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Spectroelectrochemistry of plasmonic nanoantennas

by

Chad P. Byers

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APPROVED, THESIS COMMITTEE

Christy F. Landes, Chair
Associate Professor
Department of Chemistry and Department of Electrical & Computer Engineering

Stephan Link
Associate Professor
Department of Chemistry and Department of Electrical & Computer Engineering

Rafael Verduzco
Louis Owen Assistant Professor
Department of Chemical and Biomolecular Engineering

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ABSTRACT

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The optical properties of metal nanoparticles make them useful in the fundamental study of light-matter interactions at the nanoscale. These nanoparticles can behave as antennas for optical electromagnetic radiation and can be used to investigate nanoscopic processes by measuring the optical spectral response of individual nanoantennas. In this thesis, original research is presented that expands our knowledge and understanding of how plasmonic nanoantennas respond to electrochemical potential control. In addition to minor spectral shifts from charge density tuning, nanoparticle plasmons respond very strongly to potential-controlled chemical reactions at the nanoparticle surface. With this knowledge, nanostructures were engineered to produce desired optical characteristics that are switchable via electrochemistry. The optical responses can then be used to either sense electrochemical processes occurring at the nanoscale or to create desired optical phenomena. Two engineered systems were studied to this end. First, single nanospheres and pairs of closely spaced nanospheres called dimers were placed onto two working electrode substrates and the effects of the substrate on sensitivity
to potential-controlled electroadsorption of sulfate anions was investigated. The most sensitive nanoantenna geometry was then used to develop and demonstrate a single-nanoantenna analog to bulk electrochemistry’s cyclic voltammogram (CV). Using this technique, the single-nanoantenna CV analog was used to detect the potential controlled adsorption and desorption of sulfate, acetate, and perchlorate anions. A simpler intensity-based alternate method was also tested to increase the accessibility and applicability of the single-nanoantenna technique. In another application, a core/shell strategy was employed in which the shell was electrochemically switchable between a semiconductor and a pure metal. This method was employed for both Au nanospheres and dimers. In the case of a dimer fused by an Ag bridge, the bridge was found to be electrochemically switchable between electrically conductive and nonconductive, allowing a change in the plasmonic coupling mechanism using only electrochemical potential control. The scattering spectra of these dimers experienced large changes during this switching process and dynamic measurements allowed the observation of the first in situ switchable and tunable charge transfer plasmon resonance mode. In sum, the work presented in this thesis demonstrates the value of single-nanoantenna spectroelectrochemistry both for fundamental research and application.
I would like to thank my committee members Christy Landes, Stephan Link, and Rafael Verduzco for their help and guidance during my graduate career and in this thesis. I want to thank Christy and Stephan for their years of tutelage and support, and most importantly their challenges to grow as a scientist. I also thank Wei-Shun Chang, Peter Nordlander, and Naomi Halas for their roles as mentors. I have been fortunate to work with many fantastic collaborators. I want to specifically thank Hui Zhang, Ben Hoener, Dayne Swearer, Da Huang, and Bo Shuang for their critical roles in joint projects. Many thanks to the past and present members of the Landes and Link research groups for support, feedback, and for being good friends. I also thank my friends outside of Rice for their support and genuine interest in science and my work.

I want to thank my partner Alina for being a wonderful and loving companion throughout my PhD. For her roles as a sounding board, adviser, and breadwinner, I am eternally grateful. Thank you to my parents Paul and Paula who always encouraged me to pursue my dreams and to keep aiming higher. I want to thank my brother Tim and his wife Val for their support and for hosting many weekend getaways from the city. Finally, I thank my niece Sam and my nephew Will who was born the first week that I came to Rice. Over the past 5 years, he's been a great playmate, huge fan, and since he started his battle with Sanfilippo Syndrome, a major inspiration. I dedicate this thesis to him.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>CV</td>
<td>cyclic voltammogram</td>
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<tr>
<td>CCD</td>
<td>charge coupled device</td>
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<tr>
<td>sRGB</td>
<td>standard Red Green Blue (color space)</td>
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<tr>
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<td>CTP</td>
<td>charge transfer plasmon</td>
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<td>HAADF-STEM</td>
<td>high angle annular dark field scanning transmission electron microscopy</td>
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Chapter 1

Introduction

1.1 Motivation

Metal nanoparticles possess unique optical properties due to their ability to interact with light waves much larger than their physical dimensions. Metal nanoparticles have inadvertently been used by artisans for thousands of years in pigmentation and in the manufacturing of stained glass. The scientific study of the optical properties of metal nanoparticles was pioneered by the great scientist Michael Faraday in the 1850s. The much more recent study and engineering of these optical properties is the subject of the field of plasmonics. Nanoparticles and nanoscopic devices that exhibit plasmonic properties have already been utilized in energy harvesting, medical diagnostics and treatment, and for photodetection. The sensitivity of plasmonic nanoparticles’ optical response to environmental and structural changes has inspired research into nanoscale sensing and optical
modulation in a variety of subfields. One young subfield focuses on the plasmonic response to electrochemical processes occurring at nanoparticle surfaces. The focus of this thesis is the development of plasmonic systems that are highly tunable and sensitive to various electrochemical processes. With these systems, we can not only learn about the fundamental principles of electrochemical plasmon tuning and sensing, but we can also study more complex systems to develop better sensors and novel systems with electrochemically tunable optical properties.

### 1.2 Background

The size and electronic properties of metallic nanoparticles allow special optical properties which are central to this thesis. In this chapter, I will provide a brief overview of these properties with more emphasis given to the properties, mechanisms, and ideas central to the original research presented in Chapters 2 - 4. Specific introductions and background are also included in each chapter.

Electromagnetic antennas now play an integral role in our modern connected world; e.g. over-the-air transmission of television programs, near-blanket cellular phone coverage, and most recently drone warfare. The electromagnetic waves associated with these communication applications are radio waves with wavelengths on the order of a tens to hundreds of centimeters. By comparison, electromagnetic radiation that humans can visually perceive has wavelength several orders of magnitude shorter, just hundreds of nanometers (400 – 700 nm). Analogously to radio antennas, metal antennas for light can also be constructed by
scaling down antenna dimensions by the same ratio.\textsuperscript{7, 11-12} At just tens to hundreds of nanometers in dimension, these structures are called nanoantennas. As in macroscopic antennas, oscillating electric fields of electromagnetic radiation drive electrons in nanoantennas at the same frequency as the incident light. However, due to the extremely small scale, the oscillation of electrons in small nanoantennas is a coherent process.\textsuperscript{14} The coherent oscillation of conduction band electrons is known as a surface plasmon. As its name suggests, the surface plasmon is confined to a surface, specifically the interface at which the real part of the dielectric function changes sign.\textsuperscript{15} A resonance condition can be reached in which the driving electric field matches the natural frequency of oscillating electrons. Beyond this generic surface plasmon resonance condition, the optical and electronic properties of a nanoantenna are determined by the geometric and material properties of the nanoantenna and its local dielectric environment.\textsuperscript{15} Although plasmons couple strongly to incident light, they decay rapidly through various dephasing mechanisms.\textsuperscript{16-21} Hence, the oscillation of electrons can be modeled using the damped driven harmonic (Lorentzian) oscillator model of classical physics.

Most generally, the optical response of any nanoantenna can be fully characterized by solving Maxwell’s equations. Analytical solutions of Maxwell’s equations exist for a small number of relevant plasmonic nanoparticle geometries. The most notable solution is for spheres, known as Mie theory.\textsuperscript{22} Spherically symmetric plasmonic nanoparticles are a powerful tool but represent only a small subset of the “nanoparticle zoo” that has been invented through wet chemistry, photolithography, electron beam lithography, and other techniques, e.g. nanorods,
nanoshells, spiky nanoshells, nanostars, nanocubes, nanoplates, nanorice, nanodumbbells, nanocages, etc. Many of these nanoparticles can be fabricated in a variety or mixture of metals, gold, silver, platinum, copper, palladium, aluminum, etc. The scale of such nanoparticles can range from just a few to hundreds of nanometers.

With so many nanoparticle geometries supporting surface plasmons but so few geometries with analytical solutions, computational numerical methods are used to simulate optoelectronic properties of plasmonic nanoparticles by solving Maxwell’s equations using a variety of computational models and simplifying assumptions. The development of techniques for numerical solution is a challenging and very active field of plasmonics research. With regard to the electromagnetic simulations in this thesis, I performed the Mie theory-based calculations of Chapter 2. All finite element method simulations of Chapter 4 were skillfully executed by my collaborator Dr. Hui Zhang in the Nordlander Nanophotonics Group at Rice University.

Though full-wave electrodynamic simulations capture optoelectronic properties of nanoantennas, numerical solutions sometimes offer little intuition or insight into plasmon resonance modes or the properties thereof. For assemblies of nanoparticles, these properties can be difficult to predict. One model that can bring intuition to complex nanoantenna optical responses is the plasmon hybridization theory. Within this theory, nanoparticle plasmons are treated analogously to molecular electron orbitals in the molecular hybridization theory. In
this way, plasmon resonance modes can be described and predicted as a hybridization of primary plasmon resonance modes. In addition to being a useful framework for naming and visualizing plasmon resonance modes in electronically coupled nanoantennas, the plasmon hybridization theory also provides numerically accurate analytical solutions for a number of nanoantenna geometries. In this thesis, the general ideas and naming conventions of the plasmon hybridization theory are used to describe the plasmon coupling interactions between nanoparticle dimers in the capacitive and conductive electronic coupling regimes as well the interaction between film plasmons and nanosphere plasmons.

Plasmonic nanoparticles in very close proximity exhibit interesting optical properties due to the electronic coupling between the individual nanoantennas. The simplest coupled antenna is the nanoparticle dimer consisting of two neighboring nanospheres. If the spheres are sufficiently close (gap width less than approximately their diameter) but far enough apart to prevent electron tunneling (greater than ~2 nm), the nanospheres are said to be capacitively coupled. In this case, the dipolar plasmon resonance modes interact to produce lower energy bonding modes. If the separation between nanoparticles is decreased such that electrons can tunnel between the nanoparticles, the individual spheres of the dimer no longer remain charge neutral and the optical frequency electric current between the nanoparticles decreases the strength of plasmon hybridization. If the spheres are brought into physical contact or a conductive bridge is produced, optical frequency current can pass between the two nanospheres in a classical manner. This conductive coupling leads to a drastic decrease in plasmon hybridization
between nanoparticle dipoles and leads to the emergence of new plasmon resonance modes.\textsuperscript{31} In this thesis, common names for all capacitive and conductive hybridized plasmon resonance modes are used.

While the plasmonic properties of nanoparticles can be easily designed and manufactured using modern synthetic chemistry techniques or a host of lithographic techniques, the optical properties of such structures typically remain static after fabrication. Post-fabrication control of nanoantenna optical properties is the goal of the active plasmonics research.\textsuperscript{37, 44-50} Tunable plasmonics have found potential applications such as boutique optical surface components, tunable optical filters, and spectrally controllable optical elements for photodetection.\textsuperscript{7-8, 50} The mechanisms for active plasmonic nanoantenna tuning vary considerably by application, but primarily rely on just a few tuning mechanisms. 1) By changing the dielectric properties of the nanoantennas’ surrounding medium, 2) By changing the dielectric properties of the nanoantennas themselves,\textsuperscript{51} and 3) By changing the morphology of the nanoantennas.\textsuperscript{52-54} All three of these tuning mechanisms are used in this thesis, so I will briefly introduce each concept. More detailed introduction and discussion are included as needed in Chapters 2-4.

The dielectric properties of the medium can be changed to affect the plasmonic response of nanoantennas.\textsuperscript{50, 55} This is the simplest and longest understood mechanism, but can be difficult to quickly and reversibly control \textit{in situ}. The local dielectric function dependence was captured in Mie’s sphere solution as the refractive index of the embedding medium. In practice, the local dielectric
function of materials can be changed in a variety of ways. For example, embedding dielectric environments can be replaced by immersing nanoantennas in a solution or by altering the refractive index thereof.\textsuperscript{56} Alternatively, the dielectric function of some solid-state semiconductors can be changed by field effect as in MOSFET devices.\textsuperscript{44, 49} As a final example, the dielectric environment of the nanoantennas can be switched by employing an anisotropic medium along with anisotropic nanoantennas.\textsuperscript{55, 57} In this scheme, optical properties of the nanoantennas can be changed by aligning or anti-aligning the optical axes of the medium and the antenna.\textsuperscript{55, 57}

Tuning of the dielectric properties of nanoantennas themselves has been demonstrated in a variety of ways, the most popular of which has been through charge density tuning.\textsuperscript{58-66} In these methods, the number density of conduction band electrons is increased or decreased using chemical or electrochemical charging schemes. An example of this methodology is presented in Chapter 2. Several authors have predicted that for large changes in free charge density (~10\%), plasmon resonance and scattering intensity should change significantly.\textsuperscript{59, 67-68} In experiment, researchers have struggled to realize broad tunability, primarily due to the physical inability to achieve the enormous changes in free charge density assumed in simulation-based studies.\textsuperscript{69} Electrochemically, changes in charge density are limited by the interfacial capacitance at the nanoparticle/electrolyte interface.\textsuperscript{59} For example, the number density of free electrons for a 50 nm diameter spherical gold nanoparticle in aqueous electrolyte is limited to approximately 0.5\% by the interfacial capacitance achievable by the electric double layer (~ 50 \(\mu F/cm^2\)). This
physical limitation confines the applicability of charge density tuning of optical properties in metal nanoparticles. The use of significantly smaller nanoparticles\textsuperscript{67-69} can overcome this interfacial capacitance limitation by achieving higher fractional charge density changes for a given interfacial capacitance. However, the use of significantly smaller nanoparticles is not compatible with the spectroscopic methods used in this thesis because the scattering cross-section of plasmonic nanoparticles scales with the square of the nanoparticle volume. Alternatively, plasmonic systems with just a few free electrons such as polycyclic aromatic hydrocarbons\textsuperscript{70-71} can entirely avoid the interfacial capacitance limitations. However, small molecule plasmonic systems suffer from short lifetimes and high chemical reactivity.\textsuperscript{71} Despite these challenges, both examples will undoubtedly be hotly investigated in the near future.

In contrast to the small optical effects of charge density tuning, the dielectric properties of nanoparticles themselves can also be changed by chemically altering their material properties and in turn their optoelectronic properties. Changes in chemical identity of all or part of the nanoantenna can be difficult to engineer but can result in very large tunability. In Chapter 4, an example of this strategy is employed by using nanoparticles and nanoparticle assemblies consisting of spherical Au cores with thin conformal Ag shells. The Ag shells were easily converted to AgCl under electrochemical potential control, yielding large optical tunability. Just as in macroscopic materials, the change in oxidation state or chemical identity of materials at the nanoscale also results in changes in a host of
material properties, ranging from density to electrical conductivity. These effects in turn alter the nanoantennas’ optical properties.

Another powerful method for tuning plasmonic nanoantenna spectral properties is to control the coupling strength between adjacent nanoparticles. The capacitive coupling strength between nanoparticle plasmons increases exponentially with decreasing interparticle gap width,\textsuperscript{72} making separation control an attractive tuning method. The active control of gap width has been achieved using multiple methods, affording a variety of control and tunability. In one very clever study and application, Huang and Baumberg arranged 250 nm diameter sphere dimers on a stretchable substrate.\textsuperscript{37} By then stretching the substrate, the gap width between the constituent disks in the array could be reversibly tuned. The difficulty of this approach is in finding robust substrate materials that 1) are compatible with nanostructure fabrication techniques, 2) have compatible optical properties, and 3) can withstand repetitive stress and strain without deleterious material breakdown, even at the nanoscale. Despite these limitations, research groups have had great success using closely related.\textsuperscript{52-54,73}

In order to study the effects of plasmonic coupling when nanoantennas come into very close proximity or make contact, researchers have employed several clever approaches. These approaches range from pushing Ag colloidal nanoparticles into contact using a high energy electron beam\textsuperscript{42} to fabricating plasmonic nanostructures on macroscopic atomic force microscope tips and co-positioning them.\textsuperscript{74} From these studies, we know that when nanoparticles are moved to within
~2 nm, electron tunneling leads to observable changes in the optical and electronic spectra of the nanoparticle pairs, diverging from models employing only classical electrodynamics. When optical frequency electric currents flow between the closely spaced or touching nanoparticles, a new low energy dipolar hybridized mode is formed, known as the charge transfer plasmon (CTP). The boon of these studies was their ability to decrease the interparticle separation until contact while observing the evolution of electronic or optical spectra. However, as with all techniques there are inherent drawbacks.

In the case of pushing Ag nanoparticles with the electron beam of a scanning transmission electron microscope, the same electron beam used for nanoparticle manipulation was also used to intermittently image the dimer to record the morphology corresponding to the current electron energy loss spectra. Though the intermittent imaging was essential in determining the morphology of the dimer, imaging also caused morphological changes in the dimers. As a result, spectra before and after pauses for imaging were not identical, demonstrating that the spectral series recorded did not capture the entire spectral evolution. Despite this limitation, the study was invaluable in providing a morphology-based dynamic observation of evolving plasmonic modes for an individual nanoparticle dimer.

In the case of the AFM tip-mounted antennas, the tip structures themselves were very large (>200 nm diameter oblate spheroids). While the technique was successful in establishing a well-controlled cavity mode, the structures used to do so were not by definition nanostructures (possessing at least one dimension less than
100 nanometers). Additionally, the tip features were extensions of macroscopic metallic structures. As a result, direct comparison to true nanoscopic systems is difficult. Specifically, plasmon resonance modes were very broad and did not correspond to resonance modes familiar to simple dimer systems. However, the use of macroscopic AFM tips allowed the researchers to continuously track the separation between tips, force exerted on the tips at contact, and electrical current passed between the two structures. This amount of control and concurrent measurements methods has been unrivaled in preceding or subsequent experiments.

Though there are many distinct methods and mechanisms for tuning the optical properties of plasmonic nanoparticles and nanoparticle assemblies, it can be very difficult in practice to separate these mechanisms. Often, many mechanisms combine to result in a given change in observable optical or electronic properties. This is the case in Chapter 4 where electrochemical redox reactions are used to change nanoantenna morphology, electrical conductivity of nanoantenna components, and dielectric functions of both the surrounding medium and nanoantennas themselves. Spectroelectrochemistry is the study of how light/matter interactions are affected by electrochemical processes. With few exceptions, electrochemical processes are generally chemical reactions that occur as a result of charge transfer at an electrode surface. The optical properties of an experimental system component are typically studied as a function of electrochemical potential, deposition of material, redox state of an analyte, etc.
Because there are many electrochemically active chemical systems and there are also many surface localized spectroscopic techniques, the variations of possible spectroelectrochemical techniques are nearly endless. To facilitate discussion of background relevant to this thesis, I only discuss localized surface plasmon-based spectroelectrochemical techniques and important findings. Within this subfield, changes in the optical properties of noble metal nanoantennas are interrogated during electrochemical processes occurring at their surface. To clarify scope, I will use a popular spectroelectrochemical technique EC-SERS as a counterexample. In surface enhanced Raman spectroscopy (SERS), metal nanoparticles act as antennas that allow amplified sensing of nearby Raman-active molecules. Electrochemical SERS (EC-SERS) uses the same spectroscopic method to interrogate changes in the Raman scattering properties as the analyte is oxidized or reduced. In this case, the observed changes in optical properties are those of the chemical analyte and not of the nanoparticles themselves. An excellent example of EC-SERS is in the super-resolution study of the spatial distribution of electrochemical reactions on plasmonic nanoparticle arrays.\textsuperscript{76-78}

In contrast to SERS, surface plasmon spectroscopy (SPS) focuses on the optical properties of noble metal nanoparticles themselves. Combining electrochemistry with SPS results in studies of the metal nanoantenna optical properties with electrochemical modification of the nanoantennas’ local environment or the nanoantennas themselves. Because the optical spectra and localized surface plasmons are dependent on so many variables, interpreting
changes in optical spectra can be plagued with ambiguity and uncertainty. This was especially the case in early ensemble spectroscopic studies.

