of the main themes of this dissertation was to use electrochemical size analysis, including ASV and electrochemical SA/V measurements to study the ripening behavior of different-sized Au NPs immobilized onto the electrode surface. We carried out electrochemical and thermal ripening (or thermal sintering) studies. Chapter III describes the size-dependent electrochemical ripening of 1.6, 4.1 and 15.1 nm average diameter Au NPs. The positive shift in \( E_p \) in the ASV and the decrease in the electrochemically-measured SA/V provided a clear indicator of an Au NP size increase occurring during repetitive electrochemical surface oxidation-reduction cycling in acid. We observed a size-dependent rate of transformation for the NPs upon electrochemical
cycling in acidic solution up to 1000 times, where smaller sized NPs displayed a faster size increase compared to larger ones. Based on the rate of change in SA/V, the ripening rate was found to be higher within first 200 cycles, with an increase in size of the NPs by 1.44%, 0.53%, and 0.46% per cycle for 1.6, 4.1, and 15.1 nm Au NPs, respectively. Further, the NPs were found to increase in size by a factor of 7.5, 3.5, and 2.6 for 1.6, 4.1, and 15.1 nm Au NPs after 1000 cycles, confirming their size-dependent ripening behavior. The effect of cycling scan rate, NP coverage on the electrode, and potential holding provide valuable insights about the electrochemical ripening process. The NPs undergo electrochemical Ostwald ripening, which requires the full oxidation and reduction cycling and is enhanced by higher NP coverage and smaller sized NPs.

Chapter IV describes the low temperature thermal sintering behavior of weakly-stabilized 0.9, 1.6, 4.1, and 15.1 nm diameter Au NPs. Au NPs that showed a single peak for electrooxidation before heating started to show a second peak with more positive $E_p$, indicating that some of the NPs grew into bigger sizes. The peak current at the higher $E_p$ was found to increase continuously with increased heating time and temperature. A plot of the peak current ratio at higher $E_p$ to that at lower $E_p$ ($I_{p,f}/I_{p,i}$) against temperature was then utilized to determine the sintering transition temperature for 0.9, 1.6, and 4.1 nm diameter Au NPs, defined as the inflection point of the sigmoidal-shaped curve. From this, the onset of sintering as well as the sintering transition temperature of the different-sized NPs were estimated. The transition temperature of 0.9, 1.6, and 4.1 nm diameter Au NPs was 109, 132, and 509 °C, respectively, showing some agreement with the theoretical size-dependent melting points of Au NPs reported in the literature. This provides another potential application of ASV in the characterization of ultra-small metal NPs/nanoclusters directly on electrode surfaces, which is very difficult by microscopy or other methods of
analysis but very important in terms of gaining a full understanding of metal size stability. Also, the electrochemically determined SA/V of the NPs decreases with an increase in temperature and heating time, consistent with an increase in size upon thermal sintering. A plot of size versus heating temperature shows that a dramatic size transformation occurs in the temperature range of 100-150 °C for 1.6 nm NPs while 4.1 nm and 15.1 nm Au NPs are stable up to 400 °C. Scanning electron microscopy (SEM) images confirm the electrochemical and UV-Vis size analysis, providing further confirmation of our electrochemical results.

Chapter V describes the effect of a strong ligand stabilizer on the size-dependent stability of Au NPs against bromide-induced electrooxidation (dissolution). A comparison of the size-dependent oxidation behavior of weakly-stabilized citrate-coated 4.1, 15.1, and 50.3 nm diameter Au NPs with those that were coated with alkanethiolate self-assembled monolayers (SAMs) showed that the strongly-stabilized alkanethiolate Au NPs had a reverse size-dependent oxidation stability compared to the weakly-stabilized citrate-coated Au NPs. For NPs treated with alkanethiolate SAMs exposed to conditions where electrochemical dissolution in Br⁻-containing acidic electrolyte occurs, the smaller Au NPs were more stable than the larger Au NPs (4.1 > 15.1 > 50.3 nm). For citrate-stabilized NPs, the stability trend is the opposite (50.3 > 15.1 > 4.1 nm). CV showed that the oxidative stripping of Au by Br⁻ is hindered significantly for all Au NPs when coated with butanethiolate (C4S), decanethiolate (C10S), and hexadecanethiolate (C16S) ligands. The resistance to oxidation was found to increase with increasing alkanethiolate chainlength. When comparing sizes, as mentioned above, the 4.1 nm thiolate-coated Au NPs showed greater resistance to oxidative stripping compared to the 15.1 nm and 50.3 nm diameter Au
NPs coated with the same thiols. Chronocoulometery (CC) experiments show that 15.1 and 50.3 nm diameter thiol-coated Au NPs oxidize to a much greater extent in acidic Br\(^-\) within 1000 s at 1.0 V vs Ag/AgCl compared to 4.1 nm Au NPs. These results are opposite of the trend as produced by weakly-stabilized citrate-coated Au NPs, where the smaller sized NPs undergo electrooxidation more easily than the bigger ones.

