Nanoscale Characterization and Mechanism of Electroless Deposition of Silver Metal

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NANOSCALE CHARACTERIZATION AND MECHANISM OF ELECTROLESS DEPOSITION OF SILVER METAL

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry in the College of Sciences at the University of Central Florida Orlando, Florida

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Major Professor: Stephen M. Kuebler
ABSTRACT

This dissertation is an investigation of the nanoscale characteristics and mechanism of electrolessly deposited silver metal seeded by gold nanoparticles. The process of growing seed-nanoparticles on a polymer surface was studied. Several bifunctional amines and organic reducing agents were used to explore how these chemical factors affect the size and distribution of gold nanoparticles formed at the interface. The nanoparticles were characterized by transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). An electroless deposition (ED) bath developed by Danscher was selected to study electroless deposition of silver in detail. The chemical species in the bath were varied to determine how concentration, nature of the carboxylate buffering species, and the presence and absence of gum arabic affect the morphology of silver metal formed by ED and the overall rate of deposition at the surface. The kinetics of deposition using the Danscher bath was studied in detail to elucidate the mechanism of ED. Knowledge generated from this investigation can be used to expand applications of silver ED where strict control over the nanoscale morphology of the deposited metal is required to obtain specific chemical and physical properties.
EXTENDED ABSTRACT

Electroless deposition (ED) is a means for conformally depositing metal onto nonconductive surfaces that has been used widely for decades in many industries to provide improved surface properties of plastic parts. More recently, ED has been used in applications where higher control over the morphology of the deposited metal surface is required, but there have been few reports on the nanoscale morphology (NSM) of ED metal. Several aspects of ED, using silver metal ED bath in particular, are studied so a greater understanding of what factors affect the ED process can be attained.

The first area of study in this dissertation focuses on in situ reduction of metal ions bound at a polymer surface. It is shown that in situ reduction of metal ions at a polymer surface can form nanoparticles within the polymer matrix as well as at the interface, and the size and distribution of nanoparticles between the interface and subsurface depends upon the choice of reagents and reaction conditions. Tetrachloroaurate ions were bound to cross-linked SU-8 films that were functionalized using a variety of multi-functional amines, then reduced using one of several reagents. Reduction using sodium borohydride or sodium citrate generates bands of interspersed gold nanoparticles as much as 40 nm deep within the polymer, indicating that both the Au ions and the reducing agent can penetrate the surface enabling formation of nanoparticles within the polymer matrix. Nanoparticle formation can be confined nearer to the polymer interface by reducing with hydroquinone, or by processing the polymer film in aqueous media using high molecular-weight multifunctional amines that confine the gold ions at the interface.

The second section of this dissertation shows how transmission electron microscopy can be used as a quantitative method to measure the shapes, sizes and volumes of gold nanoparticles
created at a polymeric surface by three different in situ synthesis methods. The atomic number contrast (Z-contrast) imaging technique reveals nanoparticles which are formed on the surface of the polymer. However, with certain reducing agents, the gold nanoparticles are additionally found up to 20 nm below the polymer surface. In addition, plan-view high-angle annular dark-field scanning transmission electron microscopy images were statistically analyzed on one sample to measure the volume, height and effective diameter of the gold nanoparticles and their size distributions. Depth analysis from high-angle annular dark-field scanning transmission electron microscopy micrographs also gives information on the dominant shape of the nanoparticles.

The third section of this dissertation focuses on the NSM of ED silver based on a metallization bath first reported by Danscher. This metallization bath produces small spherical nanoparticles (~20 nm) that aggregate to form rice-grain like features. Removal of gum arabic (GA) from the deposition bath increases deposition rate, but still provides small, spherical nanoparticles. However, the aggregates produced in the absence of GA are significantly longer. Using a monocarboxylate in place of citrate to buffer the bath in the absence of GA resulted in faster deposition, producing nanoparticles that are highly faceted. Dicarboxylate buffers produce faceted particles of smaller overall size and smaller facet size when compared to monocarboxylate buffers. These results show that as the chelating ability of the buffer increases, the as-deposited nanoparticles tend to exhibit less faceting and smaller size. Optical measurements of deposited films in the visible region showed absorptions associated with silver nanoparticles. Conductivity measurements of as deposited films show a conductivity approximately five orders of magnitude less than that of bulk silver. After low temperature annealing, conductivity of films increased to within 1% of the bulk metal.
The penultimate section discusses the kinetics of the ED bath first reported by Dasncher without GA, and proposes a mechanism by which ED using this bath occurs. Fractional orders with respect to Ag\(^+\) and the citrate buffer were found, indicating that there is an equilibrium occurring between these two ions before ED the reduction step occurs. The order with respect to hydroquinone (HQ) was found to be approximately one, with agrees with theory that HQ undergoes two successive single electron reductions, both governed by first order kinetics. A non-constant order with respect to H\(^+\) concentration was found, caused by a combination of H\(^+\) affecting the equilibrium between Ag\(^+\) and citrate and the reduction potential of HQ. Based on these findings a mechanism is proposed. The dissertation concludes with an outlook for ED, discussing how these findings could potentially affect applications already using ED and additional challenges that must be addressed so a greater understanding of ED can take place.
ACKNOWLEDGMENTS