Early work on the spectroelectrochemical properties of gold nanoparticles utilized ensemble extinction spectroscopy and electroreflectance measurements. To maximize electrode area and optical cross-section, the first studies of gold nanoparticle electrode spectroelectrochemistry were performed on films of gold nanoparticles. Early works using thick films of gold nanoparticles found that under potential modulation, repeatable changes in transmission and reflectance could be measured. However, the changes could not be well-modeled because of the inhomogeneous broadening and complex line shapes that result from electronic coupling in nanoparticle films. Later, Chapman et al. found that by embedding silver nanoparticles in weakly conducting polymer films, they could tune the reflectance of the silver nanoparticles using electrochemical potential control. However, the film protecting the Ag nanoparticles limited ion access to nanoparticle surfaces and led to slow tuning kinetics. Despite the added chemical and physical stability that the film provided, most future work including the works of this thesis, focused on the use of ‘naked’ nanoparticles directly adsorbed to a conductive substrate and accessible to electrolyte ions.

Throughout the 2000s, several groups published on similar systems of nanoparticle films, monolayers, and eventually submonolayers to probe the effects of electrochemical charge density tuning in plasmonic nanoparticles. Researchers in 2002 used electroreflectance measurements of submonolayer 11 nm Au gold
nanoparticles under electrochemical potential control to correlate the bulk capacitive response of the entire working electrode with the amount of charge density tuning calculated using a simple Drude model dielectric function (more details in Appendix section A.1). In 2010, another group used the same submonolayer ensemble spectroscopy approach to study the effects of multiple electrochemical processes on Au nanoparticles rather than limiting to only charge density tuning. This study served as important motivation for the work in Chapter 2 of this thesis, because it made a distinction between the electrochemical tuning of plasmonic nanoparticles by charge density tuning and by chemical means. The paper also served as an important motivation to change the way nanoparticle spectroelectrochemistry is performed. Though the authors used submonolayer coverage, SEM included in their manuscript showed that nanoparticles often formed aggregates, and generally were within strong electronic coupling range of neighboring nanoparticles. As this study was one of the finest controlled ensemble spectroelectrochemical studies of its time, it stands to reason that previous studies had sample heterogeneity and complexity of at least the same level. Ideally, individual nanoparticles should be sparse on a substrate in order to minimize electronic coupling. However, very sparse samples have low optical density and thus low signal to noise ratios in ensemble spectroscopy. The solution to this problem is to probe individual nanoparticle spectra as they are tuned electrochemically in order to avoid unwanted coupling, inhomogeneous broadening, and overcome low optical densities. This single nanoparticle
spectroelectrochemistry approach forms the basis of all experimental results in this thesis.

Because plasmonic nanoparticles have high scattering cross-sections, scattered light from individual gold nanoparticles as small as 30 nm can be observed using a standard dark-field microscope. The dark field microscope has enabled much work in the field of plasmonics and is the primary instrument for all work presented in this thesis. Dark field microscopes rely on a condenser to deliver incident light at an angle oblique to the sample plane. An objective lens with a collection angle smaller than the incidence angle ensures that all light collected by the objective was scattered by the sample. By sparsely placing metal nanoparticles on a supporting substrate, the high scattering cross-section of the nanoparticles allows light scattered from a single nanoparticle to be collected. To a human observer, the light scattered by individual silver and gold nanoparticles is sharply colored. Depending on the size, shape, etc. the individual nanoparticles can appear blue, red, green, or some combination. By directing the light scattered from individual nanoparticles to a spectrometer, the light can be dispersed by an optical grating and the scattering spectrum can be collected using an imaging array (Section 2.2.2).

Single particle and ensemble nanoparticle spectroscopy both have advantages and disadvantages. Ensemble spectroscopy typically features straightforward optical geometries and instrumentation, often consisting of a traditional UV-Vis spectrometer. On the other hand, single-particle spectroscopy
requires stable microscopes with often complex optical paths.\textsuperscript{59,86} As a result, single-particle spectroscopy can be much more costly to implement than ensemble spectroscopy. In terms of scientific merit, both techniques serve specific uses and strengths. Ensemble spectroscopy typically produces strong, easy to measure spectra, allowing fast collection times and much experimental design flexibility.\textsuperscript{51,87} However, heterogeneity in nanoparticle populations leads to optical spectra becoming broader than the individual spectra of the components.\textsuperscript{17,61,88} This effect is known as inhomogeneous spectral broadening and is common to many ensemble spectroscopies. In addition to inherent heterogeneity in nanoparticle and nanoantenna optical properties, the application of surface plasmon spectroscopy to sense chemical and especially electrochemical processes introduces the possibility of heterogeneous activity levels within nanoelectrode populations. If the sum optical response is treated as the ensemble response the most and least active nanoelectrodes are lost in the averaging process. This has large implications in the search for active electrocatalysts and in investigating heterogeneous populations such as bottom-up engineered nanoparticle assemblies, as in this thesis. Single-particle spectroscopic techniques avoid all inhomogeneous broadening effects and allow the study of nanoantennas from heterogeneous samples.\textsuperscript{59-61,86,88} The penalty of course in using the light scattered or absorbed by a single nanoparticle is that the detected signal is extremely weak. This constrains experimental design to minimize noise. For the same reason, single-particle spectroscopy often requires long exposure times, limiting applications of the technique to static or quasi-static processes.\textsuperscript{61}
By performing single-particle spectroscopy in a thin spectroelectrochemical cell, Novo et al. paved the way for many future studies, including those featured in this thesis. In their 2009 paper, Novo et al. tracked the spectral evolution of individual gold nanorods on ITO support in KCl electrolyte as a function of electrochemical potential. By applying potentials negative to their Ag/AgCl quasi-reference electrode, the authors increased the free electron densities of the gold nanorods, thereby causing a measurable increase in plasmon resonance energy. Their work marked a major breakthrough both in single particle spectroscopy and in spectroelectrochemistry. In one sense, their use of single nanorod spectra allowed them to unequivocally determine the effects of electrochemical tuning on the plasmon resonance. Despite their experimental breakthrough, the authors did not leverage one major benefit of single-particle spectroscopy. As opposed to ensemble spectroscopy, the line shape of individual plasmonic nanoparticle scattering spectra reflects the true Lorentzian nature of nanoparticle plasmons. Though the authors fit their spectra with single Lorentzian functions, they didn’t report the changes in intensity or line width, opting for a model that only reported changes in plasmon resonance wavelength as a function of applied potentials. Despite theoretical shortcomings, future works including those found in this thesis were certainly inspired and enabled through the excellent experimental breakthroughs of this seminal work.

In 2012, Dondapati et al. published an important paper using a similar single-particle scattering spectroscopic approach. The authors used a simplified spectroelectrochemical cell to study the optical response of gold nanorods to
electrochemical potential control over a much larger potential range than investigated by Novo et al. The authors constructed thin electrochemical cells by sandwiching scotch tape and KCl electrolyte between two ITO-coated glass slides, one of which carried CTAB-coated gold nanorods. By applying electrochemical potential steps and acquiring scattering spectra, they found the spectral response of individual nanorods over a large potential range. Because of their choice of a 2-electrode electrochemical cell, the actual electrochemical potential of the nanorods was unknown. However, at high anodic potentials, they observed sharp red shifts and increased spectral width. The authors attributed these large spectral shifts to gold oxidation formation. The authors demonstrated a fully reversible plasmon resonance shift in KCl electrolyte but all other electrolytes (NaClO₄, and NaNO₃) tested showed only partial reversibility. The true strength of the paper was in their fitting algorithm to quantify the changes in plasmon damping with gold oxide formation. Later work within the field has given increased focus to the modeling and experimental investigation of chemical interface damping.51, 61

In 2014, our research group published research extending the work of Novo et al.61 In our study, we used gold nanospheres on ITO and in NaCl electrolyte. While Novo et al. used single-particle spectroscopy to investigate the optical response to cathodic potentials, we investigated nanoparticles at both cathodic and anodic potentials. Our use of a three-electrode electrochemical cell allowed us to directly compare between the seminal results of Novo et al.59 and also to know the actual electrochemical potential of the working electrode. In contrast to Klar et al.16 this enabled us to calculate the interfacial capacitance and link the spectral shift to
charging at the nanoscale. We also developed a new technique for dynamic investigations by collecting scattering spectra of individual nanoparticles during cyclic voltammetry. In doing so, we were able to demonstrate both the reversibility and repeatability of the potential-induced spectral changes. We tested the theory put forth by Novo et al. that the spectral shifts could be fully explained by potential-induced changes in nanoparticle charge density. To do so, we combined the Drude dielectric model and the Mie theory of scattering from spheres to create a numerical model of the plasmonic response to changes in charge density. By comparing the changes in various properties of the scattering spectral response to potential control, we revealed that the spectral width and scattering cross-section behave in the opposite manner than predicted by the charge density tuning model (Mie-Drude). This work is the subject of Chapter 2, and the results inspired the work found in Chapter 3 and Chapter 4.

Recently, Brown et al. used ensemble spectroelectrochemistry and an iterative fitting algorithm with the aim of determining the contribution of the many mechanisms involved in spectroelectrochemistry of plasmonic nanoparticles. Applying a bias between parallel ITO coated microscope slides, they measured the optical extinction of gold nanospheres as a function of applied bias. The main contribution of the manuscript was in establishing a complex fitting algorithm to fit many parameters to optical extinction spectra. Their overarching conclusion was that although there are small changes in free charge density and local refractive index, the dominant effect of electrochemical potential control is an increase in plasmon damping at anodic potentials. This finding is in qualitative agreement with
those of Dondapati and our own, as well as classic plasmon damping literature. The authors were unable to determine a mechanism for the increase in damping, but future work using their technique applied to single-particle spectroelectrochemical observations may provide much-needed insight into the mechanisms of chemical interface damping.

Also in 2015, Chirea et al. published an article important to the work presented in Chapter 4. In this study, the authors reported on the controlled electrodeposition of Ag onto Au nanostars. In their correlated study, they were able to deposit small amounts of Ag metal onto the nanostars by applying increasingly cathodic electrochemical potentials, all while monitoring the dark field scattering spectra of an individual nanostar. By then characterizing the same Au/Ag nanostar with scanning electron microscopy, they were able to show that silver deposits on the entirety of the nanostar. Simulations performed on an idealized geometry showed that the spectral changes were due primarily to silver deposition.

All single-nanoantenna spectroelectrochemical studies discussed so far used ITO substrates as the substrate supporting the nanoparticles or nanoparticle assemblies of interest. ITO is a heavily doped n-type semiconductor with a large bandgap (\(\sim 4\,\text{eV}\)). Because of this large bandgap, ITO thin films are nearly transparent throughout the visible range. As a thin film on glass microscope slides or coverslips, they have optical transmission as high as 90% and resistivity ranging from tens to hundreds of Ohms depending on the film thickness. Importantly, ITO is available from a large number of commercial suppliers with custom properties and
substrate dimensions. Additionally, ITO films are chemically stable over a broad pH range and even under large electrochemical potentials. The most common failure mode for ITO films in electrochemical cells is by leaching of In or Sn at high cathodic potentials (below -1 V vs. standard hydrogen electrode). These chemical changes lead to drastically diminished optical transmission and electrical conductivity. The susceptibility to electrochemical degradation is exacerbated in strongly acidic electrolytes. However, at anodic potentials and more neutral pH, ITO is optically and electronically stable. In Appendix section A.2, we consider the potential for ITO charge carrier tuning playing a role in single-nanoparticle spectroelectrochemical tuning and find that it is not a significant contributor to spectroelectrochemical tuning of plasmonic nanoantennas.

While ITO has rightfully served as the workhorse for plasmonic nanoparticle spectroelectrochemistry, many other substrates are employed in other branches of spectroelectrochemistry. For example gold thin films form a model system for anion adsorption in bulk transmission and reflectance spectroscopies due to the relatively noble characteristics of charge-neutral Au along with its rich optical spectra and many easily attained structural varieties. Some early works used semitransparent Au thin films as a substrate for nanoparticle film spectroelectrochemical studies, but the optical response of the Au film to electrochemical processes was not considered. In reality, the optical frequency electronic interactions between an Au film and a single Au particle can be quite complex, let alone an entire film of nanoparticles. We investigated the role of using Au thin films in conjunction with individual nanospheres and pair of
nanospheres as sensors for spectral detection of electrochemical potential-controlled adsorption and desorption of anions. Details as well deeper background and discussion on this topic can be found in Chapter 3.

1.3 Specific Aims

This thesis has the following specific aims: 1) Develop single-particle spectroelectrochemical techniques to study the fundamental optical effects of electrochemical surface plasmon tuning; 2) Develop practical spectroelectrochemical techniques to study electrochemical processes at single metal nanoelectrodes; 3) Use single-particle spectroelectrochemistry to develop active plasmonic systems possessing large optical tunability and rich physics.

1.4 Overview

This thesis contains chapters that are based on journal publications accomplishing the specific aims. In Chapter 2 a spectroelectrochemical method for studying heterogeneous nanoparticle electrodes was developed and used to study the spectral response to both static and dynamic electrochemical potential control. Experimental observations of electrochemistry’s effect on the localized surface plasmon were compared to an existing model and inconsistencies were identified to highlight the potential for future work in electrochemical tuning beyond charge density fluctuations.
In Chapter 3, single-particle spectroelectrochemical methods developed in Chapter 2 were employed to study the effects of sulfate adsorption to gold nanoparticle electrodes. Using individual gold nanosphere monomers and dimers in conjunction with two supporting electrode materials, the sensitivity of four nanoantenna geometries to potential-controlled sulfate electroadsorption were investigated. Single-nanoantenna spectral responses were interpreted using theoretical models and bulk spectroelectrochemical literature results. The most sensitive nanoantenna geometry was then used in the development of a novel single-particle analog for cyclic voltammetry to sense the potential-driven adsorption and desorption of sulfate, acetate, and perchlorate anions. Given the complexity of single-particle spectroscopy and the applications that would benefit from the concurrent monitoring of many nanoantennas in parallel, a scattering intensity based method was also demonstrated to sense the same effects at the single-nanoantenna level.

In Chapter 4, individual and pairs of closely spaced Au nanoparticles electroplated with Ag were used to drastically alter the optical properties of individual nanoantennas by simply changing the electrochemical potential. The change in potential drove oxidation (reduction) of the Ag (AgCl) shells to change the local dielectric properties of single nanoparticles. In dimers, the electrochemical switching of the shell material led to switching of the electronic coupling mechanism. Fine control of this effect along with full-wave electrodynamic simulations enabled study of the electrochemical rates of reaction at individual nanoantennas and the spatiotemporal evolution of the electrochemical shell
conversion process. Fine structure in these experimental observations was also compared to quantum calculations of similar systems to identify novel applications for the study of quantum plasmonic effects.

1.5 Summary

The work presented in this thesis is a culmination of efforts by my mentors, my collaborators, and I to further our understanding of the rich optical phenomena of metal nanoparticles and assemblies in electrochemical applications. The findings herein have expanded and sometimes corrected the current models for nanoparticle electrode behavior. The impending rapid development in this budding field will undoubtedly uncover exciting findings and applications.
Spectroelectrochemistry of single plasmonic nanoparticles

A hyperspectral imaging method was developed that allowed the identification of heterogeneous plasmon response from 50 nm diameter gold colloidal nanoparticles on a conducting substrate in a transparent three-electrode spectroelectrochemical cell under non-Faradaic conditions. At cathodic potentials, we identified three distinct behaviors from different nanoparticles within the same sample: irreversible chemical reactions, reversible chemical reactions, and reversible charge density tuning. The irreversible reactions in particular would be difficult to discern in alternate methodologies. Additional heterogeneity was

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observed when single nanoparticles demonstrating reversible charge density tuning in the cathodic regime were measured dynamically in anodic potential ranges. Some nanoparticles that showed charge density tuning in the cathodic range also showed signs of an additional chemical tuning mechanism in the anodic range. The expected changes in nanoparticle free-electron density were modeled using a charge density-modified Drude dielectric function and Mie Theory, a commonly used model in colloidal spectroelectrochemistry. Inconsistencies between experimental results and predictions of this common physical model were identified and highlighted. The broad range of responses on even a simple sample highlights the rich experimental and theoretical playgrounds that hyperspectral single-particle electrochemistry opens.

2.1 Introduction

With the growing focus on charge transfer and storage applications using nanostructures, a fundamental understanding of the physical and chemical processes governing charge transfer at the nanoscale is of paramount importance. Because the catalytic properties of nanoparticles are derived from their ability to store and transfer charge, nanoelectrodes prepared by attaching metal nanoparticles at sub-monolayer coverage on conductive substrates can be used to experimentally test the catalytic properties of nanoparticles. Electrochemical methods afford unrivaled control of surface chemistry at metal electrodes, but are classically built upon bulk electrochemical current, potential, and charge relationships. Changes in surface charge density of gold nanoparticles can
also be detected through changes in the surface plasmon resonance energy.\textsuperscript{59-60, 62, 66} The use of these spectral characteristics to infer electrochemical processes is the subject of nanoparticle plasmon spectroelectrochemistry.

Nanoparticle size and morphology have proven to be critical in the design and engineering of efficient nanocatalysts.\textsuperscript{24-25, 114-123} Chemically prepared nanoparticles are inherently heterogeneous in size and shape even under identical growth conditions, leading to heterogeneity in catalytic and electrochemical activity within nanoparticle populations.\textsuperscript{104, 108-109, 124-125} Additionally, surface defect sites have been shown to increase nanocatalyst activity.\textsuperscript{126-127} The synthesis of nanocatalysts has historically relied heavily on iterative trial and error optimization schemes.\textsuperscript{128} Several groups have recently taken advantage of theoretically-predicted shape-dependent activity in their quest to make better catalysts.\textsuperscript{114, 128-129} If scientists and engineers could resolve heterogeneous activity within populations of nanoparticles, study of highly active subpopulations could then be used to inform design principles and further optimize catalytic properties of entire populations, increasing total activity and yield.

Single-particle surface plasmon sensing of catalytic and electrochemical charging was first demonstrated by the Mulvaney group,\textsuperscript{59-60, 65} and later reported by the Klar group\textsuperscript{130} with a focus on the ability to tune the plasmon resonance of single nanoparticles with static potential control. A related technique utilizing the surface plasmon resonance of thin films has also been used to study electrocatalytic behavior of adsorbed single nanoparticles and the metal film itself.\textsuperscript{131-132} Hill and
Pan recently demonstrated the use of single-particle dark field spectroscopy in tracking the synthesis of single silver nanoparticles via electrodeposition\textsuperscript{133}. Without the deleterious effects of inhomogeneous spectral broadening due to sample inhomogeneity as in ensemble measurements, surface plasmon resonance and homogeneous line width responses directly probe changes in free electron density and plasmon damping due to surface chemistry\textsuperscript{59-60, 130}. According to the charge density tuning model, changes in free charge density affect the bulk plasma frequency of the metal, resulting in shifts of the surface plasmon resonance\textsuperscript{59-60, 62}.\textsuperscript{64-66} However, recent ensemble spectroelectrochemical studies suggest that chemical mechanisms might play an equally or more important role in electrochemical tuning of the surface plasmon resonance\textsuperscript{82, 107}. We hypothesize that because nanoparticle size and surface heterogeneity play important roles in charge transfer and storage at nanoparticle interfaces, disparities between the charge density and chemical tuning interpretations can be addressed by resolving nanoparticle heterogeneity\textsuperscript{134}. Ideally, one would want to statistically sample the overall nanoparticle population but also have the ability to study subpopulations at the single-particle level if multiple mechanisms are identified.