8.1.2. **Atomic Level Doping and Reactivity.** In Chapter VI, we studied the size and electrocatalytic stability of electrode-confined AuAg and AuCu NPs prepared by atomic level doping through AGR reaction. The amount of Cu and Ag incorporated into the different-sized Au NPs/NCs was varied from ~70 to ~1% as determined by ASV. We discovered that Au, Cu, and Ag in the resulting nanostructures maintain size stability after multiple replacement cycles on the same NPs/NCs. This is evidenced by a constant \(E_p\) for Au in the ASV. This indicates that low level doping of Ag and Cu is possible on to sub-2 nm diameter Au NPs without significantly altering the structure of the clusters. No size ripening of Au NPs occurred during low level doping even for multiple cycles of Ag or Cu exchange.

The peak current for the oxygen reduction reaction (ORR) in 0.1 M KOH increased by a factor of ~7 when the 1.6 nm Au NPs were doped with 1% of Ag by AGR, which interestingly did not increase further with more Ag. This suggests that Ag sites created at low doping levels act as the most catalytic sites on the NCs. The onset potential for ORR was ~0.75 V vs RHE. Also, the ORR activity of AuAg NCs remained stable for at least 100 cycles while the activity degraded significantly in the case of pure Ag NPs. The improved ORR activity and stability of AuAg NCs prepared by AGR demonstrates the ability to engineer sub-2 nm Au NCs for potential applications. ASV and CV are critical
in characterizing the AGR reactivity, metal composition, size stability, and catalytic stability in this study.

8.1.3. Electrochemical Sensing. We used the combination of Au NP-analyte binding, EPD, and ASV of Au NPs for the selective and sensitive electrochemical detection of trivalent chromium and melamine in aqueous medium as discussed in Chapter VII. The EPD of citrate-stabilized Au NPs occurred on indium tin oxide (ITO)-coated glass electrodes by the release of protons upon electrochemical oxidation of hydroquinone (HQ). The binding of Cr$^{3+}$ to the citrate stabilizer surrounding the Au NPs inhibits the EPD either by inducing aggregation of the Au NPs or reducing the negative charge of the Au NPs, which could lower the effective NP concentration of the Au NPs for the former or the electrophoretic mobility for both. The lower oxidation charge in the ASV of Au accordingly acts as a signal for Cr$^{3+}$. The amount of Au measured by ASV decreased linearly with increasing Cr$^{3+}$ with a limit of detection (LOD) of 21.1 ppb and 16.0 ppb when using 15.1 and 4.1 nm Au NPs, respectively. The amount of Au also decreased linearly with increasing melamine concentration with a LOD of 45.7 ppb with 4.1 nm Au NPs, which is below the EPA recommended level. Further optimization led to 1 ppb level detection limit of Cr$^{3+}$ with potential further optimization. Our combination of EPD and ASV of Au NPs is an advancement over optical methods of detection and are potentially useful for the detection of many biomolecules and inorganic species and hence provides a new sensing strategy in electroanalytical chemistry.

All these studies clearly demonstrate that electrochemical methods of analysis (ASV, CV, CC, and EPD) are powerful tools to study the ripening behavior of metal NPs, stability against oxidation in the presence of various stabilizing agents, and reactivity of
ultra-small Au NPs towards galvanic replacement. We also demonstrated electrochemical sensing of Cr(III) and melamine using EPD and ASV of citrate-stabilized Au NPs by a unique strategy. Since these studies have been carried out on electrode-attached NPs, their behavior is relevant to what is expected in real-life applications. This provides fundamental insights into NP behavior during their applications, allowing judgements to be made about their suitability in terms of stability when considering their practical use. Importantly, the electrochemical methods used in this dissertation are simple, cheap, fast, and sensitive. They are applicable to a wide-range of metallic NPs and easily employed by any lab, requiring only a potentiostat.