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Williams, Dr. Jennefin Digaum, and Dr. Casey Schwarz all provided important and meaningful discussion along the way as fellow graduate students and post-docs in the lab.

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<th>Description</th>
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<tr>
<td>AEP</td>
<td>N-aminoethylenepeparazine</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge coupled device</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>ED</td>
<td>Electroless deposition</td>
</tr>
<tr>
<td>EDA</td>
<td>Ethylenediamine</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FCC</td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>GA</td>
<td>Gum arabic</td>
</tr>
<tr>
<td>HAADF-STEM</td>
<td>High-angle annular dark field scanning transmission electron microscopy</td>
</tr>
<tr>
<td>HQ</td>
<td>Hydroquinone</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>KED</td>
<td>Kinetic energy discrimination</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>NSM</td>
<td>Nanoscale morphology</td>
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<tr>
<td>RSD</td>
<td>Relative standard deviation</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SERS</td>
<td>Surfaced-enhanced Raman spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TEPA</td>
<td>Tetraethylenepentamine</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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INTRODUCTION

1.1 State-of-the-art on electroless deposition

Noble metal nanostructures display fascinating phenomena such as surface-enhanced Raman scattering (SERS), plasmon resonance absorption, and metal enhanced fluorescence. These phenomena have attracted considerable attention and are becoming widely applied in several emerging technologies, including SERS microscopy, optical sensing, biological labeling, optical wave guiding on chips, and nano-optics. Many reports indicate that these phenomena are sensitive to size, shape, and space between nanostructures of metal. Controlling the surface nanoscale morphology of metal is thus required for these applications.

Colloidal metal-particle surfaces can be used for SERS, biosensing, and related applications, but the instability of the metal surface due to the random aggregation of colloidal metal limits their performance and widespread use. An ideal metallization method would provide control over particle shape, size, orientation, and inter-particle spacing. Techniques for achieving this level of control remain elusive. Vacuum evaporation and sputter-deposition of metal are widely used. These techniques yield stable metal-particle films that are well packed, with controlled thickness, but particle sizes are generally small and the shape of the particles cannot be controlled well. For some applications, specific particle sizes are required to achieve the best result. For instance, it has been shown that silver nanoparticles surfaces having a high surface roughness, so called “hot spots”, can provide large surface enhancement when excited at optical frequencies. Several research groups have attempted to use high temperature annealing of sputter-coated metal to control surface morphology. However, the procedure itself is
difficult to control, and high temperature annealing can damage supporting substrates or devices. This is particularly true for micro-devices fabricated using soft-lithography technologies.\textsuperscript{20-21}

An alternative path to colloidal metalized surfaces is by a process called electroless deposition (ED) of metal. ED is a process in which a reducing agent reacts with a metal ion at an activated surface, without the use of an external current, generally in aqueous media.\textsuperscript{22} There are a number of ED baths that deposit several different metals, with nickel,\textsuperscript{23-24} silver,\textsuperscript{25-28} gold,\textsuperscript{29-30} copper,\textsuperscript{31-32} and several alloys\textsuperscript{33-35} being the most common.

ED is widely used in industrial applications to improve hardness, corrosion and wear resistance, and electric and magnetic properties of manufactured parts, including both plastics and metals.\textsuperscript{36 37} In 2016, the value of the coatings market, which includes electroless deposition and several other coating techniques, was values at USD 840 million, and was projected to grow to USD 1,307 million by 2022.\textsuperscript{38} Applications include coatings of valves in corrosive environments, rotors, drive shafts, optical coatings, including mirror production, and decorative coatings for kitchen utensils, door knobs and bathroom fixtures.\textsuperscript{36 37}

The main problem with ED is that while the mechanism of some of the deposition processes is known, such as with Tollens’-type ED baths, where an aldehyde is used as a reducing agent,\textsuperscript{27} many of the other ED baths are a “black box”. This means a metal ion is mixed with a mild reducing agent in the presence of an activated polymeric surface and a metallized surface is obtained after some time, without any mechanistic knowledge of the process by which the metallized surface was obtained. Many of the applications described above require strict control over the size and shape of the deposited NP. Greater knowledge of the mechanism of ED could allow for better control of NP size and shape. Several groups have already reported ways to control
NP size by simple ED baths. Yet few reports of particle shape control of nanostructures by ED are present.