We have developed a methodology and complimentary techniques to study electrochemical heterogeneity both of a statistical distribution and within subpopulations of chemically prepared single gold nanoparticles. By combining dark field hyperspectral imaging and short exposure single-particle spectroscopy under electrochemical control, we probed electrochemical processes of single 50 nm gold colloidal nanoparticles over a broad range of time scales and over two distinct
potential ranges. Previous studies have focused on a few selected single nanoparticles measured serially and are thus blind to heterogeneous behavior across nanoparticle populations, particularly with regard to irreversible processes. Because our methodology measures many nanoparticles in parallel, we identify and illuminate the heterogeneous nature of electrochemical plasmon resonance tuning that has not been shown in existing literature.\textsuperscript{59, 130} We identified three different subpopulations of nanoparticles in the cathodic potential range on the basis of their spectral response, and concluded that previous studies involving single-particle spectroelectrochemistry focused on the least populous group. By extending our dynamic spectroelectrochemical investigation of these nanoparticles into the anodic potential range, we observed multiple nanoparticle-dependent spectral tuning mechanisms. In light of the multiple mechanisms and processes identified in this system, we report on both the classification of the broader processes present and further study of electrochemically reversible processes. The process-specific activity of individual nanoparticles shown clearly in this work demonstrates the value of the methodology and technique, and findings herein pave the way toward further understanding of nanoparticle electrochemistry critical for guiding the design of nanoparticle electrodes and catalysts.
2.2 Materials and Methods

2.2.1 Spectroelectrochemical cell preparation

An optically transparent electrochemical cell was fabricated for use in transmission dark field geometry. A hybrid working electrode was constructed by depositing 50 nm gold nanoparticles onto clean ITO (Thermo Scientific). The ITO coverslip along with an uncoated glass coverslip were cleaned by soaking in a 10% NaOH aqueous solution at 55° C for 30 minutes. The slides were then rinsed in deionized water, washed twofold in an ultrasonic bath of deionized water for 10 minutes, and finally rinsed extensively in Millipore filtered deionized water. The slides remain in an ultrasonic bath until being removed and dried quickly with a directed dry N₂ jet.

50 nm gold nanoparticles were drop cast from water onto the ITO surface and dried with a dry nitrogen jet. To remove excess gold nanoparticles and surfactant, a threefold rinsing step was performed with 200 μl of Millipore-filtered deionized water micropipetted onto the ITO surface. The large water drop was held on the slide surface for 30 seconds and then removed. The ITO coated slide with adsorbed gold nanoparticles was then plasma cleaned in an O₂ plasma at 200 mTorr for 40 seconds to destroy remaining surfactant.

The transparent electrochemical cell was built stepwise in a custom aluminum sample holder. Copper magnet wire was soldered to short electrode leads that form the various electrodes: silver wires (Sigma Aldrich) for counter electrode,
quasi-reference electrode, and as an intermediate lead to the ITO/gold colloid hybrid working electrode.

Two doubly adhesive silicone spacers (25×25×0.12 mm ID: 13 mm) and one non-adhesive silicone spacer (25×25×0.5 mm ID: 15 mm) (Grace BioLabs) were stacked atop the ITO/gold nanoparticle working electrode. A silver wire lead to the working electrode made ohmic contact with the ITO surface via physical connection and a secondary layer of silver paint (SPI Supplies). The reference electrode was located < 0.12 mm from the working electrode but was not in contact with the working electrode surface. The counter electrode was electrically isolated from the reference and working electrodes as well as their leads and was coiled into a radially symmetric pattern around the circumference of the cell. The cell was overfilled with electrolyte, the top coverslip was placed, and excess electrolyte was removed prior to sealing the cell. A top plate sealed the cell mechanically and remained assembled. Before each experiment, the cell’s open circuit potential was measured and the cell underwent 50 voltammetric cycles in the cathodic range prior to spectroelectrochemical measurements. Routine cyclic voltammetry measurements were performed to ensure uniformity between cells.

2.2.2 Single spectrum processing and analysis

Several optical and electronic effects justified the correction of scattering spectra. Because the Tungsten-Halogen excitation lamp had a non-flat spectral output through the visible range, the measured scattering spectrum of a nanoparticle was a linear convolution of the scattering spectrum, the spectrum of
the illumination source, and the instrument response. Spectra were corrected for local background due to diffuse light scattered from out-of-focus areas of the sample or from the substrate, and for the non-flat lamp spectrum according to:

\[
\text{Particle Scattering Spectrum} = \frac{\text{scattering spectrum} - \text{background spectrum}}{\text{lamp spectrum} - \text{dark counts}}
\]

Following the spectral processing, a single Lorentzian curve was fit using a non-linear least squares fitting algorithm implemented in Matlab. All spectral fitting was performed on an energy scale.

### 2.2.3 Single nanoparticle spectroelectrochemical tuning measurements

To investigate electrochemical tuning of plasmonic nanoparticles during cyclic voltammetry on the second time scale, single nanoparticles were observed by positioning the spectrometer slit at the center of a particular nanoparticle in the image with a 100 μm slit width, corresponding to a square integration area of 2.52 μm² (1.59 μm side length). The vertical dimension of this area was achieved programmatically by selecting and binning the corresponding CCD pixels rows.

The electrochemical workstation was controlled through Labview automation software. In order to preserve the internal timing of both the potentiostat and the Labview spectral acquisition program, a transistor-transistor-logic (TTL) pulse was generated using a data acquisition card (National Instruments) to trigger the internal function generator of the electrochemical
workstation. Figure 2.1 shows a diagrammatic representation of the dark field hyperspectral microscope with full electrochemical integration.

![Diagram of spectroelectrochemical hyperspectral dark field microscope](image)

**Figure 2.1** Instrument setup diagram for the spectroelectrochemical hyperspectral dark field microscope. WE: working electrode, RE: reference electrode, AE: auxiliary/counter electrode.

### 2.2.4 Hyperspectral implementation and analysis

The dark field hyperspectral microscope was composed of three main hardware components: an inverted dark field microscope, an imaging spectrograph, and a linear translations stage. The role of the translation stage was to programatically move the entrance slit of the imaging spectrograph through the
image of the sample produced by the microscope. This configuration is known as a pushbroom imaging scheme as the sensor array (an imaging spectrograph in this case) sweeps along the image plane and builds a data cube serially.\textsuperscript{135}

Nanoparticles in the electrochemical cell were excited with white light under a transmission dark field geometry. Scattered light was collected by an oil immersion objective and could be directed to the eyepiece for visual inspection or for image capture with a mounted digital SLR camera (Canon). Scattered light could also be directed to one of two side ports. At the left side port, there was the imaging spectrometer setup. The CCD camera had 400 rows and 1340 columns of 20×20 μm pixels. The imaging spectrograph was also equipped with an adjustable bilateral entrance slit with minimum width of 10 μm and two electronically addressable and controllable diffraction gratings. The grating used for all measurements in this work was a 300 lines/mm echellette grating that is efficiency optimized for first order refraction at 500 nm (blaze angle: 4.30\(^\circ\)).

To move the entrance slit through the image plane at the microscope side port, the entire spectrograph was mounted onto a stack of two orthogonal linear translation stages. The stage with axis of motion perpendicular to the image plane was fitted with a manual micrometer, and was used to position the spectrograph entrance slit in the image plane. The second linear translation stage with translation axis parallel to the image plane was outfitted with a programmatically controlled linear actuator. The actuator had a travel speed of 1 mm/s and a minimum step size and precision of 50 nm. The step size used in hyperspectral imaging was 20 μm. This
corresponded to a position uncertainty on the order of 0.25% and an actual travel
time of 20 ms. Given that the acquisition time per exposure in hyperspectral image
acquisition was rarely less than 500 ms, the scan speed and position precision of
this stage were more than adequate.

Finally, in order to align the entrance port of the spectrograph with the left
side exit port of the microscope, the entire microscope was raised with custom solid
aluminum legs. Due to the Cartesian nature of this setup, alignment of the
spectrometer entrance slit travel plane and the image plane at the microscope side
port was of paramount importance. Once alignment was achieved, all components
were hard mounted to an active vibration isolated optical table.

In hyperspectral imaging, it is useful to refer to the 3-dimensional data set as
a data cube. Two dimensions of the cube consist of spatial information. For
simplicity, we will call these dimensions x and y. The third dimension is light energy.
We will call this the c dimension, short for color. Therefore, each plane (x-y) normal
to the energy (c) dimension is simply a spatial map of the light intensity for a
specific energy window. In a push broom collection scheme, spectra are collected in
parallel along the extent of the sensor. For each exposure, one y-c plane of the data
cube is populated. The sensor is then moved in the x direction, and takes another
exposure. In this manner, the data cube is populated in parallel in the y dimension
and in serial in the x dimension. Practically, this adds time dependence to the
acquired data. Because each x-c plane of data is acquired in separate exposures, the
hyperspectral image records data over a time period roughly equal to the number of
exposures multiplied by the sum of the exposure time and the stage movement time. Other small time constants also contribute to the total acquisition time including control software delays, CCD camera readout time, and data transfer time.

In the current setup, many of these processes were parallelized in order to minimize the impact of compounding time delays. For instance, following an exposure, the register of a CCD camera must clear each column of pixels and convert these to a readable binary signal in serial. The readout time for the CCD camera is therefore dependent on the amount of data that it must read at each exposure. For large images, the CCD camera clearing time can be of the order of the stage movement time (tens of milliseconds). By parallelizing stage movement with CCD camera clearing, data transfer, and storage, the major time components were reduced to stage movement time and exposure time.

For each exposure, ~ 50 to 300 spectra were recorded. I designed the software interface to provide the operator with useful information about the incoming data in real-time and also to allow quick post-acquisition processing. This gave the user access to data metrics such as signal-to-noise (SNR) and signal-to-background ratios (SBR), background corrected spectra, and data cube sectioning to make on the fly adjustments to any of the instrument’s many parameters. For instance, in order to increase the SNR, the user could make an informed decision of whether to increase the exposure time, decrease the CCD camera clearing rate to reduce shot noise, or decrease the wavelength or spatial resolution. These
parameters were adjustable, allowing a user to maximize data quality while minimizing data acquisition time.

2.2.5 Reconstructed true-color RGB images from hyperspectral data

Hyperspectral imaging allowed the user to collect large amounts of spectral information in little time. One data analysis technique involved identifying nanoparticles and extracting single nanoparticle scattering spectra from the hyperspectral data cube, as discussed in Section 1.2 and 1.3. This analysis scheme broke down the data set into small usable pieces. In order to get a general overview of the entire hyperspectral image, another analysis technique was needed to condense the data into a visible image representation. For this purpose, I created color images from the hyperspectral data cube.
To convert a resolved spectrum to its constituent red, green, and blue components, the spectral response functions for the sRGB colorspace were multiplied by each constituent spectrum of the hyperspectral image. The red, green, and blue components were then summed separately to compile the three layer RGB image. By using the background and flatfield corrected spectra in this calculation, the resultant image represents the true color of scatterers as they would appear under flat white illumination.
2.3 Results and Discussion

Our custom setup allows hyperspectral imaging of many nanoparticles and single-particle cyclic Coulometry with specified potentials, realized for both cathodic and anodic conditions (Figure 2.3). A sealed optically transparent thin layer electrochemical cell with 50 nm gold nanoparticles dispersed on the working electrode forms a three-electrode cell with a 100 mM sodium chloride (NaCl) electrolyte (Figure 2.3a). Silver wires were used as an auxiliary electrode and a quasi-reference electrode. A three-electrode potentiostat controlled the potential difference at the interface of the electrolyte and the gold nanoparticle/indium tin oxide (ITO) working electrode. Detailed information on the construction of the electrochemical cell and experimental details can be found in 2.2.1. The electronic free charge densities of the gold nanoparticles changed to establish each prescribed potential difference, and were manifested as shifts in the localized surface plasmon resonance. Resonantly scattered light from individual nanoparticles was resolved with a 63× oil-immersion objective and directed to a thermoelectrically-cooled back-illuminated CCD imaging spectrograph.\textsuperscript{59-60, 62, 66} By using a very thin spectroelectrochemical cell (total thickness: 1 mm) with nanoparticles directly adjacent to the collection optics, out of focus light was minimized, leading to high signal-to-noise ratios (SNR ~ 425) of the dark field scattering signal. In combination with Lorentzian fitting, our instrumentation and experimental geometry allowed us to measure shifts in single-particle plasmon resonances as small as 1 meV within a few seconds. The spectrograph was mounted atop a linear translation stage, and
both the spectrograph and stage were programmatically controlled and synchronized to construct hyperspectral images of sample regions containing many nanoparticles (Instrument details are provided in 2.2.3 and 2.2.4). Using a pushbroom hyperspectral imaging scheme, tens to hundreds of single-particle spectra were acquired in parallel under potential control. In Figure 2.3b, a representative 50 x 50 pixel RGB image of ITO-supported gold nanospheres is shown. The RGB image was reconstructed from a hyperspectral data cube, shown in cartoon form behind the image. Details for RGB construction from hyperspectral data can be found in 2.2.5. Collection of a hyperspectral image at a fixed electrochemical potential took 108 seconds (2 seconds/pixel row, 54x284 pixel image) with additional 60 seconds of equilibration time between scans at two different static potentials. In this manner, potential-dependent spectral traces from each nanoparticle were collected as a series of hyperspectral data cubes, each at a prescribed electrochemical potential. Two example potential controlled spectra from a single nanoparticle are shown in the right panel of Figure 2.3b.
Figure 2.3 - Cathodic and anodic spectroelectrochemistry of single gold nanoparticles. (a) Optically transparent thin electrochemical cell for dark field spectroscopy of single 50 nm gold spheres on an ITO working electrode (WE) under electrochemical potential with auxiliary and reference electrodes (CE, RE) composed of silver wire. (b, left) Steady-state hyperspectral imaging of many single nanoparticles under potential control (32 × 32 μm). (b, right) Normalized spectra at potential vertices for a single nanoparticle along with Lorentzian fits. (c) Non-Faradaic cathodic (blue) and anodic (red) potential ranges with predicted charging mechanisms shown schematically.
Using the above setup, single-particle spectra were collected under two potential ranges (Figure 2.3c). In the cathodic range ($U < 0$ V, shown in blue in Figure 2.3c and throughout this work), electrons were injected into each nanoparticle from the conductive ITO substrate.\textsuperscript{59} The nanoparticles had a net negative charge, corresponding to a higher free electron density than a neutral nanoparticle. According to the Grahame model for electrode/electrolyte contact, a positively charged Stern layer composed primarily of hydrated cations forms at the surface of the nanoparticles as well as at the surface of the ITO (Figure 2.3c).\textsuperscript{136} In the anodic range ($U > 0$ V, shown in red in Figure 2.3c and throughout this work), electrons are extracted from the nanoparticles by the potentiostat circuit, yielding lower free electron densities and net positively charged nanoparticles. In order to screen the positively charged gold surface, hydrated chloride anions form a negatively charged Stern layer.\textsuperscript{136} The two potential ranges were arbitrarily defined with 0 V (vs. Ag/AgCl quasi-reference electrode) as a common vertex as a matter of convention set by seminal work.\textsuperscript{59}

In the cathodic potential range investigated (0 to -800 mV), the only known Faradaic process for gold electrodes in a NaCl solution is the overpotential deposition of hydrogen cations and subsequent hydrogen evolution reaction (HER). These coupled reactions are unavoidable at cathodic overpotentials and have been shown to rely heavily on crystal lattice structure and the presence of defects.\textsuperscript{134, 137} Protonation of the gold surface is electrochemically reversible, whereas HER is electrochemically and chemically irreversible. As such, we expect nanoparticle heterogeneity to result in a variety of observed spectral tuning behaviors in the
cathodic potential range. However, existing literature reports only on nanoparticles following the charge density tuning model.\textsuperscript{59, 130} In the anodic potential range ($U > 0$ V), multiple reactions occur at gold electrodes in NaCl solutions.\textsuperscript{137} With a pH-neutral NaCl solution, the lowest potential anodic oxidation reaction is that of chloride ions, which occurs at $\sim 530$ mV (vs. Ag/AgCl reference electrode), as detected in ensemble spectroelectrochemical measurements.\textsuperscript{107} In an attempt to avoid this reaction and target charge density-related surface plasmon resonance shifts, we limited our upper potential vertex to $+400$ mV. Because of the above mentioned (and other possible) coupled reactions, we examined the cathodic and anodic regimes separately. We began with cathodic potentials to explore heterogeneous nanoparticle responses under potential control.
Figure 2.4 - Cathodic hyperspectral steady-state electrochemical tuning of gold nanoparticles on ITO support. (a) Real-color RGB image of 50 nm gold nanoparticles at open circuit potential. Nanoparticles that did not exhibit a Lorentzian scattering spectrum were not classified. Image size: 90 × 17 μm.

(b) Classification of single-particle behavior based on reversibility of potential-dependent spectral changes. (c) Scattering spectra at potential vertices for a single nanoparticle from subgroup Reaction One. (d) Spectra for a nanoparticle from subgroup Reaction Two. (e) Spectra for a nanoparticle showing charge density tuning of the plasmon resonance. (f) Mean peak resonance shift and associated standard error for seven nanoparticles exhibiting charge density tuning, shown as a function of applied potential. Arrows indicate applied potential scan directions.

Potential-dependent hyperspectral imaging gave us the means to observe heterogeneity within a nanoparticle population (Figure 2.4). A series of hyperspectral images at each potential was used to identify the steady-state potential induced plasmon resonance shift. Figure 2.4a shows an example spectral
image compiled at open circuit potential, with circled nanoparticles noting subsets identified by their potential-dependent spectral behavior. Each scattering center in the series was located and fit with a single Lorentzian function. Single gold nanoparticles were distinguished from clusters by imposing a coefficient of determination cutoff, $R^2 > 0.95$. Because we achieved a large signal-to-noise ratio, spectra were well-fit. This allowed us to reliably and repeatedly detect spectral shifts as small as 1 meV.

By investigating many nanoparticles under potential control in this cathodic range (0 to -800 mV), we found that the majority of nanoparticles demonstrated behavior not predicted by charge density tuning, as shown in Figure 2.3b. We expected the plasmon resonance of all gold nanoparticles to blue shift linearly upon application of negative electrochemical potentials, due to an increase in free electron density that results from electrons flowing from the potentiostat circuit into the nanoparticles and substrate in establishing the electrical potential difference between the bulk electrolyte and the nanoelectrodes. Upon exposure to cathodic potentials, spectra for half of the single gold nanoparticles that met the selection criteria ($R^2 > 0.95$) showed significant irreversible changes in their scattering spectra including significant resonance broadening, large increases in scattering intensity, and the loss of their original Lorentzian response. These nanoparticles are highlighted with red circles in Figure 2.4a and representative spectra at the potential vertices are shown in Figure 2.4c. We attribute this to an electrochemically irreversible reaction (Reaction One).
Further identified in Figure 2.4a and b, one-fourth of the nanoparticles also showed large increases in intensity, spectral broadening, and plasmon resonance red shifts not predicted by the charge density tuning model. In contrast to nanoparticles undergoing Reaction One, the scattering spectra of nanoparticles in this subset maintained their Lorentzian line shape throughout the entire experiment, but their scattering spectra only returned to initial conditions after the application of a sufficient positive potential. These nanoparticles are highlighted by cyan circles in Figure 2.4a and example spectra are shown from a single nanoparticle in Figure 2.4d. Further investigations are required to elucidate the mechanisms and potentially complex behaviors that we refer to collectively as Reactions 1 and 2.