8.2. FUTURE DIRECTIONS

There are several interesting directions that could be explored in follow up studies of this dissertation work. Our electrochemical stability studies discussed in Chapter III could be extended to < 1 nm diameter metal nanoclusters, termed atomically-precise nanoclusters (APNCs), which are often better candidates for catalytic and sensing applications. The synthesis of thiol- or phosphine-coated Au, Ag, and Pd NPs or NCs are available in the literature. These metals and a variety of other metal nanostructures with different ligand stabilizers, obtained through ligand replacement reactions, could be synthesized and tested in the laboratory. It would be interesting to study the effect of shape, size, and more variety of ligands on the electrochemical stability of the metal nanostructures. An extensive electrochemical ripening study of these nanoscale metals could be a future study. The ripening study could be further extended to bimetallic NPs, such as CuAu and AuAg, with a low level doing of Cu and Ag. Besides electrochemical
ripening, the thermal ripening/sintering of these metal NPs or NCs could be studied as described in Chapter IV of this dissertation. The effect of ligands on the thermal sintering behavior of metal NPs would be an interesting study in the future. NPs of Cu, Ag, Pd, and Pt, which have potential catalytic, sensing and engineering applications, could be studied to determine their sintering temperature and melting point by our method of analysis. These types of studies on ultra-small metal nanostructures are tedious, complicated, and often impossible by microscopy or other methods of analysis. The great benefit of electrochemistry is the simplicity, low cost, and speed.

The size-dependent electrooxidation behavior of Au NPs described in Chapter V of this dissertation provides valuable information related to enhancing the stability of ultra-small metal NPs. Since we used straight chain alkanethiols for this study, the study could be extended to branched chain and aromatic thiols. This would reveal whether dense ligand packing is necessary for stability and what extent of metal-S bonding is needed for high stability. If high stability can be achieved with low ligand density, one might be able to find conditions where the NPs are highly stable and catalytically active. Besides thiols, a comparison of the stability of metal NPs stabilized with amine, phosphine and several other surfactants is also possible. This would provide ideas about how to maintain NP stability while also retaining high catalytic activity over long periods of time. Besides Au, this strategy could be extended to other metal NPs, such as Pt, Ag, and Pd. Thin film applications could be enabled by improving NP stability using the methods developed in this dissertation.

Some important future work could be explored on the anti-galvanic replacement (AGR) of Au NPs with several other metals in addition to Cu and Ag as discussed in
Chapter VI of this dissertation. Besides 4.1 nm and 1.6 nm Au, the galvanic exchange could be explored with smaller atomically precise metal nanoclusters such as Au$_{60}$, Au$_{25}$ and Au$_{11}$, whose synthetic protocols are available in the literature. The choice of other hetero metals for AGR could be Cu, Pd, Co, Ni, and Fe. The metal replacement reaction could be carried out by direct AGR or though underpotential deposition of a second metal followed by galvanic exchange or AGR. Since Cu is reported to be a good catalyst for electrochemical CO$_2$ reduction, it would be interesting to perform single or few atom doping of Cu onto Au clusters via AGR and measure the electrocatalytic activity for CO$_2$ reduction. The CO$_2$ reduction products could be analyzed by gas chromatography-mass spectrometry or nuclear magnetic resonance (NMR) spectroscopy. By varying the composition of Cu in AuCu nanoalloy clusters via AGR and analyzing the composition by ASV, it is possible to correlate the amount of Cu and possible Cu binding locations with electrocatalytic behavior. Similarly, doping of Pd onto Au nanoclusters would likely produce a significant improvement in the hydrogen evolution reaction (HER). It would again be interesting to determine the effect of doping level and location on the electrocatalytic activity. Electrochemical characterization would be a good start but other more sensitive methods of atomic level analysis would also be required.

The strategy for sensing Cr and melamine described in Chapter VII could be extended to many other biomolecules, such as leucine, isoleucine, lysine, and dopamine. The generality of the method and suitability for non-plasmonic Au NPs could be very useful for sensing a variety of molecules with a much lower limit of detection and higher sensitivity. The analytical parameters could be further improved by varying the size of Au NPs, analyte/Au NPs concentration ratio, Au NPs-analyte binding time, EPD time, and/or
combination of those. Overall, our detection method opens up a completely new avenue for sensing of different inorganic ions and biological species with high analytical interest simply by combination of EPD and ASV of Au NPs upon treatment with the analytes. The main criteria is that the analyte has to have some selective binding interaction with the Au NPs and the binding has to alter the EPD of the Au NPs. As mentioned, the EPD and ASV acts as a detector of the analyte-metal NP binding interaction but does not require spectroscopy, so it does not require the metal NPs to be fluorescent or plasmonic. An even more sensitive approach than demonstrated might be one where the analyte-metal NP binding interaction improves EPD by making the Au NPs more highly charged.