While there are many ED baths, a bath utilizing silver, which has the highest electrical conductivity of all metals, originally formulated by Danscher showed promise for wide-spread application in metallizing high-aspect ratio microstructures fabricated in SU-8. Silver is also the preferred metal for SERS and related bio-analytical applications. The Danscher bath is preferred over other ED baths because the chemicals used are not acutely harmful and can be handled without taking special precautions, unlike other baths which use concentrated ammonia and other hazardous chemicals. The Danscher bath is potentially also preferable, as other ED baths can form silver azide if the solvent is allowed to evaporate, which is a highly explosive compound.

The original application of the Danscher bath was for staining of biological tissue to increase contrast in scanning electron microscopy and tunneling electron microscopy. Gold ions were injected into rats and mice to determine where gold ions collect in the body, then after some time, the rats were killed and samples of their tissue was taken. The gold ions were then reduced using UV light, which generated Au NPs. Development using silver was achieved using a protecting colloid (gum arabic), a citrate buffer, reducing agent and silver ion source while keeping the specimens at 26 °C in complete darkness. In the present application, rather than using UV light to reduce Au, a method developed by McCarley and Henry was used, where Au was attached to surface bound amines, then reduced with NaBH₄. The Au NPs generated in this process are then used as seeds to nucleate deposition of metal from the Danscher bath. The overall process to generate a metallized silver surface is illustrated in Figure 1.
1.2 Thesis Overview

The purpose of this dissertation is to study the process of electroless deposition. Understanding the electroless deposition process can aid in engineering metallic surfaces that are useful in many areas including metal fluorescence, SERS and plasmon resonance absorption. In Chapter 1, the state-of-the-art of electroless deposition and the determination of the reaction rate is discussed. Chapter 2 discusses the experimental methods used in this dissertation. Chapter 3 studies the effect the amine binding group and the identity of the reducing agent will be studied to determine how Au NP seed morphology and distribution can be affected. Chapter 4 discusses additional nanoscale characterization of the Au NP surface. Chapter 5 details the nanoscale morphology of the electrolessly deposited Ag layer under different deposition conditions,
including varying time, the presence of gum arabic, the concentration of Ag\(^+\) and the identity of the carboxylate buffer. Chapter 6 discusses the kinetics of ED and proposes a mechanism for the ED process. Chapter 7 summarizes this dissertation and provides the future outlook for ED and the technology applications now that a mechanism is known.

1.3 References


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2 EXPERIMENTAL METHODS

2.1 Preparation of silvered films

2.1.1 Cross-linked substrate preparation

Square 25 mm × 25 mm glass substrates were cleaned by immersing in aqueous 1.0 M KOH (Fisher, CAS# 1310-58-3) for one hour, rinsing with copious deionized water, and drying in the oven (at 100°C). Cross-linked SU-8 substrates were prepared by spin coating SU-8 2035 resin (Microchem) onto cleaned substrates (Ramp 1: 100rpm/s; hold 500 rpm for 10 s; Ramp 2: 300 rpm/s; hold at 4000 rpm for 30 s). Substrates were cured by baking to remove solvent at 65 °C for 3 min followed by 95 °C for 6 min; irradiating for 3 min using a broad-band UV source (Loctite ZETA 7411-5, 400 W metal halide source, 315 nm – 400 nm) with a long-pass filter (Omega Optical, PL-360LP, cut-off 360 nm); then baking after exposure for 60 s at 65 °C, 15 min at 95 °C, and 60 s at 65 °C.

2.1.2 Functionalization of polymer surface with bifunctional amines

The cross-linked polymer surfaces were functionalized with bifunctional amines for subsequent binding of gold Au-NPs. Amine functionalization was achieved by immersing the cross-linked polymer sample into a solution of 20 vol-% 1,2-diaminoethane (Acros, CAS# 107-15-3) in ethanol for 60 min, rinsing with copious ethanol, and drying in the oven.1 In Sections 3 and 4, additional amines are used to functionalize the cross-linked polymer surface to study the effects of the bifunctional amine. Functionalization with tetraethylenepentamine (Acros, CAS# 112-57-2) or N-aminoethylenepeparazine (Acros, CAS# 140-31-8) was achieved by
immersing the cross-linked polymer sample into a solution of 20 vol-% of the amine in ethanol for 60 minutes, rinsing with copious ethanol, and drying in the oven.