Finally, just under a quarter of the single gold nanoparticles followed the predicted charge density tuning model. These nanoparticles are indicated by green circles in Figure 2.4a and example spectra from a nanoparticle in this subset are shown in Figure 2.4e. Nanoparticles in this subset were well-fit throughout the experiment ($R^2 > 0.95$), show small changes in FWHM ($\Delta \Gamma < 20$ meV) and demonstrated completely reversible plasmon resonance shifts. The change in peak resonance energy as a function of potential for this subset of nanoparticles is shown in Figure 2.4e as a mean resonance shift with associated standard error for all nanoparticles in this subpopulation. The return to initial resonance energy is a strong indicator that the spectral tuning mechanism for this subset of nanoparticles is electrochemically reversible, fitting the charge density tuning model. By design, this experiment observed the initial response of nanoparticles to electrochemical
modulation. The relatively large populations of nanoparticles demonstrating potential dependent spectral responses other than those predicted by the charge density tuning model indicates that future work will be necessary to model and fully understand the irreversible and semi-irreversible spectral tuning observed here in the cathodic potential range. Previous studies of single-particle spectroelectrochemical tuning under static potential control have only reported on the behavior of this particular subset of nanoparticles.59,130

The most valuable electrochemical techniques are not steady-state techniques, but rather are dynamic in nature.113 The ability to precisely and quickly vary the potential at an electrode surface allows researchers to characterize electrodes, investigate fine potential structure, and determine reaction kinetics. For the same purpose, in this work we developed dynamic single-particle spectroelectrochemistry. By measuring single-particle spectra under dynamic potential control, we recorded spectral changes on the order of seconds rather than minutes as with steady-state experiments. While the value of hyperspectral potential-controlled imaging experiments lies in studying many nanoparticles simultaneously, the strengths of dynamic measurements are three-fold: 1. Fast collection times allow many potential cycles to be measured, allowing us to probe the repeatability and reversibility of potential-dependent spectral shifts. 2. By investigating the potential scan-rate dependence of spectral response, the time scale of reaction kinetics can be interrogated. 3. Reactions with partial chemical reversibility can be probed by limiting the amount of time spent with significant electrochemical overpotentials. From a practical standpoint, recording spectra on
the time scale of seconds vs. minutes allows greater potential resolution to be achieved in a realistic time frame. Therefore, dynamic measurements illuminate fine potential/resonance structure not possible using static measurement techniques.

Figure 2.5 - Single-particle measurement of dynamic electrochemical tuning in the cathodic range (0 to -800 mV). (a) Electrochemical potential of the working electrode relative to the reference electrode as a function of time. Sweep rate: 10 mV/s. (b) Scattering spectra under dynamic potential control. The fitted resonance energy, $E_{\text{Res}}$ (solid white line) and full width at half maximum, $I'$ (dotted white lines) are superimposed. (c) Reversible, cyclic $E_{\text{Res}}$
response as a function of potential $U$ shown as mean with standard error for three consecutive cycles. (d) Average $\Gamma$ over 3 cycles as a function of potential. (e) Mie-Drude model simulations, the number of electrons transferred from the conductive substrate to the nanoparticle is calculated. Error bars indicate propagated standard error in $E_{\text{Res}}$. Arrows indicate the scanning directions of the applied potential.

Investigations under dynamic potential control in the cathodic potential range showed that the subset of nanoparticles described in Figure 2.4e and f also demonstrated reversible spectral tuning, consistent with the charge density tuning model (Figure 2.5). In this experiment, the potential was swept in a sawtooth pattern at 10 mV/s between 0 and -800 mV, as shown in Figure 2.5a. Scattered light from a single nanoparticle was directed to the spectrograph and spectra were recorded every 2.5 seconds. Each spectrum was independently fit with a single Lorentzian and the parameters of the fit determined the resonance energy, $E_{\text{Res}}$, and full width at half maximum, $\Gamma$. $E_{\text{Res}}$ and $\Gamma$ are shown in Figure 2.5b as solid and dashed white lines, respectively.

The mean and standard error for $E_{\text{Res}}$ and $\Gamma$ for three consecutive potential cycles after initial stabilization are shown as a function of applied electrochemical potential in Figure 2.5c and d, respectively. $E_{\text{Res}}$ blue shifted linearly with increasingly negative potentials and returns to the initial resonance as the potential $U$ was swept back to 0 V ($dE_{\text{Res}}/dU = -3.9$ meV/V). A small but measurable potential-independent hysteresis is also apparent. To test whether this hysteresis was related to double layer formation kinetics, the scan rate was varied, but no effects due to changes in scan rate were observed (Figure 2.6).
Figure 2.6 - Comparison of the spectral response to varying scan rates in the cathodic range. (a) Change in peak resonance energy as a function of applied potential for three scan rates. There are small variations in the peak energy shift vs. potential slope but no systematic trend is observed. (b) The changes in plasmon resonance width as a function of applied potential for the three scan rates are nearly identical.

We conclude that because no scan rate dependence was found for these values, transient cell and double layer dynamics occurred faster than the rate of potential changes, as expected from theory. By corollary, observed spectral shifts for these nanoparticles in this potential range probed changes in equilibrium charge densities. These results are in good qualitative agreement with the charge density tuning model.

Using the charge density-modified Drude dielectric function model along with Mie scattering theory (Mie-Drude model), we calculated the excess charge on the nanoparticle from $E_{Res}$ throughout the potential range applied in our study (Figure 2.5e). In these calculations, a model Drude dielectric function was modified to
reflect changes in the nanoparticle free electron density and then used to simulate the plasmonic response as a function of applied electrochemical potential. Details and derivation of the full Mie-Drude model are found in the Appendix. At negative potentials, the nanoparticle was negatively charged and therefore had a higher free electron density, as shown in Figure 2.5e. Over this potential range the number of excess electrons fluctuated by ~ 20,000 electrons, which is still less than 0.5% of the total conduction electrons in the nanoparticle, but corresponded to a surface capacitance of ~ 50 μF/cm². Figure 2.5d shows that $\Gamma$ decreased linearly with applied potential, with $d\Gamma/dU = 3.2$ meV/V. However, the trends in $\Gamma$ and scattering intensity predicted by the Mie-Drude model scattering simulations were completely opposite to the experimental results (for more details see Section 0). For this reason, we suggest that significant theoretical work is still needed to unravel the dependence of resonance width and intensity on applied potential. In the calculation of free charge density fluctuation, each nanoparticle was assumed to be electrically neutral at the open circuit potential of the working electrode. The actual point of zero charge for each nanoparticle is unknown and likely varies slightly from nanoparticle to nanoparticle. It should be noted that previous studies have confirmed that changes in refractive index do not play a significant role in electrochemically induced plasmon resonance tuning by varying the cationic species and observing no change in cathodic charge density tuning response.\textsuperscript{107} From a survey of 13 nanoparticles in this potential range obeying the charge density tuning model, we found that the response was linear but $dE_{\text{Res}}/dU$ varied greatly among nanoparticles from -2 to -16 meV/V, indicating that the nanoparticles’ ability to
store charge varied or that contact heterogeneity between the conducting substrate and metal nanoparticles played a limiting role in overall charging. For these nanoparticles, $d\Gamma/dU$ also varied from 0.2 to 12 meV/V.

Figure 2.7 - Two distinct plasmonic responses to anodic charging. (a,f) Scattering spectra collected during dynamic potential control shown with $E_{Res}$ and $\Gamma$ superimposed with solid and dashed white lines, respectively. (b) Electrochemical potential of the working electrode as a function of time. Sweep rate: 10 mV/s. (c,g) Average $E_{Res}$ over 3 consecutive cycles shown as a function of potential. (d,h) Average $\Gamma$ is shown as a function of potential. (e,i) The number of electrons transferred from the nanoparticle to the substrate is
shown as a function of potential, calculated using the Mie-Drude model scattering simulations and \( E_{\text{Res}} \). Error bars indicate propagated standard error in \( E_{\text{Res}} \).

When the nanoparticles found to undergo charge density tuning at cathodic conditions were examined within the anodic range with dynamic potential control, a heterogeneous spectral response was observed (Figure 2.7), indicative of multiple processes occurring. In the anodic potential range of 0 to +400 mV, well below the chloridation onset potential expected from ensemble measurements (~ 530 mV vs. Ag/AgCl)\(^{82}\), some nanoparticles exhibited nonlinear spectral tuning, inconsistent with the charge density tuning model. Figure 2.7a illustrates a series of spectra as a function of time varying potential for two separate nanoparticles demonstrating the two observed behaviors. Particle 1 showed apparent charge density tuning in the anodic potential range. \( E_{\text{Res}} \) and \( \Gamma \) are shown as solid and dotted lines, respectively. The electrochemical potential was again swept at 10 mV/s between 0 to 400 mV as shown in Figure 2.7b. Take note that large modulations of the scattering intensity with potential produce an illusion of resonance narrowing at higher potentials, when in fact the opposite is true – \( \Gamma \) increases with increasing potential. Figure 2.7c plots the plasmon resonance energy as a function of potential averaged over three consecutive cycles. The resonance energy decreased linearly with increasing potential as predicted by the charge density tuning model (\( dE_{\text{Res}}/dU = -7.3 \text{ meV/V} \)). Again, in Figure 2.7d, \( \Gamma \) increases linearly in contrast to predictions by Mie-Drude model scattering simulation for charge density depletion (\( d\Gamma/dU = 10.6 \text{ meV/V} \)). Using this model and applying it to the change in resonance energy (Figure 2.7c), the
nanoparticle’s net electron flux is reported as a function of potential in Figure 2.7e, but needs to be treated with care for the reasons already given. From the 13 nanoparticles investigated in the anodic potential range all of them underwent reversible plasmon resonance shifts, but only 8 nanoparticles displayed linear resonance shifts and broadening with potentials like Particle 1. For these nanoparticles \( \frac{dE_{\text{Res}}}{dU} \) varied from -0.5 to -8.7 meV/V. \( \frac{d\Gamma}{dU} \) for these nanoparticles varied from 2 to 32 meV/V, nearly 3 times larger than seen in the cathodic range. We attribute this increase in resonance broadening to interface damping, resulting from the much higher polarizability of chloride ions compared to sodium ions.\(^{21}\) The other 5 nanoparticles showed a nonlinear plasmonic response to the applied electrochemical potential (Particle 2 shown in Figure 2.7) and will be discussed next.

Scattering spectra for Particle 2 are shown in Figure 2.7f under the potential modulation given in Figure 2.7b. \( E_{\text{Res}} \) and \( \Gamma \) are indicated with solid and dotted white lines, respectively. Figure 2.7g illustrates the mean and standard error for \( E_{\text{Res}} \) as a function of potential over three consecutive cycles after initial stabilization. In contrast to Particle 1, \( E_{\text{Res}} \) for Particle 2 decreased nonlinearly with increasing potential in the anodic range and exhibited two distinct resonance vs. potential slopes. From 100 to 220 mV, \( \frac{dE_{\text{Res}}}{dU} = -23.2 \text{ meV/V} \), nearly six times larger than the linear shift observed for the nanoparticle in the cathodic potential range (Figure 2.5) and more than two times larger than that of Particle 1. After this initial shift, \( E_{\text{Res}} \) settled and shows less than 1 meV shift with increasing potential. Following the reversal of the potential sweep direction at 400 mV, almost no change in the
resonance peak position occurred until a critical potential was met, below which $E_{\text{Res}}$ returned to its initial value ($dE_{\text{Res}}/dU = -24.8 \text{ meV/V}$). Most importantly, the nonlinearity and hysteresis were segmented in potential, indicating that the change points for $dE_{\text{Res}}/dU$ have differing electrochemical potentials depending on scan direction. This behavior indicates that the mechanism responsible for these more drastic resonance shifts is likely chemical in nature and the resonance shift change points correspond to single-particle onset potentials. In addition to potential-dependent hysteresis and tuning rates for $E_{\text{Res}}$, $\Gamma$ shows similar trends in Figure 2.7h. From 0 to 250 mV, nearly no change in plasmon resonance width occurs ($d\Gamma/dU = 2 \text{ meV/V}$). From 250 to 400 mV, broadening increases nearly linearly with $d\Gamma/dU = 23.8 \text{ meV/V}$. The plasmon resonance remained broadened until roughly 200 mV on the reverse potential scan, at which point $\Gamma$ decreases with a slope close to its initial value ($d\Gamma/dU = 14.4 \text{ meV/V}$). These change points roughly correspond to the observed change points for the $E_{\text{Res}}$.

The consistent bimodal $dE_{\text{Res}}/dU$ and $d\Gamma/dU$ behavior shown in Figure 2.7g and h indicates that at least one additional process along with charge depletion is occurring. Non-Faradaic charge density tuning on this nanoparticle resulted in relatively small resonance shifts and was overshadowed by the additional process that, we propose, was chemical in nature rather than physical. In a single-particle steady-state experiment involving nanorods in 100 mM NaCl on ITO, Dondapati et al. also observed larger shifts in the plasmon resonance at small positive potentials compared to expected shifts based on the Mie-Drude model. They attributed this effect to adsorbate damping due to hydration of the gold surface and excluded
reactions between gold and chloride ions from their treatment. In their experiment, they covered a very large potential range (-1 V to +2 V, no reference electrode), preventing them from observing the type of hysteresis seen here in the more limited potential range. Unfortunately, their use of a two-electrode electrochemical cell precludes the direct comparison between reported applied potentials and other literature values or the present study due to unknown interfacial potential differences and considerable iR drop across the low concentration electrolyte. In a series of dynamic ensemble spectroelectrochemical studies of many gold nanoparticles on ITO support in NaCl, Sannomiya, Dahlin et al. investigated the formation of a gold chloride surface complex. By measuring the ensemble absorption spectrum of thousands of nanoparticles in parallel, they accessed scan rates as high as 1 V/s. They concluded, by observing strong scan rate dependence even below +600 mV, that metal-halide formation dominated the plasmonic response almost entirely. Because the ensemble absorption spectra were comprised of the collective absorption of many thousands of nanoparticles, it is unreasonable to expect a clearly defined onset potential for this chloridation process based on our own observations. In considering these explanations, we note that both tuning models attribute resonance shifts at small anodic potentials to a process other than charge density tuning. However, the adsorbate damping model attributes resonance shifts and spectral broadening to a physical effect, whereas metal halide formation obviously is a chemical process that then results in damping due to an electro-optically lossy layer of gold chloride. For comparison, we performed an otherwise identical experiment using a more inert
electrolyte, aqueous sodium phosphate (Figure 2.8). In the cathodic and anodic potential ranges, we observed only linear changes in $E_{Res}$ and $\Gamma$.

**Figure 2.8** - Linear surface plasmon resonance tuning of a 50 nm Au nanoparticle to potential modulation with an inert electrolyte in a combined cathodic and anodic potential range (-400 to +400 mV). (a) Electrochemical potential of the working electrode relative to the reference electrode as a function of time. Sweep rate: 10 mV/s. (b) Scattering spectra under dynamic potential control. (c) Reversible, linear $E_{Res}$ response as a function of potential $U$ shown as mean with standard error for five consecutive cycles. (d) Average $\Gamma$ over five cycles as a function of potential. Electrolyte: 44 mM Na$_2$HPO$_4$. All potentials relative to silver/silver chloride quasi-reference electrode.
The effect of refractive index modulation of the ITO substrate as a result of electrochemically-gated charge carrier concentration changes by electrochemical gating was considered through simulations (Appendix A.1). The Drude-Lorentz model was used to find the carrier concentration-dependent refractive index of ITO. This result was then used for the embedding dielectric medium in Mie Scattering simulations of a 50 nm Au sphere. Even in the limiting case of a sphere completely embedded in ITO, we found that the measured resonance energy shifts would require charge carrier concentration modulation over six orders of magnitude larger than those reported in the relevant electrochemical ITO gating literature. We concluded that potential-dependent refractive index changes of the substrate are insignificant in our system. Additional details and calculation results are shown in Appendix section A.1.

Our experiments showed that even at limited positive potentials, some nanoparticles showed clear onset potential behavior, while others showed only linear plasmon shifts consistent with the charge density tuning model. Although we cannot exclude interface damping as a tuning mechanism, the heterogeneous onset potentials shown in some nanoparticles (e.g. Particle 2) suggest that at least one mechanism is chemical in nature, possibly metal halide formation. In terms of this working model, we postulate that the onset potential for Particle 2 was within the potential range, while the onset potential for Particle 1 was likely above the upper potential vertex (+400 mV). We conclude that even within a very narrow subset of nanoparticles chosen based on behavior in the cathodic potential range, further heterogeneity is apparent in the limited anodic potential range investigated. In light
of these results, disagreement between previous single-particle and ensemble spectroelectrochemical measurements is inevitable. More importantly however, our results show that electrochemically induced changes to nanoparticle plasmons and the associated physical and chemical mechanisms differ greatly within populations of nanoparticles.

2.4 Conclusions

This study shows that spectroelectrochemical tuning of the plasmon resonance is the result of multiple mechanisms, and that the presence and distribution of mechanisms varies from nanoparticle to nanoparticle. Under steady-state cathodic potentials, the majority of nanoparticles demonstrated behavior inexplicable within the charge density plasmon resonance tuning model. Fewer than 25% of the nanoparticles observed obeyed this model. These nanoparticles were investigated under dynamic potential control and their plasmonic response to an applied electrochemical potential was found to be completely reversible. For positive potentials, some of these nanoparticles showed signs of an additional tuning mechanism, likely chemical rather than physical in nature. This result suggests that some combination of nanoparticle or nanoparticle/substrate properties of these nanoelectrodes dictate their charge transfer or charge storage capability. The methodology and techniques developed herein allow the quantitative study of catalytic and electrochemical activity of single nanoparticles, both statistically and dynamically. We hope that this proof of principle study of heterogeneous single-particle electrochemistry will inspire future investigations
and serve as a tool in informing design principles for the engineering of specific
electrochemical and catalytic nanoparticles and nanostructures. Ongoing work
focuses on in-depth study of the multiple mechanisms first reported on here by
measuring the effects of other electrolytes, ion concentrations, nanoparticle
morphology and size, potential ranges, and electrode materials.

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Chapter 3

Individual plasmonic nanoantenna electroadsorbate sensing

Assemblies of plasmonically active nanoparticles and thin films have recently enabled precise sensing through their high sensitivity to their local dielectric environments. In order to develop plasmonic spectroelectrochemical sensors at the single-nanoantenna scale, we investigated several geometries under test reaction conditions. By testing the combination of both ITO and Au thin film substrates with nanosphere monomers and dimers, we identified the value of the Au film substrate in sulfate electroadsorbate sensing. Using nanosphere dimers on Au film, we conducted single-nanoantenna dynamic spectroelectrochemistry to develop a sensing strategy. We compared bulk cyclic voltammetry (CV) and a single-nanoantenna CV analog for sulfate, acetate, and perchlorate adsorption sensing. In order to make the technique more accessible, we also demonstrated the successful use of the total scattering intensity fluctuation of single nanoantennas in sensing the same anions. Our technique extends
dynamic spectroelectrochemical sensing to the single-nanoantenna level using both individual plasmon resonance mode and total scattering intensity fluctuations.