Clearly there are many possibilities for further electrochemical studies of metal NPs/NCs related to their stability, reactivity, electrocatalysis, and potential sensing applications. These studies are directly carried out by attaching the metal nanostructures onto the electrode surface of interest, which mimics their real-life conditions. In addition to the analysis occurring under real conditions, the simplicity of operation, cost-effectiveness, and high sensitivity of the electroanalytical methods described in this dissertation make it highly likely that these methods will be generally applied to future studies in nanoelectrochemistry, nanomaterials science, and nanotechnology in general.
REFERENCES

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APPENDIX

LIST OF ACRONYMS AND ABBREVIATIONS

AAS: Atomic absorption spectroscopy
AGR: Anti-galvanic replacement
APNCs: Atomically-precise nanoclusters
APTES: 3-(Aminopropyl) triethoxysilane
ASV: Anodic stripping voltammetry
CA: Chronoamperometry
CC: Chronocoulometry
CE: Counter electrode
CV: Cyclic voltammetry
DLS: Dynamic light scattering
DPASV: Differential pulse anodic stripping voltammetry
DPV: Differential pulse voltammetry
DSC: Differential scanning calorimetry
ECD: Electrochemical deposition
ECSTM: Electrochemical scanning tunneling microscopy
EDS: Energy dispersive spectroscopy
EPD: Electrophoretic deposition
FESEM: Field emission scanning electron microscope
FT-IR: Fourier transfer infrared spectroscopy
HER: Hydrogen evolution reaction
HMM: Homogeneous melting hypothesis
HQ: Hydroquinone
ICP-MS: Inductively coupled-plasma mass spectrometry
IPA: Isopropanol
ITO: Indium tin oxide
LNG: Liquid nucleation and growth
LOD: Limit of detection
LSM: Liquid skin melting
LSPR: Localized surface plasmon resonance
NCs: Nanoclusters
NMR: Nuclear magnetic resonance
NPs: Nanoparticles
NSs: Nanospheres
ORR: Oxygen reduction reaction
ppb: Parts per billion
ppm: Parts per million
RE: Reference electrode
SACs: Single atom catalysts
SAMs: Self-assembled monolayers
SD: Standard deviation
SEM: Scanning electron microscopy
STEM: Scanning transmission electron microscopy
STM: Scanning tunneling microscopy
TEM: Transmission electron microscopy
TGA: Thermogravimetric analysis
THPC: Tetrakis(hydroxymethyl) phosphonium chloride
TPPS: Triphenyl phosphine sulphonate
UV-Vis: Ultraviolet-Visible spectroscopy
WE: Working electrode
Size-Dependent Ripening of Gold Nanoparticles through Repetitive Electrochemical Surface Oxidation-Reduction Cycling

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Google scholar link: https://scholar.google.com/citations?user=8gAbhTgAAAAJ&hl=en


12. Mainali, B.P; Zamborini, F.P. “Synthesis of Phosphine Stabilized Au Nanoclusters Containing <5 Atoms” Ongoing Project
13. Mainali, B.P.; Puzhakkaraillah, A. M; Zamborini, F.P. “Ligand Effect on the Anti-Galvanic Replacement of ≤4 nm Diameter Au Nanostructures with Cu and Ag” Ongoing Project

**SCIENTIFIC EXPOSURE**

- Poster Presentation - Pittcon, New Orleans, March 2021.
- Oral Presentation – Graduate Student Regional Research Conference (GSRRC), University of Louisville, Louisville, KY, Feb 2019.
- Poster Presentation – 249th National Meeting of the ACS, Denver, CO, March 2015.