2.1.3 Functionalization of polymer surface with gold nanoparticles

Gold nanoparticles (Au NPs) were attached to amine-functionalized polymeric surfaces by either (1) binding Au$^{3+}$ cations to the amine sites and reducing with aqueous NaBH$_4$ or (2) separately preparing citrate-capped Au colloids and binding these to the amine sites. All depositions were carried out on in situ-produced Au NPs unless otherwise stated.

2.1.3.1 NaBH$_4$-reduced (in situ) Au NPs

The amine-functionalized polymeric sample was treated with 5.3 × 10$^{-4}$ M aqueous HAuCl$_4$ (Acros, CAS# 16961-25-4) for 30 min, rinsed with copious deionized water, immersed in 0.1 M aqueous NaBH$_4$ (Fisher, CAS# 16940-66-2) for 60 s, rinsed with copious deionized water, and allowed to dry by standing in air.$^2$

2.1.3.2 Citrated Au-NPs

A suspension of citrate-capped gold colloids was prepared using the method of Grabar et al.$^3$ Amine-functionalized polymer samples were then immersed into the gold colloid suspension for 60 min, rinsed with copious deionized water, and dried in air.
2.1.3.3 Additional in situ Au NPs

In Sections 3 and 4, additional reducing agents are used for the in situ preparation of Au NPs. Reduction using citrate was accomplished by immersing samples for 8 h in aqueous 1% (w/v) sodium citrate (Fisher, CAS# 6132-04-3)\(^4\). Reduction with hydroquinone was achieved by immersing samples in aqueous 0.1 M hydroquinone (Acros, CAS# 123-31-9) for 1 hour\(^5\). After reduction, samples were rinsed with copious water and allowed to dry by standing in air.

2.1.4 Silver electroless deposition

Silver deposition was achieved using a formulation originally reported by Danscher and co-workers\(^5\), which will hereafter be referred to as the "standard bath." Conditions were varied as needed to explore how the nanoscale morphology of the deposited metal is affected by type of metallization bath, Ag\(^+\) concentration, and the presence or absence of gum arabic, a deposition retardant, and various other carboxylates.

2.1.4.1 Standard bath

Sufficient gum arabic (Aldrich, CAS# 9000-01-5) was dissolved in hot deionized water, cooled, and filtered giving a 33 wt-% solution. A citrate buffer (pH = 3.8) was prepared consisting of 1.5 M citric acid (Aldrich, CAS# 5949-29-1) and 0.5 M trisodium citrate (Aldrich, CAS# 6132-04-3). An aqueous silver nitrate solution having a concentration of 222 mM was prepared by dissolving the parent salt (Aldrich, CAS# 7761-88-8) in deionized water. Sufficient hydroquinone (Aldrich, CAS# 123-31-9) was dissolved in deionized water to give a 0.52 M solution. A reductant solution was prepared by combining 7.5 mL of citrate buffer, 11.25 mL of
hydroquinone solution, and 45 mL of gum arabic solution. The reductant solution and 11.25 mL of the appropriate silver nitrate solution were then equilibrated at 20 °C ± 1 °C and rapidly combined immediately prior to use, giving a final Ag⁺ concentration of 33.3 mM. Substrates were removed once a completely reflective silver film was formed and subsequent substrates were removed at regular intervals.

2.1.4.2 Variations of the standard bath

ED baths were also prepared in which [Ag⁺], the presence/absence of gum arabic, and the identity of the carboxylate buffer were each varied. For depositions in which [Ag⁺] was varied, concentrations were fixed at 5.6 mM and 16.7 mM. For depositions in which gum arabic was not used, an equivalent amount of deionized water was used. For depositions in which carboxylate buffer was varied, the total carboxylate concentration in the ED bath was 200 mM, and the pH was adjusted to 3.8, matching the conditions of the standard bath. Additionally, the order in which the chemicals were combined differs from that used to prepare the standard bath. In cases where the buffer was insoluble, the undissolved solid was filtered off. The AgNO₃ solution was combined with pH adjusted buffer solution and 45 mL of water and allowed to equilibrate at room temperature. The hydroquinone solution was rapidly added immediately prior to use. Films were left to deposit until a nontransparent film was achieved and subsequent films were removed at regular intervals. The identity and structure of additional carboxylate buffers used is given in Figure 2.
2.1.4.3 Kinetics studies

For all kinetics studies, an apparatus was designed that allowed for up to 12 films to be placed into the same ED bath, and allowed for removal of a single film at a time, giving data over a potentially long time domain in a single trial. The ED reaction was quenched by removing a film from the ED bath and placing the film into a large volume of water, which rinsed any remaining ED solution from the film and diluted the reactants to a point where the ED reactions essentially stop.