3.1 Introduction

Electrochemistry gives unrivaled control of metallic and semiconductor surfaces, enabling fine control of electrode/electrolyte interfaces. Electrochemical sensing ability has improved greatly over the past 50 years due in large part to the continuous miniaturization and homogenization of electrodes.\textsuperscript{140-141} Nanometer-scale electrodes present the formidable challenge of measuring extremely small electrochemical currents.\textsuperscript{51, 59, 139} Currently, the direct readout of current from a single nanoparticle has only been accomplished using a scanning tunneling microscope tip.\textsuperscript{142} However, the ideal method for monitoring electrochemical reactions at individual nanoparticles would be compatible with a range of heterogeneous catalytic reactions. For metal nanoelectrodes, the plasmon resonance has been shown to report on the primary and secondary effects of electrode reactions.\textsuperscript{61, 63, 83, 93} Because nanoparticle plasmons report on their extremely local dielectric environment (nanometer range),\textsuperscript{9-10, 143} they make ideal candidates for electrochemical reaction sensing.\textsuperscript{16, 51, 82-83, 87, 144-146} In addition, nanoparticle plasmons have high scattering cross-sections and do not undergo deleterious photophysical processes such as blinking or bleaching like fluorescent dyes and quantum dots.\textsuperscript{143, 147}

In this work we characterized the sensitivity of localized surface plasmons to anion adsorption and demonstrated a novel technique useful in the study of nanoscale electrochemical sensing. We used electrochemically controlled sulfate adsorption onto gold nanoantenna working electrodes under single-nanoantenna spectroscopy to develop
an effective plasmon-based sensor to track electrochemical adsorption processes. Analogous bulk spectroelectrochemical methods have been successful in sensing sulfate adsorption on planar gold electrodes via second harmonic generation (SHG), two dimensional Fourier transform infrared spectroscopy (2D FTIR), and surface enhanced Raman spectroscopy (SERS). In contrast to bulk spectroscopic methods, anion adsorption on single nanoparticle surfaces can be detected through changes in nanoparticle plasmon resonances. Based on previous work on the role of substrates in the engineering of plasmonic nanoantennas and plasmonic sensing applications, we set out to experimentally investigate the role of substrate optoelectronic and electrochemical properties in single-nanoantenna plasmonic electrochemical sensing.

We chose to investigate two substrates common to spectroelectrochemistry, thin films of Au and ITO. While thin film spectroelectrochemistry focuses on the optoelectronic properties of the films themselves, nanoparticle-based spectroelectrochemical studies typically use these films purely as a physical support and electrical contact. The development and choice of transparent conductive substrates for spectroelectrochemistry is an active and enduring research area. In this work we investigate two of the most common supports used in spectroelectrochemical studies, in part to demonstrate the capability of even the most simple nanoantenna geometries for single-nanoantenna spectroelectrochemical sensing through alternate substrate selection. ITO has a strong foothold in the spectroelectrochemical arena due to its optical transparency from the UV into the near infrared and its impressive chemical, optical, and electronic stability in the often harsh
conditions of electrochemical cells. ITO is also a favored substrate in the plasmonics community because its electrical conductivity allows electron beam lithography and characterization in scanning electron microscopes. Because the plasmon resonance of ITO thin films is typically >1600 nm, interactions between film plasmons and nanoantenna plasmons are typically minimal and the optical properties of the nanoantennas can be interrogated through the optically transparent film using various optical transmission spectroscopies. For these reasons, ITO has been a natural choice of substrate for many plasmonic nanoparticle spectroelectrochemical studies.

In contrast to the non-interactive relationship between nanoparticle plasmons and ITO, Au thin films and adjacent nanoparticles interact strongly to produce rich optical properties. The interaction of nanoparticles and metal planar surfaces including thin films has been the focus of many studies on the fundamental nature of plasmonic coupling. In addition to the interesting plasmonic properties of nanoparticle/film systems, gold thin films hold a special place in spectroelectrochemistry because of the opportunity electrochemistry provides to make Au behave in non-noble ways. When positively charged by electrochemical potential control, Au becomes more reactive, allowing significant tunability of its electronic and optical properties through chemical modifications. In contrast to the electrochemical and optical stability of ITO at anodic potentials, sulfate and other anions readily adsorb to the anodically polarized Au film substrate. However, the combination of Au nanoparticles and thin films for spectroelectrochemical study has been limited to bulk spectroelectrochemical studies.
In combination with the ITO and Au thin films, we investigated nanosphere monomers and dimers for their practicality as single-nanoantenna electrochemical sensors. After identifying a highly sensitive nanoantenna/substrate geometry, we reversibly controlled and probed sulfate anion adsorption on Au at the single-nanoantenna level during cyclic voltammetry (CV). Using this dimer on Au film single-nanoantenna structure, we correlated the spectral response to sulfate ion electroadsorption to the bulk cyclic voltammetry measurements. Fluctuations in single plasmon resonance mode scattering intensity and integrated scattering intensity were developed as methods for monitoring electro-adsorption/desorption at the single-nanoantenna level. Finally, we demonstrated the nanoantenna’s applicability in sensing the adsorption and desorption of additional anions, acetate and perchlorate, and under electrochemical potential control.

3.2 Methods

3.2.1 Dimer Preparation

Au nanoparticle dimers were prepared using a nonspecific aggregation method and electrophoretic enrichment as described previously.\(^{147}\) 500 μL of stock citrate-stabilized 50 nm Au colloids (BBI Solutions) were washed with Millipore filtered deionized water and concentrated 10x by centrifugation at 1400 rcf for 5 min. 200 μL of acetonitrile was added to the suspension and stirred for 30 min. 5 μL of 10 mM 11-mercaptoundecanoic acid (11-MUA, Sigma) was added, followed by 30 min. of stirring. The solution was centrifuged and the supernatant was removed. Sedimented nanosphere aggregates were suspended in 500 μL Millipore filtered
deionized water then washed and concentrated 10×. 10 μL 40 w/v% sucrose solution was added to increase solution density before loading into electrophoretic gel separation wells. Samples were electrophoretically separated in 1% agarose gel at 135 V for 30 minutes in 0.5× TAE Buffer. The second band was manually removed with a razor blade and aggregates and dimers in the removed gel were removed using a published electroelution method at 250 V. Extracted nanosphere monomers and dimers were centrifuged, washed and concentrated for deposition. TEM analysis showed that the resulting solution contained 23% dimers with gap widths ranging from 1 to 5 nm.

3.2.2 Au Film Preparation

Semi-transparent conductive thin films were fabricated on clean glass coverslips by electron-beam evaporation of a 2 nm Ti adhesion layer followed by a 20 nm Au thin film. Film thickness was measured during deposition using a quartz crystal microbalance. Au thin films were found to be free of optical scatterers via dark-field spectroscopy.

3.2.3 Spectroelectrochemical cells

Nominally 50 nm Au nanosphere monomers and dimers were drop cast onto conductive substrates and ligands were removed chemically prior to cell assembly in NH₄OH : H₂O₂ : H₂O at 40° C for 10 minutes. Working electrodes were rinsed with copious amounts of milli-pore filtered water and dried under dry nitrogen jet. Cells were assembled as described in previous work. Briefly, thin
optically transparent thin electrochemical cells were prepared by sandwiching an insulated Pt wire (A-M Systems) quasi-reference electrode, Pt wire (Sigma Aldrich) counter electrode, and appropriate silicone spacers (Grace BioLabs) between the thin-film coated glass coverslip and a top glass coverslip. All electrolytes were prepared using ACS grade reagents (Sigma Aldrich). The cells were filled with desired electrolyte and pressure sealed using a custom sample holder to accommodate an oil immersion objective and dark-field condenser in an inverted microscope geometry.

### 3.2.4 Spectroelectrochemistry Experiments

Series of single-nanoantenna scattering spectra were acquired during time-correlated chronocoulometry and cyclic voltammetry experiments. Nanosphere monomers and dimers were excited by white light from a tungsten-halogen lamp through an oil immersion dark-field condenser. Light scattered by individual nanosphere monomers was collected by a variable NA 63× Plan Achromat oil immersion objective (Zeiss) on an inverted microscope (Zeiss Axio-Observer m1). Scattered light was directed to an Acton SpectraPro 2150i imaging spectrograph mounted atop a programmatically controlled linear translation stage (Newport). A custom control program (LabView, 2011) enabled the potential- and time-dependent collection of scattering spectra of individual nanosphere monomers and dimers under electrochemical potential control. For chronocoulometry experiments, potential steps were applied via the potentiostat (C.H. Instruments model 630D). For cyclic voltammetry, a sawtooth potential was applied to the working electrode.
and current passed from the working electrode was recorded in the form of a cyclic voltammogram. Single-nanoantenna spectral series and electrochemical measurements were temporally synchronized by a transistor-transistor logic (TTL) pulse supplied by the LabView automation and data acquisition program.

To account for differing optical transmission properties of the ITO and Au thin film spectroelectrochemical cells, the transmission spectra of a clean glass slide was compared to the transmission spectra of full spectroelectrochemical cells with each working electrode. The normalized transmission spectra are shown in Figure 3.1A. By dividing the normalized cell transmission spectra by that of the glass slide to correct for the emission spectrum of the lamp, the actual transmission spectra of each cell were obtained (Figure 3.1B).
Figure 3.1 - Normalized transmission spectrum of a glass slide compared to electrochemical cells built using ITO or Au thin film working electrodes. All spectra were acquired using illumination from a 100 W Tungsten-halogen lamp and were subsequently divided by the CCD dark counts. Spectra in A are close to the emission spectrum of the lamp. (B) By dividing the transmission spectrum of each cell by the Glass slide spectrum in A, the combined transmission spectra of the thin film and electrolyte was found.
Based on the early spectroelectrochemical reports on changes in Au film light scattering and absorption with applied potential, we used the same technique as in Figure 3.1 to measure changes in the Au film transmission spectrum as a function of applied potential. Across the entire spectral range, transmission of the Au film spectroelectrochemical cells was lower at anodic potentials than cathodic (Figure 3.2). The decrease in transmission was not uniform for all wavelengths, and reached a maximum difference at 515 nm. This observation is in accordance with electroreflectance studies which reported that the greatest normalized changes in reflectance at a gold/electrolyte interface upon potential modulation was at the 5d→6s interband transition (2.4 eV, 515 nm).166

Figure 3.2 - Transmission spectrum of electrochemical cell built with Au film and 0.1 M NaSO4 as a function of applied potential. (A) The transmission spectrum through an Au film electrochemical cell was collected at both -0.4
and 0.4 V. Dark counts were subtracted from both spectra and were subsequently divided by the lamp standard as described in Figure 3.1.

3.3 Results

Single-nanoantenna spectroelectrochemistry, in which scattering spectra of individual nanoantennas were collected under electrochemical potential control, revealed that the optoelectronic properties of the substrate played a critical role in sensing sulfate electroadsorption (Figure 3.3). We deposited Au nanosphere monomers and dimers onto two optically transparent conductive substrates to test the role of the substrate in plasmonic adsorbate sensing. The first substrate was commercial tin-doped indium oxide film (ITO, ~140 nm thick, Evaporative Coatings, Inc.) on a glass coverslip. ITO is a popular substrate in nanoparticle spectroelectrochemistry due to its broad transparency window (UV-NIR) and its impressive chemical, optical, and electronic stability in the often harsh conditions of electrochemical cells. The second substrate was composed of a 20 nm Au thin film evaporated onto a glass coverslip. An underlying 2 nm Ti adhesion layer was first deposited to ensure film quality. In contrast to the non-interactive relationship between nanoparticle plasmons and ITO, Au thin film plasmons and nanoparticle plasmons interact strongly to produce rich optical properties. Also unlike the ITO substrate, anions readily adsorb to gold at anodic potentials causing large changes in optical and electronic properties of the thin film. Nanosphere monomers and chemically assembled dimers were deposited onto the two substrates, and surface ligands were chemically removed from the monomers and dimers to leave the nanoantennas in electrical contact with the
substrates (Section 3.2.3).\textsuperscript{174} The thin film substrates with attached nanosphere monomers and dimers were then used as the working electrode in thin optically transparent three-electrode spectroelectrochemical cells (Figure 3.3A, Section 3.2.3).\textsuperscript{16, 59, 61, 93} Pt wires formed a quasi-reference electrode and counter-electrode.\textsuperscript{177} Cells were filled with 0.1 M Na$_2$SO$_4$ electrolyte, allowing the bare nanoparticles and conductive substrates to be directly accessed by ions in the electrolyte solution.

By controlling the electrochemical potential difference between the working electrode and the reference electrode via a potentiostat, sulfate ions were reversibly electroadorsbed to the Au surfaces of the working electrode.\textsuperscript{99-100, 148, 175} From the results of \textit{in situ} FTIR spectroscopy and cyclic voltammetry of sulfate adsorption on polycrystalline Au,\textsuperscript{148} the predicted equilibrium potential for sulfate adsorption in our cells was 140 mV vs. Pt. Thus, for static measurements, we chose potentials straddling this equilibrium potential to clearly distinguish sulfate adsorption state based on applied potential (-0.4 V, desorbed; +0.4 V, adsorbed). The effects of potential-driven adsorption and desorption of sulfate were observed in bulk electrochemical measurements.
Figure 3.3 - The effects of reversible potential-controlled sulfate electroadsorption on plasmonic nanoantennas was strongly substrate-dependent. Diagram of transparent spectroelectrochemical cell for single-nanoantenna spectroscopy with counter, reference, and working electrodes (CE, RE, WE).

Our spectroscopic method detected changes in the scattering spectra of individual nanoantennas as a function of applied potential (Figure 3.3 B,C). Based on the work of Persson,\textsuperscript{89} Henglein,\textsuperscript{90-92} and many researchers since,\textsuperscript{16, 82-83, 87} we interpreted the potential-dependent spectral changes as increased electronic damping of surface plasmons and adsorbate induced shifts in local dielectric coefficient due to reversible sulfate electroadsorption.\textsuperscript{16, 51, 89-90}
Potential dependent changes in the scattering spectra for nanosphere monomers and dimers on ITO substrate were measureable but very small (Figure 3.3B). Scattering spectra of sphere monomers on ITO showed one dipolar plasmon resonance mode (Figure 3.3B, top), while dimers showed two modes – a hybridized bonding dipolar mode (~1.9 eV) and a higher energy transverse mode (Figure 3.3B, bottom). Because ITO is incapable of supporting optical frequency currents, electronic coupling between the adjacent nanospheres of the dimer was capacitive. Single-nanoantenna spectra of both geometries were collected and fit with single or double-Lorentzian functions to find the resonance energy \( E \), full-width at half maximum \( \Gamma \) and intensity \( I \) as a function of applied potential (Section 3.2.4). For all 11 nanosphere monomers measured, the plasmon resonance red shifted \( \Delta E = -5.0 \pm 0.6 \) meV, broadened \( \Delta \Gamma = 4.6 \pm 0.7 \) meV, and decreased in intensity, \( \Delta I = -2.6 \pm 0.3\% \). As expected, the dimer’s longitudinal mode had larger mean changes for the 16 dimers measured, \( \Delta E = -11.7 \pm 1.0 \) meV, \( \Delta \Gamma = 14.8 \pm 1.1 \) meV, \( \Delta I = -8.6 \pm 0.9\% \). The increased sensitivity to local dielectric changes of the dimer’s longitudinal bonding mode is well known from its use as a refractive index sensor.

In contrast to the measureable but very small responses of the nanoantennas on ITO, the potential-dependent changes in the scattering spectrum of nanosphere monomers dimers on Au thin film was very large (Figure 3.3C). The sphere monomer on film system has been the subject of many recent experimental and theoretical studies. For consistency, we use the terminology of the plasmon hybridization model for discrete localized surface plasmon states interacting with the Au thin film surface plasmon continuum of states. Under our dark-field excitation geometry (57°
unpolarized white light), the $m = 0$ hybridized plasmons (perpendicular to Au film surface) were excited, resulting in a prominent low energy hybridized plasmon mode at $\sim 1.6$ eV (Figure 3.3C, top).\cite{33, 35} Because the thickness of the film is significantly smaller than the nanoparticle diameter, the film cannot fully support the well-known image charge bonding dipolar mode.\cite{33, 35, 158} However, because the thin film plasmonic density of states varies with thickness, the degree of hybridization can be engineered through the relative dimensions of the sphere and film.\cite{35} Specifically, the low energy hybridized mode red shifts strongly with decreasing film thickness in relation to nanoparticle radius.\cite{33, 35} Using this knowledge, we used a 20 nm Au film in conjunction with a 50 nm diameter sphere to retain the low energy mode’s resonance energy within our silicon photodetector’s spectral detection range (1.2 to 3 eV) to enable this study.

In addition to the design tunability, the optoelectronic properties of the Au film can also be tuned \textit{in situ} by the potential-induced adsorption of sulfate and other anions.\cite{98, 100, 148, 167, 176} Indeed, the bulk transmission spectrum of the Au film substrate was found to decrease at anodic potentials, with the maximum fractional change occurring around the interband transition energy (Figure 3.2), in agreement with classic electroreflectance literature.\cite{166, 179} Switching from cathodic to anodic potentials, the low energy hybridized mode showed large spectral shifts (Figure 3.3C, top), likely due to changes in the plasmonic density of states of the Au film.\cite{31, 35, 102, 180} For the 10 monomers measured, the low energy hybridized mode responded strongly to sulfate adsorption, $\Delta E = -24.2 \pm 1.8$ meV, $\Delta \Gamma = -30.6 \pm 6.2$ meV, $\Delta I = -20.7 \pm 1.7\%$. The consistent decrease in $\Gamma$ at anodic potentials is an important observation in that the application of anodic potentials typically leads to a broadening of nanoparticle plasmon
To reconcile the narrowing of the low energy hybridized mode at anodic potentials, recall that plasmon hybridization theory predicts that the overlap between thin film plasmonic density of states and the discrete nanoparticle plasmonic states controls the degree of hybridization. According to this model, the observed narrowing of the hybridized mode would imply a stronger interaction due to increased overlap of states. Electrochemical tuning of a sphere/film system has not been modelled in the literature, but may merit theoretical study for its potential to probe changes in the plasmonic density of states using an experimentally feasible system with simple yet highly tunable geometry.

Unlike the ITO substrate, the Au thin film substrate supports optical frequency electrical currents, so Au sphere dimers on the metallic substrate supported oscillating charge transfer between nanoparticles. The substrate-mediated screening current resulted in a longitudinal screened bonding (SB) dipolar plasmon mode at significantly higher resonance energy than the unscreened longitudinal bonding mode of the dimers on ITO (Figure 3.3C, bottom). Theoretical and experimental studies have shown that the resonance energy and absorption cross-section of the SB mode can be tuned via the optical-frequency electrical conductivity of the substrate. Anodic sulfate adsorption on Au film is known to decrease electrical conductivity of the film due to adsorbate scattering, so we posited that changes in the SB mode scattering properties should report strongly on potential-induced sulfate adsorption. Liu et al. predicted that with decreasing electrical conductivity of the conductive pathway, the SB mode should red shift, broaden, and show decreased scattering intensity. Our experimental observations of the SB mode perfectly match their theoretical predictions.
For all 9 dimers measured, the SB mode responded strongly to anodic potential application, \( \Delta E = -18.3 \pm 0.9 \text{ meV}, \Delta \Gamma = 20.3 \pm 1.8 \text{ meV}, \Delta I = -25.3 \pm 0.8\% \).