**Summary of Qualifications**

- 5+ years of experience in wet chemical synthesis of nanoscale materials and characterization
- Experience in general electrochemical techniques, scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), transmission electron microscopy (TEM), Raman spectroscopy, ultraviolet-visible spectroscopy (UV-vis), atomic absorption spectroscopy (AAS), IR-spectroscopy, dark field optical microscopy, thermogravimetric analysis (TGA), sputtering, spin coating, X-ray diffraction (XRD), X-ray photoelectron spectroscopy, gas chromatography
- Electrochemistry of nanomaterials for study of stability and reactivity and applications in catalysis and sensing
- *Software*: MS Office Package, Origin Pro, Igor Pro, Sigma Plot Pro, Adobe Photoshop.
• **Leadership skills:** Led several successful projects as a senior graduate student research associate that resulted in peer-reviewed journal publications.

• **Communication skills:** Excellent in both verbal and written communication in English; have experience writing several peer-reviewed journal articles and technical reports; presented several posters and talks at conferences.

### EXPERIENCE

**Research Experience**

Graduate Research Assistant, Department of Chemistry

University of Louisville, Louisville, KY  
Aug 2015 to present

- Chemical synthesis of Au, Ag, Cu, Pd and Pt nanoparticles/nanoclusters and their alloys and characterization by electrochemical techniques (anodic stripping voltammetry, cyclic voltammetry, chronoamperometry, chronocoulometry, rotating disc electrode, electrochemical impedance spectroscopy, electrodeposition), UV-vis, SEM, STEM, TEM.

- Electrochemical study on the stability, and electrocatalytic and sensing applications of weakly coated ultra-small metal nanoparticles/nanoclusters and their alloys.

Graduate Teaching and Research Assistant, Department of Chemistry, Middle Tennessee State University, Murfreesboro, TN, Aug 2013 to July 2015

- Synthesis of semiconductor quantum dots (QDs) and characterization, fabrication of core/shell QDs by cation exchange and study of its effect on optical and electronic properties of the QDs.

- Experience in atomic absorption spectroscopy (AAS), X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR), X-ray fluorescence (XRF), FT-IR, schlenk line and glove-box.

- Use of *Sigma plot*, *Origin*, and *Igor pro* for data storage, analysis and visualization.
Teaching Experience

- Mentored several graduate and undergraduate students for research on electrochemistry of metal nanoparticles/nanostructures for several semesters, Department of Chemistry, University of Louisville, Louisville, KY, Fall 2017 till date
- Teaching Assistant: Assisted in introductory level chemistry lab courses for several semesters in the Department of Chemistry at the University of Louisville. August 2017 till date
- Teaching Assistant: Assisted in CHEM 201, CHEM 202, CHEM 210, and CHEM 243 in the Department of Chemistry, Middle Tennessee State University, TN, Aug 2013 to July 2015
- Lecturer: Dhulikhel Medical Institute, Kathmandu University, Kavre, Nepal (responsibilities include working as chemistry department chair, teaching chemistry courses with special topics to the undergraduate students, assigning and grading of homework, quizzes and exams, biannual and annual evaluation, report writing) July 2010 to July 2013
- Lecturer: Chaitanya Multiple Campus, Banepa, Kavre, Nepal (responsibilities include working as science program coordinator, teaching general chemistry courses to the undergraduate students, assigning and grading of homework, quizzes and exams, biannual and annual evaluation, report writing) July 2009 to June 2011

AWARDS

- ‘Dissertation Completion Award’ for Summer 2021, University of Louisville
- ‘Undergraduate Research Mentorship Award’ University of Louisville, Feb 2021
- ‘Student Travel for Best Research Award’, Society for Electroanalytical Chemistry, Pittcon, Chicago, March 2020
- Doctoral student graduate school fellowship and teaching/research assistantship, University of Louisville, August 2015 till date
- Graduate school council travel award from the University of Louisville, 2018, 2020
• Travel award from the American Chemical Society, 70th Southeastern Regional Meeting of the American Chemical Society, Augusta, GA, Oct 2018

• Master student tuition fellowship and research assistantship, Middle Tennessee State University, August 2013 to July 2015

ADDITIONAL ACTIVITIES

• ‘Volunteer-Judge in a Tri-Service Sponsored Competition ‘Junior Science and Humanities Symposium’’ University of Louisville, KY, Jan 2020

• Vice-President: Nepalese Student Association, University of Louisville, 2016 to 2017

• Chair, Department of Chemistry, Dhulikhel Medical Institute, Kathmandu University, Dhulikhel, Kavre, Nepal, 2011 to 2013

• Science Program Co-ordinator, Chaitanya Multiple Campus, Banepa, Kavre, Nepal, 2009 to 2011