2.2 Measurement of Deposited Silver

Deposited silver films were digested using 20 mL of 4 M trace metal grade HNO₃ (Fisher, CAS# 7697-37-2). Films were digested for 5 min, though all films were digested in generally less
than 20 s. Solutions were then diluted with sufficient deionized (DI) H₂O so 2% HNO₃ was present. Dissolved silver was measured using a Thermo Fisher Scientific iCap Qc inductively coupled plasma mass spectrometer (ICP-MS) with QCell technology and operated in kinetic energy discrimination (KED) mode of analysis with helium as the collision gas. Calibration-, internal-, and quality-control standards (Inorganic Ventures) were prepared in 2% trace metal grade nitric acid. Rhodium and indium were used as internal references in both standards and samples.

2.3 Scanning Electron Microscopy (SEM) Analysis

Substrates deposited with silver were imaged using the Zeiss ULTRA-55 FEG SEM located at the Materials Characterization Facility (MCF). The acceleration voltage was 5.0 keV. A standard 30 µm beam aperture and the In-lens detector were used for all images. The working distance varied for each image, but was generally between 2.5 mm and 3.0 mm. Energy dispersive X-ray spectroscopy (EDX) was also carried out in this instrument, and accelerating voltages were increased to 20 keV. Spectra were obtained for a total of five minutes.

2.4 Particle Size Determination

The sizes of particles and aggregates were obtained by hand-measurement of 100 features in SEM images of silver deposited under a given condition. Images obtained at x25,000 (x100,000) magnification were used to measure features larger (smaller) than 100 nm. For ellipsoidal particles, the lengths of both the major and minor axes were measured. These data were used to obtain particle-size distribution and average particle size. The uncertainty reported
corresponds to one standard deviation of the mean, unless otherwise indicated. The error of individual particle measurements was found to be significantly less than the standard deviation of the ensemble.

2.5 Sample Preparation for Transmission Electron Microscopy (TEM)

To increase contrast of cross-sectional images in TEM the Au deposited samples were first coated with carbon for 30 s in a vacuum evaporator (Jeol JEE 4X, Japan). To improve conductivity and contrast in the Focused Ion Beam (FIB), the C-coated samples were coated with an Au-Pd alloy for 3 min – 4 min in a sputter coater (Emitech K550, UK) which uses a 60 mm diameter and 0.1 mm thick magnetron target assembly giving fine grains without the need to cool the specimen.

An FIB (FEI, Hillsboro, OR, U.S.A.) system operating at 30 kV was used to prepare cross-sectional TEM samples of the Au samples. The FIB system can be operated at low-beam currents for imaging or high-beam currents for site-specific sputtering or milling and can reach a lateral resolution of 5 nm. A 1-μm thick platinum layer was deposited on the sample surface on a typical rectangular area of 20 μm (length) × 1 μm (width) to protect the interior of the FIB cross section from gallium ion implantation with the help of the Pt deposition system within the instrument. Milling is carried out on the desired rectangular area with precise control by using smaller ion beam sizes with lower currents in the final steps 6-9. Currents as low as 50 pA were used for the final thinning of the sample to prevent back deposition of gallium ions and to limit the thickness of the amorphous (radiation damaged) layer forming at the surfaces of the FIB cross section 10-11. The typical dimensions of the final sample were 16 μm (length) × 4 μm (height) × 50 nm
A Mitutoyo (Japan) VM Zoom 40 optical microscope equipped with hydraulic micromanipulators was used for ex-situ lift out from the bulk and for placement of the TEM sample on a holey carbon-coated Cu grid.\textsuperscript{12} The FIB technique of preparing cross sections was not used to produce the plan-view samples. Instead, a portion of the Au-deposited film on the glass substrate was scraped off with tweezers and placed directly on the Cu TEM grid.