Comparing the potential-induced spectral responses by substrate, both monomers and dimers on Au thin film had much larger changes than those on ITO (Figure 3.3B,C). The low energy hybridized mode of the monomer on Au film had the largest mean resonance energy shifts, while the dimers on Au film had the largest mean intensity modulation. Due primarily to the lower transmission of the Au film (~60% of that of ITO film, Figure 3.2B) and the much larger scattering cross-section of nanosphere dimers than monomers, \(^{32,147}\) dimer scattering spectra were significantly easier to acquire, especially at anodic potentials where scattering intensity was greatly decreased. The differences in spectral quality can be qualitatively ascertained from the relative noise levels in the normalized scattering spectra of Figure 3.3C. Quantitatively, the signal to noise ratio for a typical monomer/film low energy hybridized mode at its resonance peak ranged from 9 to 29 (at +0.4 V and -0.4 V), while the screened bonding mode of a dimer on Au film had signal to noise ratios ranging from 42 to 91 under identical experimental conditions. For its strong potential-controlled spectral response and high signal to noise ratio, the dimer on Au film was chosen for dynamic potential-resolved sulfate adsorption sensing.

Changes in scattering spectra of an individual dimer on Au film during a cyclic voltammetry (CV) experiment were used to detect the dynamic spectral response from potential-controlled sulfate electroadsorption and desorption (Figure 3.4). The electrochemical potential was swept linearly at 10 mV/s between -0.4 and 0.6 V for 5 full cycles while scattering spectra were recorded every four seconds. The scattering spectra
for the dimer changed dramatically with potential, predominantly through the broadening and attenuation of the SB mode (Figure 3.4A). However, the background scattering of the Au film itself was found to not change with applied potential.

Figure 3.4 - Dynamic spectral response of a dimer on Au film during reversible potential-controlled sulfate adsorption/desorption. (A) Scattering spectra of a dimer
on Au thin film at cathodic (left) and anodic potentials (right). (B) Mean changes in $E$, $\Gamma$, and $I$ over 5 cycles for SB mode (red) and T mode (blue) relative to values at -0.4 V. (C) Bulk current as a function of potential showing sulfate adsorption and desorption along with hydrogen related reactions (black). Dimer SB mode - $dI/d\Phi$ as a function of potential (red). Signal inverted for clarity.

Potential-dependent changes in the Lorentzian fits for both plasmon modes indicate that $E$, $\Gamma$, $I$ all exhibited well-defined steps corresponding to the adsorption and desorption of sulfate, as measured through conventional CV (Figure 3.4B,C). $\Delta E$, $\Delta \Gamma$, and $\Delta I$ of both modes traced out reversible highly hysteretic trajectories. We and others have previously found that changes in slope of the Lorentzian fit parameters of single-nanoantenna spectra during electrochemical potential sweeps can be related directly to the onset of chemical reactions.\textsuperscript{16, 61, 87} Rather than evaluating the slope over segmented potential ranges, we aimed to visualize the dynamic spectral response to sulfate adsorption and desorption by calculating the slope at all potentials. Because of the high signal to noise ratio and applicability to intensity-based sensing, we focused primarily on the fluctuations of the SB mode scattering intensity.

The potential-dependent rate of change in the SB mode intensity was found to coincide with the adsorption and desorption of sulfate as measured using conventional CV (Figure 3.4C). Conventional CV of the Au film/Au nanoparticle working electrode clearly showed the adsorption and desorption of sulfate along with protonation, hydrogen evolution reaction (HER), and deprotonation of the entire working electrode (black line). Just as the voltammogram is the time-derivative of the coulomogram (charge passed at the entire working electrode as a function of time or potential), we took a two-point differential of the SB mode peak scattering intensity to obtain $dI/d\Phi$. Using the
directionality (shown by arrows in all plots) and known potential, we can clearly identify the peaks associated with adsorption and desorption of sulfate ions (Figure 3.4C). Recalling the predicted sulfate adsorption potential of 140 mV,\textsuperscript{148} we see excellent agreement between literature values, our single-nanoantenna CV analog, and concurrently measured conventional CV. A similar differential approach was used to establish a bulk surface plasmon based electrochemical sensor using macroscopic gold diffraction grating electrodes and observed changes in the surface plasmon polariton wavevector.\textsuperscript{176}

Using our single-nanoantenna CV analog, we can relate the electrochemical activity at the single-nanoantenna level to that of conventional CV. It is important to note that $dI/d\Phi$ does not report strongly on the protonation, HER, or deprotonation of the gold electrode surfaces as the conventional CV (Figure 3.4C). Bulk studies on similar systems have reported the same insensitivity to hydrogen-related reactions.\textsuperscript{176} Likewise, conventional CV has a large non-faradaic component corresponding to the charging of the electrochemical capacitor.\textsuperscript{113} This time-dependent charging current is not immediately apparent in the single-nanoantenna CV analog. The spectral responses to charge density tuning alone have been found to be significantly smaller and are linear in potential over a broad range, in accordance with the Drude model.\textsuperscript{16, 51, 59, 61} Because the plasmonic response to anion adsorption is significantly larger than that of charge density tuning, the single-nanoantenna CV analog minimizes this deleterious effect present in conventional CV. The natural combination of conventional CV and the single nanoantenna CV analog allows researchers to separate the role of non-faradaic currents in the electrochemical cell circuit and relevant reactions taking place at individual nanoelectrodes.
The sensitivity of the single-nanoantenna CV analog was tested for the potential-induced adsorption and desorption of two other polyoxyanions, acetate and perchlorate and performed equally well (Figure 3.5). Adsorption of perchlorate and acetate on bulk gold electrodes have also been successfully characterized via bulk spectroelectrochemical techniques.\textsuperscript{182-183} Identical electrochemical cells were prepared with 50 nm dimers on 20 nm Au thin film working electrodes with 0.1 M sodium acetate electrolyte (Figure 3.5A). As in the case of sulfate, a large cathodic current is present for the protonation of the Au film electrode and HER.\textsuperscript{176} Just as the case for sulfate adsorption, clear acetate adsorption and desorption peaks are present with much smaller signal from the hydrogen-related reactions and secondary reactions.

![Figure 3.5](image)

**Figure 3.5 - Comparison between conventional CV and single-nanoantenna CV analog for alternate anion adsorbates.** (A) CV with assigned oxidation and reduction waves for sodium sulfate (black). Concurrently acquired single-nanoantenna CV analog (red). (B) CV (black) and single-nanoantenna CV analog (red) for NaClO\textsubscript{4}. Arrows indicate scan direction.
Further tests demonstrated that the single-nanoantenna CV analog is also sensitive to perchlorate adsorption (Figure 3.5B). In the case of 0.1 M sodium perchlorate electrolyte, our use of a Pt quasi-reference electrode resulted in the interrogation of a potential range more positive than in the cases of sulfate and acetate. In sulfate and acetate electrolytes, the reference electrode operated on the same principle as the reversible hydrogen electrode, with the reference reaction being the reversible oxidation and reduction of hydrogen at the platinum surface. However, because perchlorate specifically adsorbs to Pt, this interaction served as the reference reaction. The difference between the two cases can be seen by the absence of the familiar protonation and HER currents at negative potentials in Figure 3.5B. Despite this difference in electrochemical potential window, the modulation of the SB mode intensity still reproduced the adsorption and desorption of perchlorate on the Au surfaces, in agreement with the conventional CV (Figure 3.5B).

Because the single-nanoantenna CV analog technique relies on large fluctuations in the SB mode intensity, it is most sensitive to potential-induced events causing large changes film conductivity and surface plasmon damping. As such, the single-nanoantenna technique is most sensitive to the initial adsorption of ions and not secondary reactions such as higher complexation (Figure 3.4C, Figure 3.5). For sulfate and acetate, the rates of adsorption and desorption are similar, as visible from the similar amplitude of oxidation and reduction waves (Figure 3.4C and Figure 3.5A). However, the rate of perchlorate desorption leads to peak reduction current more than twice that of initial adsorption peak current (black line, Figure 3.5B). This rate asymmetry is preserved in the single-nanoantenna CV analog, suggesting that the temporal response of
the scattering spectra may be useful in single-nanoantenna electrochemical kinetics studies given appropriate instrumentation and experiment design (red line, Figure 3.5B).

The same differential technique applied to the total scattering intensity an individual dimer on Au film yielded similar results to that utilizing the dimer’s SB mode intensity (Figure 3.6). In the current work, instrumentation, targets, and experimental conditions were designed to optimize signal quality and temporal stability for the purpose of dynamically measuring small changes in single-nanoantenna scattering spectra. The experimental geometry and conditions necessary for these measurements can limit the applicability of single-nanoantenna spectroelectrochemical techniques. One way to circumvent the experimental complexity and associated limitations is to develop techniques based on the total scattering intensity fluctuation rather than precise changes in multicomponent scattering spectra. The ability to monitor chemical processes at single nanoelectrodes using intensity fluctuation rather than spectral measurements would be both useful and convenient for wide-field monitoring of many nanoelectrodes in parallel.

To test the functionality and potential of using total intensity fluctuations as a method for single-nanoantenna electroadsorbate sensing, we integrated the scattering spectrum over the visible range and compared the rate of total intensity fluctuation to conventional CV (Figure 3.6).
Figure 3.6 - Comparison between conventional CV and total scattering intensity fluctuation based single-nanoantenna CV analog for: (A) 0.1 M Na$_2$SO$_4$, (B) 0.1 M NaC$_2$H$_3$O$_2$, (C) 0.1 M NaClO$_4$. The differential of total scattering intensity integrated from 500 to 800 nm as a function of potential is shown in blue (signal inverted for clarity). Conventional CV is shown in black. All potentials reported vs. Pt. quasi-reference electrode. Arrows indicate scan direction.

The adsorption and desorption features for sulfate, acetate, and perchlorate were largely reproduced. However, we found that that especially in the case of perchlorate, the rates of total scattering intensity fluctuation did not mimic the electrochemical current amplitude as closely as the SB mode intensity (Figure 3.6C vs. Figure 3.5B). The decreased total modulation of the total integrated intensity is due to the relative inactivity but still significant spectral weight of the transverse mode (Figure 3.4A,B). Future
experiments using anisotropic nanoantennas, such as lithographically produced dimers, could easily improve modulation depth by using light polarized along the longitudinal optical axis. Nevertheless, this proof of concept demonstrates that with sufficient knowledge of the spectroelectrochemical properties of a system, electrochemical reaction sensing could be performed for plasmonic nanoelectrodes via total intensity fluctuation measurements, allowing less restrictive experimental design and better temporal resolution.

3.4 Conclusions

In this work, we employed dynamic single-nanoantenna scattering spectroelectrochemistry to investigate the plasmonic response to sulfate adsorption of Au nanosphere monomers and dimers on ITO and Au thin film substrates. We found that the response of individual nanosphere monomers on ITO was detectable but very small. In contrast, the low energy hybridized plasmon mode of nanospheres on Au film was very sensitive to sulfate adsorption on the Au surfaces. The longitudinal bonding mode of dimers on ITO showed larger spectral shifts than monomers. Dimers on Au thin film showed even larger shifts, including high intensity modulation with sulfate adsorption and desorption. Using dynamic high-resolution spectroscopy of a single dimer on Au film during CV, we constructed a differential single-nanoantenna CV analog to track anion adsorption/desorption dynamically. Using fluctuations in the dimer’s SB mode scattering intensity, we identified the onset of sulfate, acetate, and perchlorate adsorption and desorption, in agreement with literature values and conventional CV. Finally, we demonstrated that the same technique applied to the SB mode intensity can also be used
for the total scattering intensity of single dimers, an important breakthrough to guide future applications and experiment design.

### 3.5 Acknowledgements

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The optical properties of metallic nanoparticles, particularly when in close proximity to each other, are highly sensitive to interparticle distance, frequently giving rise to dramatic, irreversible color changes. By electrochemical modification of individual nanoparticles and nanoparticle pairs, we induced equally dramatic, yet reversible, changes in their optical properties. We achieved reversible plasmon tuning by oxidation - reduction chemistry of Ag - AgCl shells on the surfaces of both individual and strongly coupled Au nanoparticle pairs, resulting in extreme but

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reversible changes in scattering line shape. We demonstrated reversible formation of the charge transfer plasmon mode by switching between capacitive and conductive electronic coupling mechanisms. Dynamic single particle spectroelectrochemistry also gave insight into the reaction kinetics and evolution of the charge transfer plasmon in an electrochemically tunable structure. Our study represents a highly useful approach for precise tuning of the morphology of narrow interparticle gaps, and will be of value for controlling and activating a range of properties such as extreme plasmon modulation, nanoscopic plasmon switching, and sub-nanometer tunable gap applications.

4.1 Introduction

Active control of the optical and electronic properties of nanoparticles is critical for many future technological applications, yet remains largely elusive. Optical tunability of metallic nanoparticles can be achieved through exploiting the sensitivity of the localized surface plasmon. Researchers in pursuit of in situ active control have employed electronic \(^ {55, 185}\), chemical \(^ {60}\), and electrochemical approaches. \(^ {16, 59, 61, 82, 87, 139}\) Recent electrochemical efforts have either resulted in small reversible modulation, \(^ {59, 61}\) or large irreversible plasmon shifts. \(^ {93, 186}\) One strategy towards achieving larger plasmon resonance shifts is through tuning the plasmon coupling strength between adjacent nanostructures. Modest tunability of the capacitive coupling between nanoparticles was achieved with lithographically prepared dimers on an elastomeric substrate by stretching the substrate. \(^ {37, 53}\) For strongly coupled nanoparticles (gaps < 1 nm), quantum effects
strongly influence the optical response and electron tunneling conductance between nanostructures depends exponentially on the gap width. If the gap is further decreased until the structures are within tunneling contact, optical-frequency electrical currents can flow through the entire joined structure, resulting in the emergence of new plasmon modes in the visible and near-IR. Transitions from capacitive to conductive coupling produce enormous spectral changes, but so far all in situ fully nanoscopic methods have been irreversible. To date, reversible tuning between capacitive and conductive plasmon coupling has only been achieved for one nanostructure at a time using nanpositioners. Significant challenges still remain for active nanophotonic control over a broad optical range.

In this report we demonstrate reversible, active plasmon control through electrochemical reduction and chloridation of Ag metal on both isolated Au nanoparticles and strongly coupled Au nanoparticle dimers. Large changes in nanoparticle optical spectra are typically irreversible, but here we demonstrate a simple and robust chemical mechanism to cause large reversible changes in nanoparticle optical properties. We tune the optical and electronic properties by electrochemically controlling the nanostructure morphology, chemical composition, electronic coupling strength, and ultimately the fundamental coupling mechanism. We initially demonstrate reversible tuning of the localized surface plasmon resonance of individual core-shell Au/Ag nanoparticles through Ag redox electrochemistry, the fundamentals of which have only recently been demonstrated (Au/Ag denotes gold core with silver shell). Here, the well-known Ag - AgCl redox chemistry allows for reversible resonance energy shifts an order of magnitude larger and intensity modulation three orders of magnitude larger than charge
density tuning. We then reversibly tune the hybridized bonding plasmon mode of strongly coupled individual Au/Ag nanoparticle dimers. Finally, by electrochemically bridging the inter-particle gap, we demonstrate fully reversible transitions between capacitive and conductive coupling regimes, as evidenced by the dynamic evolution of the charge transfer plasmon (CTP) mode. Our study represents the first demonstration of active switching between these two coupling regimes on individual nanoparticle pairs in a completely nanoscopic system as well as the first reported switchable and tunable CTP. These advances will provide a valuable tool for precise gap control and plasmon tuning, of importance for both the development of active plasmonic devices such as switches and modulators as emphasized here, and more broadly for the emerging field of quantum plasmonics which relies on precise gap control.

4.2 Materials and Methods

4.2.1 Dimer preparation

Au nanoparticle dimers were prepared using a nonspecific aggregation method and electrophoretic enrichment as described previously.\(^{194}\) 500 μL of stock citrate-stabilized 50 nm Au colloids (BBI Solutions) were once washed with Millipore filtered deionized water and concentrated to a volume of 50 μL by centrifugation at 1400 \( \text{rcf} \) for 5 min. 200 μL of acetonitrile was added to the suspension and stirred for 30 min. 5 μL of 10 mM 11-mercaptoundecanoic acid (11-MUA, Sigma) was added, followed by 30 min. of stirring. The solution was centrifuged and supernatant was removed. Sedimented nanoparticles and aggregates were re-suspended in 500 μL Millipore filtered deionized
water followed by another washing and concentration to a volume of 50 μL. 10 μL 40 w/v% aqueous solution was added to facilitate horizontal gel electrophoretic separation of aggregates consisting of various numbers of nanoparticles. Samples were electrophoretically separated in 1% agarose gel at 135 V for 30 minutes in 0.5X TAE Buffer. The second band was manually removed with a razor blade and aggregates and single nanoparticles in the removed gel were removed using a published electroelution method at 250 V. Extracted nanoparticles and aggregates were centrifuged, washed and concentrated for deposition. TEM analysis showed that the resulting solution contained 23% dimers with gap widths ranging from 1 to 5 nm. TEM images of single nanoparticles in prepared dimer solutions were analyzed to find average cross sectional area, using an algorithm adapted from Gontard et al.\textsuperscript{195} Identical procedures were followed using 40 nm Au colloids (BBI Solutions) to produce smaller dimers.

4.2.2 Electrochemical cell preparation

Single nanoparticles and dimers were drop cast onto indium tin oxide (ITO) coated coverslips and washed to remove excess nanoparticles. 11-MUA was removed from the nanoparticles by soaking in a NH$_4$OH:H$_2$O$_2$:H$_2$O solution of volume ratio 2.3:1:38.6 for 10 minutes at 40º C.\textsuperscript{174} Samples were then rinsed thoroughly with water and dried with nitrogen gas. Optically transparent sealed thin electrochemical cells were constructed using the hybrid ITO Au nanoparticle substrate as a working electrode. An insulated 0.05 mm diameter platinum wire was used as a quasi-reference electrode (A-M Systems). The counter electrode was formed by either a clean platinum or anodically chloridized Ag wire (Sigma Aldrich). All electrolytes were prepared using ACS grade
reagents (Sigma Aldrich). In the case of the Ag/AgCl counter electrode, Ag chloro-complexes were dissolved into the NaCl host electrolyte. Ag was electrodeposited onto bare Au nanoparticles and dimers.

4.2.3 Dark field scattering measurements

Single-particle and single-dimer spectra were collected on a custom instrument described previously. In short, spectra from individual scatterers were collected on an inverted dark-field microscope (Zeiss AxioObserver m1, with oil immersion dark field condenser and oil immersion Zeiss Plan-Achromat 63x, NA 0.7-1.4). Light was directed to an Acton SpectraPro 2150i imaging spectrograph mounted atop a programmatically controlled linear translation stage (Newport, model LTA-HL). A control program (Labview, 2011) linked incoming spectra with an electrochemical workstation (CH Instruments, Model 630D) allowing time/potential–correlated dynamic spectroelectrochemcial measurements. A nonlinear least squares fitting algorithm (Matlab 2013a) was used to fit single- and double-Lorentzian curves to single nanoparticle and dimer scattering spectra, respectively.

4.2.4 Electron microscopy and spectroscopy

4.2.4.1 Au nanoparticle and dimer TEM sample preparation

10 μL of an aqueous suspension containing 11-MUA coated 50 nm diameter gold nanoparticles and dimers was drop cast onto a 300 mesh Cu TEM grid pre-coated with lacey carbon films from Pacific Grid Tech (Cu-300LD) and dried in air.
4.2.4.2 Au@Ag Core-Shell nanoparticle and dimer TEM sample preparation

2 μL of an aqueous suspension containing 11-MUA coated 50 nm diameter gold nanoparticles and dimers was drop cast onto a clean ITO-coated glass coverslip (ECI). 11-MUA was removed from the nanoparticles by soaking in a NH₄OH:H₂O₂:H₂O solution of volume ratio 1 : 2.3 : 38.6 for 10 minutes at 40º C. Au nanoparticles and dimers were coated in Ag electrochemically in the spectroelectrochemical cell. After disassembly of the spectroelectrochemical cell, Au-Ag core-shell nanoparticles and dimers were removed from their ITO support by sonication into 2 mM sodium citrate solution. 10 μL of the suspension was dried onto a 300 mesh Cu gridded ultrathin TEM grid pre-coated with lacy carbon films. Excess citrate was rinsed with running Milli-Q filtered deionized water, and grids were dried with dry nitrogen.

4.2.4.3 Au nanoparticle and dimer SEM sample preparation

2 μL of an aqueous suspension containing 11-MUA coated 50 nm diameter gold nanoparticles and dimers was drop cast onto a clean ITO-coated glass coverslip (ECI). 11-MUA was removed from the nanoparticles by soaking in a H₂O₂ : NH₄OH : H₂O solution of volume ratio 1 : 2.3 : 38.6 for 10 minutes at 40º C. Au nanoparticles and dimers were cycled 50 times between -0.5 and 0.5 V in 100 mM NaCl electrolyte with no silver present. The spectroelectrochemical cell was disassembled and the ITO working electrode was rinsed with running Milli-Q filtered deionized water and dried with dry nitrogen.
4.2.4.4 Au@Ag nanoparticle and dimer SEM sample preparation

2 μL of an aqueous suspension containing 11-MUA coated 50 nm diameter gold nanoparticles and dimers was drop cast onto a clean ITO-coated glass coverslip (ECI). 11-MUA was removed from the nanoparticles by soaking in a NH₄OH:H₂O₂:H₂O solution of volume ratio 1 : 2.3 : 38.6 for 10 minutes at 40º C. Au nanoparticles and dimers were coated in Ag electrochemically. The spectroelectrochemical cell was disassembled and the ITO working electrode was rinsed with running Milli-Q filtered deionized water and dried with dry nitrogen.

4.2.4.5 SEM methods

Scanning electron micrographs (SEM) were taken with FEI Quanta 650 FEG ESEM with beam energy of 30.0 kV. All images were taken directly from the ITO working electrode after the sample preparation described in Sections 4.2.2 and 4.2.3.

4.2.4.6 TEM methods

Transmission electron microscope (TEM) images were taken with a JEOL-2100F field emission electron microscope operated at 200 kV. High angle annular dark field scanning transmission electron micrographs (HAADF-STEM) were taken using a Gatan 806 detector. Energy-dispersive X-ray spectroscopy (EDS) was performed using an Oxford Instruments EDS INCA x-sight detector and data was collected using the INCA software. Raw data from STEM-EDS was processed using HyperSpy (open source, available at www.hyperspy.org) multidimensional data analysis toolbox version 0.8. EDS
elemental maps were produced from background subtracted Au-\(M\alpha_1\) (2.12 keV) and Ag-\(L\alpha_1\) (2.98 keV) X-ray peaks using FIJI (open source, available at http://Fiji.sc/Fiji).

### 4.2.5 Simulation methods

Modeling and simulations were performed by using the Finite Element Method (COMSOL Multiphysics). An effective medium approximation was employed under homogenous refractive index as 
\[ n = \sqrt{\frac{n_{\text{water}}^2 + n_{\text{ITO}}^2}{2}} \]
where \(n_{\text{water}} = 1.33\) and \(n_{\text{ITO}} = 1.97\). The Au dimer structure consisted of two spheres with 48 nm center-to-center distance as measured by TEM (Figure 4.2). Because of non-uniform sizes of nanoparticles (Figure 4.2), a 44 nm diameter Au dimer is adopted in Figure 4.3 to match experiments, while Figure 4.5 uses 45 nm diameter Au dimers. The core-shell system investigated was an Au-core-Ag\(\_\alpha\) AgCl\(_{1-\alpha}\)-shell system with different shell thicknesses varying from 0 nm (pure Au dimer) to 1.6 nm (overlapping shell case with 0.4 nm radius rounding). The 1.5 nm shell case corresponds to the touching geometry. In order to show the evolution of modes with increasing Ag content of the bridged structure, we adopted the real experimental conditions in Figure 4.7 and Figure 4.8 (water medium, ITO substrate, and 40 nm diameter Au cores). The dielectric functions of Au and Ag were taken from Johnson & Christy\(^{197}\) which has been widely used for Au and Ag nanomaterials. The refractive index of AgCl was taken to be \(n = 2.02\) from White\(^{198}\) and Tilton\(^{199}\). Finally, an averaging procedure over a non-normal incident (56.4°) light cone was performed so that the simulation results can be directly compared with dark field scattering spectra.
4.3 Reversible electrochemical redox tuning of Au@Ag nanoparticles

We employed single-nanoparticle spectroelectrochemistry, specifically the redox chemistry of Ag/AgCl to actively tune the intensity, spectral line shape, and resonance energy of single Au/Ag nanoparticles (Figure 4.1). Ag chloro-complex ions were produced anodically from an Ag/AgCl counter electrode and reduced on cathodically polarized bare Au 50 nm spherical nanoparticles to form Au/Ag core-shell nanoparticles in a transparent spectroelectrochemical cell. The light-scattering properties of Au/Ag nanoparticles were reversibly tuned by repeatedly converting the shell between Ag and AgCl through electrochemical potential cycling (Figure 4.1).

Figure 4.1 - Reversible redox tuning of Au/Ag nanoparticles. (A) Nanoparticle shells were reversibly switched between Ag and AgCl using redox
electrochemistry. The optical response to redox tuning was measured using single-particle spectroscopy under electrochemical potential control. (B) HAADF-STEM and EDS elemental maps of a single Au/Ag nanoparticle show clear core-shell geometry. (C) Mean response over five cycles of changes in resonance energy ($\Delta E$), full width at half maximum ($\Delta \Gamma$), and intensity ($\Delta I$) as a function of applied potential at different electrolyte conditions. Inset shows small intensity response for control and thin shell cases. Shaded bounds indicate standard error.

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS) elemental maps showed clear core-shell structure of the Au/Ag nanoparticles (Figure 4.1B).

Multiple series of scattering spectra of individual Au/Ag nanoparticles were collected during cyclic voltammetry experiments. Scattering spectra displayed well-defined potential-dependent plasmon resonance energy ($E$), full width at half maximum ($\Gamma$), and intensity ($I$) (Figure 4.1C). Recently, others have shown that under specific electrolyte conditions, electrochemical oxidation of pure Ag nanoparticles resulted in complete oxidation and dissolution of the nanoparticles. In contrast, the use of the core-shell geometry and the inclusion of chloride ions in our system allowed reversible tuning between two stable states with well-defined optical properties. Here the different oxidation potentials of Ag and Au allowed us to electrochemically modify the Au/Ag nanoparticle to Au/AgCl. Mean changes of $E$, $\Gamma$, and $I$ were compared as a function of potential over five cycles (Figure 4.1C) for three different cell conditions: a bare Au nanoparticle in a cell with Pt reference and counter electrodes, thus containing no Ag (black), an Au nanoparticle in the presence of a low concentration (pink) and higher concentration (blue) Ag chloro-complex solution, achieved by using a Ag counter
electrode and tuning the Cl\textsuperscript{−} electrolyte concentration. In the control sample containing no Ag, \(E\), \(\Gamma\), and \(I\) showed small linear shifts with applied potential due to electrochemically induced charge density tuning as previously reported\(^{59,61}\). In contrast, redox tuning the Ag shells of Au/Ag nanoparticles resulted in nonlinear plasmon resonance shifts. At low Cl\textsuperscript{−} concentration, and therefore low Ag chloro-complex concentration, redox tuning induced much larger shifts than charge density tuning alone. Increasing Cl\textsuperscript{−} concentration by a factor of 10 to 1 M raised the Ag chloro-complex solubility nearly thirty-fold\(^{193}\), which led to much larger shifts because of increased Ag shell thickness. Therefore, the extent of reversible optical tuning is directly controllable via the salt concentration.

At 1 M NaCl and negative applied potentials where AgCl is reduced to Ag, we observed spectral blue shifts of 15 meV followed by large red shifts (50 meV, blue lines in Figure 4.1C). This complex response is the product of three competing mechanisms and their impacts on the nanoparticle plasmon: 1) In the AgCl shell case, the local refractive index seen by the nanoparticle plasmon is that of the AgCl dielectric shell. Once the shell is converted to Ag, the surface plasmon resides on the outer Ag surface and the medium refractive index is that of the surrounding electrolyte, resulting in a decrease from \(n_{\text{AgCl}}(s) = 2.02\)\(^{198-199}\) to \(n_{\text{electrolyte}} = 1.34\). The decrease in refractive index causes \(E\) and \(\Gamma\) to increase and \(I\) to decrease; 2) A change in nanoparticle optical properties as the dielectric AgCl is replaced by Ag metal that supports plasmon resonances in the visible. This effect causes \(E\) and \(I\) to increase, and \(\Gamma\) to decrease; 3) In the AgCl shell case, the surface plasmon resides on the Au core surface, but in the Ag shell case, the entire Au/Ag nanoparticle supports the plasmon oscillation. This increase in effective size and the elimination of the dielectric shell cause \(E\) to decrease and \(\Gamma\) and \(I\)
to increase. The opposite responses are expected when the Ag shell is converted back to AgCl. The first two mechanisms cause an initial blue shift, but as the Ag shell grows thicker, mechanism 3 causes a net red shift and increases in $\Gamma$ and $I$. In this system, our method of single-particle plasmon spectroelectrochemistry during cyclic voltammetry is crucial in analyzing nanoparticle plasmonic responses to chemical processes. Unlike cyclic voltammetry which measures the electric current passed to and from the entire working electrode, the potential-dependent plasmon resonances report on changes in composition, charge, damping, scattering cross-section, etc. of individual nanoparticles.

### 4.4 Redox tuning of strongly coupled nanoparticle dimers

The Ag-AgCl redox spectroelectrochemistry was extended to individual strongly coupled plasmonic dimers to take advantage of nonlinear gap effects. Dimers consisting nominally of 50 nm diameter Au nanoparticles were chemically assembled using a nonspecific aggregation method and enriched through electrophoretic separation.\(^1\)\(^9\), \(^2\)\(^0\)\(^5\) High resolution TEM micrographs revealed that Au dimers had gap widths ranging from 1 to 5 nm and mean core diameters of 45.5 nm with significant size and shape dispersity (Figure 4.2).
Figure 4.2 - Transmission electron micrographs showing the native structure of gold nanoparticle dimers and size analysis of single gold nanoparticles. a) TEM images of single nanoparticles in prepared dimer solutions were analyzed to find average cross sectional area, using an algorithm adapted from Gontard et al. The equivalent nanoparticle diameter $D$ was calculated in this manner for 513 nanoparticles to find a mean value of 45.5 ± 0.4 nm. b) The interparticle spacing was estimated from high resolution TEM images of individual dimers and ranged from 1 to 5 nm.

We hypothesized that the effective gap width of the dimers could be tuned by depositing a thin switchable Ag shell. Full-wave simulations using the Finite Element Method (FEM) showed that for Ag shells, the shell itself would dominate the optical response (Figure 4.3A, left). But when switched to AgCl, the Au cores should dominate (Figure 4.3A, right) (charge density maps generated at the plasmon resonance at 1.88 eV; additional details of FEM simulations can be found in Supplementary Materials). Charge primarily resides on the metallic Ag shells under electrochemically reducing conditions, and on the Au cores under oxidizing conditions, leading to a change in effective gap
width. The strong electric field enhancement caused by the cores also causes a visible polarization in the AgCl shell in the gap region (Figure 4.3A, bottom right). The nonlinear response to gap width change allows significant tuning of the longitudinal bonding (LB) dipolar plasmon mode.
Figure 4.3 - Dimer surface plasmon response to reversible electrochemical redox tuning. (A) Thin shells on strongly coupled Au dimers were reversibly switched between Ag and AgCl. Charge density maps of the core and shell surfaces show that the optical response is dominated by Au cores in Au/AgCl dimers, but by Ag shells in Au/Ag dimers. Maps were generated at 1.88 eV. (B) Scattering spectra during dynamic potential control shows clear modulation with changes in shell composition. (C) Mean longitudinal bonding (LB) mode $\Delta E$, $\Delta \Gamma$, and $\Delta I$ over 5 cycles as a function of applied potential. Shaded bounds indicate standard error (smaller than line width at most points).
The spectral response of an individual dimer’s LB mode to Ag shell redox tuning is compared to a bare Au dimer control (Figure 4.3C). In the absence of a redox-tunable Ag shell, $E$, $\Gamma$, and $I$ decreased linearly with increasing potential. These results are consistent with the single-nanoparticle charge density tuning described in Figure 4.1C (0.1 M NaCl, black lines) and reported previously.\textsuperscript{61} In stark contrast, the plasmonic response to redox tuning of Au/Ag dimers exhibited a large hysteretic response with $E$ strongly decreasing with increasingly negative potentials. This inverted trend is easily explained within the plasmon ruler model;\textsuperscript{72} as the gap between metallic surfaces decreases when AgCl salt shells are reduced to metallic Ag shells, capacitive plasmon coupling strongly increases (Figure 4.4).

![Figure 4.4 - Effects of increasing shell thickness for Ag and AgCl shells. Simulated scattering cross-sections demonstrating the effects of increasing shell thickness for both Ag and AgCl shells with constant Au core separation. In both shell compositions, increasing shell thickness leads to red shifting of the lower energy longitudinal mode due to the increase in capacitance of the dimer system. The larger red shift of Ag shell dimers compared with AgCl dimers is attributed to the narrowing of the gap width, increasing the](image-url)
capacitance of the system further. For AgCl shells, the transverse mode also red shifts with increasing shell thickness. For Ag shells, the higher energy feature shows a bimodal response with blue shifts, due to the increase of Ag content, up to 1.5 nm Ag thickness.

4.5 The plasmonic drawbridge: reversible switching between capacitive and conductive coupling

By further increasing the thickness of the Ag shells and applying sufficient step potentials, the coupling mechanism for nanoparticle dimers was reversibly switched between capacitive and conductive coupling (Figure 4.5). High resolution TEM imaging revealed the detailed structure of Au/Ag bridged dimers (Figure 4.5A). Under electrochemical potential control, the shell can be actively tuned between semiconducting AgCl and highly conductive metallic Ag. It is expected that as the advancing metallic surfaces of the nanoparticles approach contact, electron tunneling provides a charge transfer pathway between nanoparticles. Electrical contact of the two Au nanoparticles established through the Ag metal bridge results in oscillating current between the nanoparticles and multiple corresponding charge transfer plasmon modes.
Figure 4.5 - Reversible electrochemical tuning of a dimer between capacitive and conductive coupling. (A) Overlapping shells on Au dimers were switched between Ag and AgCl to create a switch between capacitive and conductive coupling. TEM image shows Au dimer enveloped by Ag shell. (B) Simulated and experimental scattering spectra show drastic optical response to switching plasmon coupling mechanism. (C) Series of scattering spectra during step potential application to switch shell composition. (D) Surface charge density plots of shell and core surfaces for screened bonding (SB) and longitudinal bonding (LB) modes. Charge plots were calculated at 2.0 eV for the SB mode and 1.67 eV for the LB mode.

Simulated and experimental spectra agree in the emergence of a new longitudinal screened bonding (SB) dipolar plasmon mode (Figure 4.5B). The SB mode is a longitudinal charge transfer plasmon mode, characterized by significant charge transfer between the Ag shells and a weak quadrupolar polarization of the cores. \(^{38, 42, 74-75, 187}\)
A series of scattering spectra of an individual Au/Ag dimer shows broad tuning of the plasmon modes in response to repeatedly forming and removing a conductive bridge between the Au cores (Figure 4.5C). The transition from capacitive to conductive coupling at negative bias is clearly visible with the emergence of significantly brighter shell-dominated SB and T modes (Figure 4.5C). By then applying a positive bias, conductive coupling was broken as the shell composition was switched to AgCl. This event is visible in the scattering spectra with the re-emergence of the core-dominated LB and T modes. This plasmonic “drawbridge” effect was reversible over at least 30 full cycles and was not observed to disappear or degrade. This effect was observed for all dimers studied and was clearly visible by eye in dark-field microscopy through changes in both color and intensity (Appendix). We also observed that the chloridation reaction (Ag → AgCl) under oxidizing potentials causes much faster spectral changes than the reduction reaction (AgCl → Ag) under reducing potentials. The asymmetric response rate may be due to sluggish Ag reduction kinetics as recently reported for the reduction of Ag ions from solution \(^{155}\).

As in the thin-shell case, simulations revealed that the Ag shell dominates the optical response in the reduced state, while the Au cores dominate in the oxidized state. Charge density plots demonstrate the relative contributions of the shells and cores for the two longitudinal modes, SB and LB (Figure 4.5D). For the SB mode, charge density on Ag shell surfaces are more than ten times greater than those of Au core surfaces (Figure 4.5D, left). For the LB mode, charges are distributed primarily on the Au core surfaces
with no current flowing between the two Au cores (Figure 4.5D, right). Again, the strong electric fields induce a visible polarization response in the AgCl shells near the gap (Figure 4.5D, bottom right).

By decreasing the size of the Au cores to 40 nm and the reductive overpotential, we characterized the spectral evolution of the pure CTP mode in addition to the SB and T modes for an individual dimer. FEM simulations correctly predicted that given the same Ag shell thickness and core separation distance, the CTP resonance energy blue shifts with decreasing Au core size due to a reduction in coupling between the Ag shells (Figure 4.6).

![Averaged Scattering vs. Energy](image)

**Figure 4.6** - Changes of averaged scattering spectra for various Au core sizes for Au/Ag bridged dimer structure. Ag shell thickness was fixed at 3nm, and the gap between Au cores was fixed at 5nm.
Additionally, by lowering the Ag/AgCl redox overpotentials, the rates of the chloridation and reduction reactions were decreased.\textsuperscript{113} The AgCl shell was slowly reduced to Ag by applying a step potential slightly more negative than the equilibrium potential (-0.22 V vs. Pt). Because of the smaller dimer, the pure CTP mode remained within the spectral detection range of our silicon photodetector. We clearly observed the formation of the SB mode at higher energy than the LB mode. The formation of the SB mode at roughly 42 s indicates the formation of a conductive pathway between the two lobes of the bridged dimer. As the shell is further converted to Ag, an increase in coupling between the Ag shells leads to a red shift of the CTP and SB modes (Figure 4.7A). Then, by switching to a chloridizing potential, the Ag shell was converted back to AgCl. As demonstrated for the larger bridged dimer (Figure 4.5), the charge density distribution for the longitudinal modes is dominated by the Ag shells. The calculated charge density plot of the CTP mode shows characteristic dipolar charge distribution on the Ag shell surface with charge strongly localized near the gap region (Figure 4.7A inset).
Figure 4.7 - Dynamic evolution of the charge transfer plasmon mode using 40 nm Au cores and decreased overpotential. (A) Experimental static (top) and dynamic (bottom) scattering observation of slow bridging evolution during conversion between AgCl and Ag shells for an individual Au/Ag dimer with 40 nm Au cores at -0.22 V. Inset: surface charge density plot of outer Ag shell surface for the CTP mode (calculated at 1.35 eV). (B) Predicted spectral evolution with electrochemical shell conversion from pure AgCl to pure Ag using isotropic dielectric mixing approximation. (C) CTP mode splitting in simulations using bridged concentric Ag growth mechanism, at the point of Ag shell overlap (full evolution shown in Figure 4.8b).