2.6 High-Resolution TEM

The samples were studied in a TECNAI F30 TEM (FEI, Hillsboro, OR, U.S.A.) equipped with a field emission source operating at 300 kV with a point to point resolution of 0.2 nm and a maximum allowable specimen tilt of $\pm 40^\circ$. Both lower magnification and high-resolution images were acquired. In the scanning transmission electron microscopy (STEM) mode, a Fischione high-angle annular dark-field (HAADF) detector with a contrast/brightness setting of 12.5\% and 46.9\% and a camera length of 80 mm was consistently used.\textsuperscript{13} This setting allowed for a quantitative calibration of the contrast of the Au NPs. Energy dispersive spectroscopy and energy-filtered TEM were employed for compositional analysis.

2.7 References


3 CONTROLLING FORMATION OF GOLD NANOPARTICLES GENERATED IN SITU AT A POLYMERIC SURFACE

Work in this chapter was published as

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3.1 Introduction

Gold nanoparticles (Au NPs) and clusters or arrays of surface-bound Au NPs have a wide variety of applications, including nanofabrication, optical devices, and catalysis.1-8 Au NPs and NP-aggregates are effective for enhancing signal via surface plasmon resonance in various spectroscopic and sensing methods.9-10 Metal NPs are used as nucleation sites in electroless metallization, which is a promising approach for creating metallized micro-electromechanical structures (MEMS) and optical MEMS devices.7,11-15 Such applications frequently involve Au-NP functionalization of a polymeric surface or structure. As such, NP synthesis and surface functionalization continue to be active areas of research that impact many established and emerging technologies.

The common approach for functionalizing surfaces with NPs involves first synthesizing colloidal particles in solution, for example by the Turkevich method1,7,9,15-18 or sodium borohydride (NaBH₄) reduction,10,17,19-22 and subsequently binding them to the surface of interest. In contrast, in-situ reduction of gold ions adsorbed onto a surface is an alternative means for
generating Au-NP-functionalized surfaces and devices\textsuperscript{1-2, 23-27}. This approach offers some advantages, including the possibility for generating smaller particles, stabilization of the NPs through surface attachment, and decreased aggregation due to immobilization on the surface.\textsuperscript{1, 27-28} Additionally, surface-bound NPs can be readily isolated from the synthesis medium or further derivitized by simple physical transfer of the supporting substrate. There are several pioneering reports of in-situ synthesis of Au NPs at polymeric surfaces.\textsuperscript{1-3, 25, 27-30} Yet in comparison to the conventional approach of separately synthesizing NPs then binding them to a surface, in-situ synthesis of Au NPs at polymeric surface remains far less explored.

In this work we show how the choice of gold-ion surface-linker and reducing agent affects in-situ formation of Au NPs at the surface of a polymer known as "SU-8". SU-8 is a cross-linkable epoxide which is increasingly employed for patterning micro- and nano-scale surfaces and creating functional devices.\textsuperscript{22, 31-33} The key findings of this work are (1) NPs formed by in-situ reduction do not reside exclusively at the liquid-polymer interface; (2) varying the reducing agent can affect both the size of the NPs and their location relative to the interface; and (3) the choice of gold-cation binding agent and how it is processed can be used to confine formation of NPs to the liquid-polymer interface.

3.2 Results and Discussion

3.2.1 Nanoparticle characteristics and surface distribution

Figure 3 shows a plan-view bright-field TEM image of Au NPs generated by reduction of gold ions bound at the polymer surface using ethylene diamine (EDA) then reduced using NaBH\textsubscript{4}. It is important to note that this imaging mode shows features in projection, so the nanoparticles
visible may be bound at the interface or \textit{within} the polymer film. Elemental analysis line scans obtained during plan-view imaging, as well as cross-sectional imaging discussed below, consistently indicate the round high-contrast features are gold. Au NPs form on or near the surface, randomly distributed, with almost no aggregation and no long range order. Although minor faceting can be observed for select particles, as a whole they appear to be agglomerations of gold atoms, which also lack a definite periodicity. However, by the very nature of the present work, the Au NPs are always viewed against a background of amorphous polymer that significantly reduces contrast relative to that achievable in conventional TEM imaging, where samples are supported on a thin grid. Consequently, the Au NPs may in fact have a definite atomic periodicity that is simply not visible for most nanoparticles.

Figure 3. Bright-field plan-view TEM micrograph of Au NPs generated in situ by binding gold ions at the SU-8 polymer surface with ethylenediamine then reducing with NaBH$_4$. 
HAADF-STEM images like that shown in Figure 4 were analyzed using integrated pixel intensity to obtain estimates for the shape and size of particles formed by \textit{in situ} reduction. Comparison of similar plan-view (as well as cross-sectional images, see below) indicate that the dispersion in particle size and spatial homogeneity seen in Figure 3 and 4 is typical for samples produced by this process. Based on the particle-size analysis, Au NPs formed by NaBH$_4$ reduction are best described as oblate spheroids. Integrated pixel intensity measurements yielded an average volume of 8.5 nm$^3$, with a standard deviation (width of particle-volume distribution) of 4.8 nm$^3$, or an RSD of 60%. This wide distribution arises from large variation observed in both the lateral and vertical radii of the particles. The measured particle heights (normal to the surface) average to 1.8 nm with an RSD of 40%. The average lateral radius is 1.4 nm with a RSD of 21%. From these values, one can calculate an average particle volume-from-height of 7.3 nm$^3$, which agrees well with the value obtained from integrated pixel intensities. These particle sizes are comparable to that obtained by synthesis of Au NPs in solution\textsuperscript{17, 19} and other reports of Au NP generated \textit{in situ} using NaBH$_4$.\textsuperscript{24-25, 27}
Figure 4. HAADF-STEM image of Au NPs generated \textit{in situ} by binding gold ions at the SU-8 polymer surface with ethylenediamine then reducing with NaBH$_4$.

3.2.2 Controlling nanoparticle size and distribution relative to the interface

We examined how the choice of reducing agent used to prepare the Au NPs affects their size and resulting distribution laterally at (or near) the polymer surface and vertically with respect to the interface. In addition to NaBH$_4$, sodium citrate and hydroquinone (HQ) were selected for this portion of the study, as they are widely used for metal cation reduction and preparing Au NPs in solution.\textsuperscript{9, 16-17, 19-20, 27, 34} From the TEM cross-sectional images of Figure 5, it is immediately obvious that the size of Au NPs generated varies substantially, depending upon the reducing agent employed. NaBH$_4$ generates Au NPs in a band that spans from the interface into the polymer film to a depth of approximately 20 nm. These particles are mostly small (radius less than 5 nm). Citrate-generated Au NPs appear to form in two distinct bands of significantly different sizes, and both are larger than those generated with NaBH$_4$. The first band consists of large Au NPs (radius $> 5$ nm) located at the polymer interface. The second band consists of small Au NPs, comparable in size to those generated by NaBH$_4$, that are spread across a band approximately 40 nm wide and centered 20 nm below the polymer interface. Reduction with hydroquinone appears to generate
only the larger Au NPs, having a diameter of 10 nm - 20 nm, consistent with reports of synthesis of Au NPs in solution using hydroquinone. Interestingly, Au NPs generated with hydroquinone reside in a single band located at or within 10 nm of the polymer interface. Repeated experiments using each reducing agent showed that the observations described above were highly reproducible.

Figure 5. TEM bright-field cross-sectional images of Au-NP decorated films prepared using (A) NaBH₄, (B) sodium citrate, and (C) hydroquinone. The scale bar is applicable to all images. The dashed lines demarcate the approximate interfaces between the polymer, carbon, and Pt layers.

The difference in size of particles generated at versus below the interface may result from the difference in species mobility within the polymer matrix versus at the interface, as well as a difference in strength of the reducing agents. Studies in solution show that strong reducing agents promote formation of small Au NPs, because rapid reduction favors nucleation over diffusion limited growth of larger particles. Values for the standard reduction potentials of NaBH₄,
hydroquinone, and citrate are $-1.37 \text{ V}$, $+0.699 \text{ V}$, and $+1.2 \text{ V}$, respectively, referenced to the normal hydrogen electrode. Consistent with this, the smallest Au NPs observed in this work are generated by NaBH$_4$, the strongest reducing agent used.

The TEM cross-sections suggest both NaBH$_4$ and sodium citrate are capable of diffusing into the polymer matrix sufficient to generate Au NPs below the surface. In contrast, hydroquinone generates Au NPs only at or near the polymer interface. Relative to NaBH$_4$ and sodium citrate, the greater rigidity and steric bulk of hydroquinone may reduce its ability to diffuse into the polymer matrix, so that Au NPs are only generated by hydroquinone at the interface.