Detailed mechanistic information can be extracted from the slow evolution of the scattering spectrum during electrochemical conversion of the bridging shell. Soon after application of a reduction potential, a rapid red shift occurred along with the disappearance of the core-dominated LB and T modes (Figure 4.7A, bottom). This
corresponds to the increasing real part of the dielectric function of the shell with increasing Ag content and the corresponding dominance of the shell-dominated plasmon resonance modes. Later, the CTP and SB modes emerged at much higher energy than the LB mode due to the formation of a conductive pathway as mentioned above. With increasing Ag content, the CTP and SB modes grew in intensity and red shifted until the shells reach full Ag content. The red shifts of the capacitively coupled modes, especially their decreasing spectral weight, and the general evolution of the conductively coupled modes with increasing Ag content can be understood from full wave simulations using isotropic dielectric mixing of Ag and AgCl (Figure 4.7B).

With increasing Ag content (from top to bottom of Figure 4.7B) the core-dominated LB and T modes gradually red shift and fade away, just as observed in single-particle spectra. The calculated scattering spectra also show the same high energy origin and red shift of the CTP mode with increasing Ag content. At the present size, however, the SB and T modes lie at very similar resonance energies in the simulated spectra, precluding a clear analysis of their evolution.

Estimates of the electrochemical reaction rates are possible via the full experimental spectral response by assuming idealized spherical cores, 3 nm conformal overlapping shells, and full conversion of shells between AgCl and Ag. With these parameters, we calculate that AgCl was converted to Ag at a rate of ~2200 atoms/s, while in the oxidation step, Ag was converted to AgCl at ~8700 atoms/s. Even at a low reaction overpotential, the conversion from Ag to AgCl was still approximately four times faster than the reverse process under our experimental conditions. The asymmetric response
rates can be explained in terms of sluggish Ag reduction kinetics as recently reported for the reduction of Ag ions from solution\textsuperscript{155} or differences in active ion transport rates.\textsuperscript{206}

It is important to note that the experimental spectral evolution at the onset of conductive coupling indicates a short-lived intermediate, labeled CTP discontinuity in Figure 4.7A, which is not predicted by the isotropic dielectric mixing model. At roughly 75 s in Figure 4.7A, a new low energy spectral feature briefly developed at 1.7 eV. For three sequential exposures (7.5 s), only one low energy peak was visible, but was abruptly replaced by the return of two peaks. With further increase in Ag content of the shells, the two peaks gradually converged to form the CTP mode. Clearly, the isotropic dielectric mixing model of Figure 4.7B cannot address this evolution near the point of contact. Short-lived intermediates in the spectral evolution were also observed in other dimer bridging experiments. These results are similar to previous investigations of the fusion of small Ag nanoparticles using electron energy loss spectroscopy, which showed evidence of splitting of the pure CTP mode near the point of physical contact.\textsuperscript{42}

Further simulations with variations in bridging geometry allow insight into these intermediates. We explored alternate Ag shell growth mechanisms including concentric sphere growth with and without a thin metal bridge (Figure 4.8). The growth mechanism of Ag content inside the shell was studied under two hypotheses: 1) isotropic dielectric mixing of Ag and AgCl (Figure 4.7B) under the Maxwell Garnett medium approximation method;\textsuperscript{207} 2) concentric spherical growth of Ag around core surfaces\textsuperscript{206, 208} (Figure 4.7C and Figure 4.8). As a bridge connecting the Au cores may be formed when the Ag content increases,\textsuperscript{43, 190} we consider three different cases in terms of bridge growth rate: i) no bridge at all unless Ag shells touch; ii) a thin bridge is formed before
the Ag shells overlap, one-tenth the width of the total bridge; iii) the Ag bridge has the same growth rate as that of Ag shells. As seen in Figure 4.7B, all modes red shift with increasing Ag content under the isotropic dielectric mixing hypothesis. Specifically, the LB and T modes of Au/AgCl gradually red shift and disappear because they are core-dominant modes. Meanwhile, new modes dominated by Ag shells (i.e., T, SB and CTP) appear and red shift with increasing Ag content. For the concentric spherical growth hypothesis on the other hand, the evolution shows a completely different behavior (Figure 4.8). When the bridge growth rate is much smaller than that of Ag shells (no bridge case, Figure 4.8A; constant ratio thin bridge case, Figure 4.7C and Figure 4.8B), the concentric growth dominates the optical response before touching, and the LB mode red shifts due to the increased coupling between the Ag shells. Upon shell overlap, an abrupt discontinuity appears and the CTP mode splits into resonances (see Figure 4.7C and boxed spectra in Figure 4.8B), consistent with what has been observed previously.\(^{38,41-42}\) After touching, SB and CTP modes blue shift due to the increase in bridge conductance.\(^{40}\) When the bridge growth rate is comparable to that of Ag shells (same growth rate, Figure 4.8C), the increase of bridge conductance dominates throughout the entire spectral evolution, resulting in clear blue shifts for LB and T modes for small Ag shells as well as T, SB and CTP modes for touching nanoparticles.
Figure 4.8 - Mode evolution with increasing Ag content under concentric spherical growth hypotheses: A) no bridge between Ag shells unless they touch; B) a thin bridge of constant width connecting the Au cores before Ag shells touch; C) bridge connecting Au cores has the same growth rate as that of Ag shells. The boxed spectra in panel b are featured in Figure 4.7C of the main text to demonstrate the splitting of the CTP mode upon contact of the Ag shells.

In summary, we found that in the case of bridged concentric sphere growth, the CTP mode splits at the point of overlap for the Ag shells (Figure 4.7C). In addition to the aforementioned experimental observation upon nanoparticle contact and observed splitting in our simulations, full quantum mechanical calculations of bridged dimers have also shown weak splitting of the CTP mode near the point of physical contact.\textsuperscript{38, 41}

Because the system dimensions and specific geometry of the gap plays a major role in the formation and evolution of charge transfer plasmons.\textsuperscript{38-39, 74-75, 188} Based on these
simulation results of our dielectric mixing and concentric shell growth models, we must conclude that the experimental system is best described by a combination of these two extreme cases.

Comparing the experimental and simulated scattering spectra for the bridged dimers, two remarks are in order. First, assuming the same shell thickness for both redox states, the tunneling conductance of Ag shells causes the SB mode to have a higher resonance energy than the LB mode. Experimentally, the resonance energy difference between LB and SB modes varied structure by structure. Along with likely dependence on individual gap geometry, the shell thickness also plays an important role. With increasing shell thickness, the LB mode always red shifts; the SB mode initially red shifts due to increased coupling strength, but then blue shifts due to increasing tunneling current (Figure 4.9).
Figure 4.9 - Evolution of the screened bonding (SB) mode with increasing Ag shell thickness. By fixing Au core size and separation (r = 22.5 nm, center-to-center separation: 48 nm), the spectral evolution with increasing Ag shell radius was found. As the overlap increases, there is an initial red shift of the SB mode as coupling increases. After 1.7 nm shell thickness (0.4 nm overlap) the SB starts to blue shift due to increased tunneling conductivity. A dotted black line is superimposed to guide the eye along the peak scattering intensity with increasing shell thickness. For AgCl shells (not shown) the longitudinal bonding (LB) mode always red shifts with increasing shell thickness.

Hence for identical core structures, larger differences between LB and SB resonance energies correspond to increased shell overlap. In the cases of isotropic dielectric mixing simulations (Figure 4.7B) and concentric sphere growth simulations (Figure 4.7C, Figure 4.8), small differences in plasmon resonance energies are observed
between simulated and experimental scattering spectra. We attribute these differences to
the known variations in nanoparticle and bridge morphology (Figure 4.2 and Figure
4.5A) which are not accounted for in the idealized geometries of simulations.

4.6 Conclusions

Using Ag redox chemistry, we have demonstrated fully reversible
active control of plasmon resonances both in isolated and in interacting plasmonic
nanoparticles. For dimers, the plasmon shifts were particularly large because our
approach allowed us to fill the junction and introduce or remove conductive
coupling between the nanoparticles. Our results show that electrochemical
modification of plasmonic nanoparticles allows predictable, reversible, and fully
controllable modulation of the intensity, line shape, and color of both simple and
complex nanostructures. In addition to providing a valuable model system for
investigating the transitions between classical capacitive coupling and quantum
mechanical effects, these results also pave the way for new research opportunities,
such as more precise and controlled studies of narrow plasmonic gap effects,
electrochemical potential-directed nanoparticle growth, electrochemical alloying, or
layer by layer (LBL) active plasmonics.

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Chapter 5

Summary and Conclusion

In this thesis, single-nanoantenna spectroelectrochemical techniques were developed and utilized for fundamental study and for the engineering of tunable plasmonic elements and sensors. Using single-particle spectroelectrochemistry techniques combined with analytical models, we found that the spectroelectrochemistry of plasmonic nanoparticles is much richer than previously known. In particular, the chemical effects of potential-controlled spectroelectrochemical tuning greatly overshadowed the purely physical effect of charge density tuning.

Building on the observed sensitivity of nanoparticle plasmons to surface chemistry effects, a coupled structure was utilized in the development of a single-
nanoantenna cyclic voltammetry analog. The sensor was composed of an Au dimer on Au thin film, where optical frequency screening currents could flow between the plasmonically coupled Au nanoparticles. Because of the large dependence of the screened bonding mode scattering spectrum on the screening pathway electrical conductance, the mode had a high sensitivity to changes in Au film conductivity. The conductivity of the film was tuned by reversibly electroadsorbing polyoxyanions via electrochemical potential. A differential technique was developed to dynamically report fluctuations in the scattering cross-section of an individual nanoantenna during cyclic voltammetry experiments. By correlating the single-nanoantenna CV analog to the concurrently measured bulk CV, the spectral response was correlated to known adsorption and desorption events. The sensitivity (and insensitivity) to electrochemical processes in multiple electrolyte systems was characterized.

By leveraging electrochemical reaction control, we engineered model systems to create large changes in optical properties and study exotic physical phenomena. We found that by bridging gold nanoparticle dimers with overlapping Ag shells, we could electrochemically switch the shell and bridge between a highly conductive state (Ag, metallic), and a capacitive state (AgCl, wide bandgap semiconductor). The use of dynamic single-nanoantenna spectroelectrochemical techniques developed in this thesis allowed us to observe the first switchable charge transfer plasmon in a fully nanoscopic system. This dynamic observation also allowed us to learn about the electrochemical reduction and oxidation mechanisms
and rates of the shell material based on the observed spectral evolution and matching full-wave electromagnetic simulations.

In sum, the work of this thesis has helped demonstrate and increase the value of single-nanoantenna spectroelectrochemistry. The tools and techniques developed herein will serve as the building blocks for future studies, while the scientific findings will inspire and guide their design. Though many answers and conclusions have been drawn, a far greater number of questions and possibilities have emerged. Like the glittering plasmonic nanoparticles and assemblies that form the basis of this work, the future of plasmonic spectroelectrochemistry for fundamental research and applications appears to be dazzling.
Appendix

Additional Methods

A.1

Charge density-modified Drude dielectric function for Mie scattering simulations

The following model was used to calculate the scattering efficiency of a plasmonically active metal nanosphere as a function of charge density. Following the general framework used in multiple works,\textsuperscript{59-60, 62, 64-66} the effect of changes in the charge density of a nanoparticle can be modeled through the frequency dependent Drude dielectric function.

\[ \varepsilon(\omega) = \varepsilon_\infty + \varepsilon_{\text{free}} \]

The free electron term depends on the free charge density via the bulk plasma frequency:
\[ \varepsilon_{\text{free}}(\omega) = -\frac{\omega_P^2}{\omega^2 + iy\omega} \]

where \( \omega \) is the incident photon frequency, \( \omega_P \) is the bulk plasma frequency, and \( \gamma \) is the damping coefficient. The bulk plasma frequency is given by:

\[ \omega_P = \sqrt{\frac{N e^2}{m \varepsilon_0}} \]

where \( N \) is the free charge density of the nanoparticle, \( e \) is the elementary charge, \( m \) is the effective mass of the electrons in the metal, and \( \varepsilon_0 \) is the free space permittivity. Through this simple model, the complex dielectric function of the metal as a function of free charge density can be found. The dielectric function of the metal can then be used to calculate the interaction of light with a nanoparticle of certain charge density using Mie Theory. In this study, the complex dielectric function of gold was calculated by subtracting the free electron term for an electrically neutral nanoparticle from smoothed Johnson and Christy tabulated optical data, then adding the free electron term for the same nanoparticle with an altered free charge density. This scheme is represented in the following equation:

\[ \varepsilon(\omega) = \varepsilon_{Jc} - \varepsilon_{\text{free\,(neutral)}} + \varepsilon_{\text{free\,(charged)}} \]

The nanoparticle of interest was assumed to be 50 nm in diameter. Gold nanoparticles in this study were supported on ITO (\( n = 1.922 \) at 550 nm) and immersed in 100 mM NaCl (\( n = 1.334 \) at 550 nm). In order to perform Mie theory calculations, the medium refractive index was treated as an adjustable parameter to
fit the spectrum of the nanoparticle at open circuit potential. This procedure resulted in an effective refractive index of 1.4803, a reasonable value based on the refractive indices of the electrolyte solution and substrate. The refractive index value was then fixed and the charge density of the gold nanoparticle became the only fit parameter in the simulation. Figure A.1 shows the large scale effect of changing the charge density of the nanoparticle. Here, simulated scattering spectra are shown for large changes to the free charge density. We found that changes in charge density were less than 1%. Mie theory simulations were performed in custom MATLAB scripts using 50 multipoles in the spherical harmonics expansion. Within the Drude model, the damping coefficient $\gamma$ was fixed at 0.07 s$^{-1}$. 
Figure A.1 - Calculated scattering spectra showing the effect of changing charge density of a gold nanosphere. A charge density-modified Drude dielectric function was used in Mie scattering calculations, which show that for increases in free charge density the resonance peak blue-shifts. (a) Full scattering spectra are shown for ±10% changes in the free charge density. Because the changes in charging were less than 1% of the total free electrons in a neutral nanoparticle during the experiment, a higher resolution excerpt is shown in (b). (b) The simulated scattering spectra for ±1% change in free electron density. Note that the x-scale is in units of wavelength and not energy and that (b) shows a much smaller wavelength range than (a).

Because the charge density changes observed experimentally were so small, the simulated trends of the plasmon resonance on changes in charge density are shown in Figure A.1. for a 50 nm gold nanoparticle. The resonance peak, the full
width at half maximum, and the intensity are shown as a function of the fractional charge density. The fractional charge density is defined here as the free charge density of the nanoparticle divided by the free charge density of the same nanoparticle with no net electrical charge, that is, the number of free electrons in the neutral nanoparticle is equal to the number of gold atoms in the nanoparticle.

A.2

**Indium Tin Oxide carrier concentration tuning simulations**

Because the Au nanoparticles are not an isolated system, the effect of changing the carrier mobility of the indium tin oxide thin film was modeled using a Drude Lorentz function to calculate the refractive index as a function of carrier density. Literature values were used for the uncharged free carrier density, and carrier scattering time ($5 \times 10^{20}$ carriers/cm$^3$, 4 fs).\textsuperscript{178, 209} The Drude-Lorenz model results matched literature results and experimental measurements.\textsuperscript{209}

Mie scattering calculations were then performed for a 50 nm Au sphere embedded in this tunable ITO medium. The free electron density of the gold was fixed in order to assess the role of ITO carrier density tuning only. It is important to note that in this model, the nanoparticle is embedded in the medium, and this can be interpreted as an upper limit for plasmon resonance modulation. In our experimental configuration, ITO only forms the substrate and therefore constitutes
a very small fraction of the nanoparticle surface area contact with its embedding medium.

Over a very large carrier density tuning range (>1 order of magnitude carriers/cm$^3$) a nearly linear dependence can be seen for resonance energy, width, and scattering efficiency. The observed trends qualitatively match the experimental trend for resonance energy but are opposite of those observed for FWHM and scattering efficiency. According to Dasgupta et al. the charge carrier density of ITO thin films under electrochemical gating only changed at a rate of $1.7 \times 10^{13}$ electrons/cm$^3$ per volt. While this $0.0000034 \%$ change in carrier density per volt was electrically measureable for Dasgupta et al., the corresponding change in the refractive index is $\Delta n = 4 \times 10^{-9}$. Mie scattering simulations were performed using a 50 multipole expansion and a carrier concentration tuned refractive index over a range of $4 \times 10^{20}$ to $6 \times 10^{20}$ carriers/cm$^3$. All scattering parameters as a function of carrier concentration were fit well with a linear regression. The fit parameters are summarized in Table A.1 along with the calculated shift in each parameter using the measured carrier density variation reported by Dasgupta et al. As can be seen in column four of Table A.1, all changes are several orders of magnitude lower than any experimental noise level and would therefore not be measureable. In order to produce the measured 4 meV shift shown in Figure 2.5 of the manuscript, the carrier concentration would need to change by $3.4 \times 10^{19}$ carriers/cm$^3$. This concentration change is roughly 6 million times larger than that measured by Dasgupta et al. over a similar potential range. Because this embedded nanoparticle model is viewed as
the upper limit for the ITO carrier concentration tuning effect, we conclude that this mechanism is not a contributor to the observed electrochemical plasmon tuning.

Figure A.2 - Mie Scattering simulations of the plasmon resonance scattering of a 50 nm Au sphere embedded in a charge carrier tunable Indium Tin Oxide (ITO) thin film. The refractive index at 2.075 eV (a), resonance energy (b), resonance width (c), and scattering efficiency factor (d) are shown as a function of the charge carrier concentration of ITO around a literature-reported charge-neutral range. Each trend was fit with a linear regression. Fit parameters are shown in Table A.1, along with predicted changes for literature-reported changes in ITO charge carrier concentration.
Table A.1 - Linear regression fit parameters for the trends in Figure A.2 are reported along with predicted values for 1 V change in electrochemical potential using literature reported changes in carrier concentration. Even for an entirely embedded nanoparticle, the resonance energy, resonance width, and scattering intensity changes would be roughly six orders of magnitude too small to experimentally probe directly with our method.

A.3

Digital camera images of Au/Ag switching
Figure A.3 - Digital color images taken with an SLR camera at microscope eyepiece at chloridizing (left) and reducing (right) conditions. Images of the same area show the change in color and intensity of many single nanoparticles and dimers as the composition of their shells changes electrochemically. At 0.5 V (left) the shells are composed of AgCl. Single nanoparticles scatter green light and dimers scatter yellow-red light. At -0.5 V, the shells are composed of metallic Ag. Single nanoparticles scatter green-yellow with much greater intensity than AgCl shell state. Dimers conductively bridged by their silver shell scatter bright white/cyan due to their high silver content and broad line shape.
Figure A.4 - Digital color images captured with an SLR camera at microscope eyepiece during initial electrodeposition of Ag metal onto bare Au nanoparticles and dimers. Images of the same area show the change in color and intensity of many single nanoparticles and dimers as Ag is electrodeposited. Before Ag is deposited, single Au spheres scatter green light and dimers scatter yellow-red light. As the Ag shell is deposited, sphere scattering becomes significantly brighter. Dimers conductively bridged by their silver shell scatter bright white/cyan due to their high silver content and broad line shape. Approximately 20 dimers and 50 monomers are shown in this region.
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