The outcome of reduction by citrate is intermediate between that observed with NaBH$_4$ and hydroquinone, in that small Au NPs are generated within the polymer matrix, yet large Au NPs are produced at the interface as well. Au ions located at the interface are expected to have higher mobility than those within the matrix, so particle growth should be more favorable at the interface, especially with weaker reducing agents. Consequently, Au NPs generated at the interface with both sodium citrate and hydroquinone are much larger than those generated within the polymer matrix. Comparing the size of Au NPs produced within the polymer matrix reveals they are larger when produced with citrate than with NaBH$_4$, consistent with the former being the weaker reducing agent. Interestingly, both the large and small Au NPs observed for in-situ reduction by citrate are

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1This value is based on one-electron irreversible oxidation of citrate observed by cyclic voltametry. Evidence for two-electron decarboxylation to dicarboxyacetone has been obtained in studies of gold nanoparticles synthesized in solution and may therefore be relevant to the present work. The corresponding reduction potential can be estimated as -0.35 V based on values for two-electron oxidative decarboxylation of malate (-0.330 V) and isocitrate (-0.375 V) at pH 7.
within the range of sizes observed when prepared in solution (5 nm - 147 nm), albeit at different reactant concentrations. This implies that the polymer matrix does not block Au NP formation, but it does affect particle sizes, which can be ascribed to diffusion-limited transport of both gold ions and the reducing agent. This suggests the size of Au NPs generated at a polymer surface by in-situ reduction and their distribution in depth relative to the interface can be controlled by choice of the reducing agent.

Alternative binding agents and surface functionalization chemistry were examined as means for confining gold-ion binding and subsequent Au-NP formation to the polymer interface. Ethanol was replaced by water as the solvent for reacting amines with the polymer because water does not swell SU-8, so it was expected to reduce transport of the binding agent into the polymer matrix. Additionally, the alternative binding agents AEP and TEPA were used in place of EDA, on the assumption that their larger size would decrease their ability to penetrate into the polymer matrix. These experiments were performed with NaBH₄ as the reducing agent and were otherwise identical in all other ways to procedures described above.

When either aqueous AEP or TEPA was used for binding agent attachment, the Au NPs form in a single layer near the interface approximately one particle-width thick (compare Figure 6A and Figure 6B with Figure 5A). If the larger amines were able to penetrate into the polymer appreciably under aqueous condition and bind gold ions below the surface, or if gold ions could embed within the polymer matrix unbound by the amine, then small Au NPs should have been observed, as in Figure 5A. The absence of Au NPs substantially below the interface supports the hypothesis that TEPA and AEP are unable to penetrate significantly into the polymer matrix and that these larger amines bind gold ions at the interface. Additionally, because the Au NPs that do form near the interface are comparable in size to those observed in Figure 5A, it provides additional
evidence that the size is largely determined by the strength of the reducing agent. This approach
decouples the effect of the reducing agent on influencing size of the NPs and the depth at which
they form. By using larger binding agents and functionalizing the surface in water, formation of
Au NPs can be confined near the interface, whereas their size can be independently controlled
through choice of reducing agent.
Figure 6. TEM cross-sections of Au NPs created when the polymer is functionalized with the alternative binding agents (A) AEP and (B) TEPA in water. The scale bar applies to both images. The dashed lines demarcate the interface between the polymer and the layer of carbon and to prepare the sample cross section. Note that the NPs reside in a single band roughly the width of the particles themselves.
3.2.3 The polymer matrix as a reservoir for metal ions

From HAADF-STEM images of Au NPs like that in Figure 4, we can calculate what the effective number of gold atoms is per projected unit surface area. It is instructive to compare this value to what the maximum coverage of gold ions at the interface could be prior to reduction, and to reflect on what this implies about the role of the polymer matrix during formation of Au NPs by in situ reduction.

Based on the number of Au NPs found per region, their average volume, and assuming gold atoms adopt a face-center-cubic packing within the NPs, the projected gold atom surface density across five different regions was found to be 10 to 13 atoms nm$^{-2}$ with a mean surface density of 12 atoms nm$^{-2}$. Now let us calculate what the maximum gold-ion coverage could be at the interface prior to reduction. First, let us assume that gold ions bind to the interface as a monolayer of AuCl$_4^-$ units packed as tightly as possible -- an hexagonally close-packed arrangement of square-planar AuCl$_4^-$ anions oriented with the coordination plane perpendicular to the surface. Based on the dimensions of the AuCl$_4^-$ anion observed for crystalline KAuCl$_4$·2H$_2$O, we can estimate that the gold-ion surface density could at most be 6 atoms nm$^{-2}$ prior to reduction. Note that this represents an upper limit because the surface-packing arrangement assumed is even denser than that found for crystalline KAuCl$_4$·2H$_2$O. Thus, HAADF-STEM images of the Au NP-decorated polymer film give a number of gold atoms observed per projected unit surface area that is twice as large as the number of gold atoms that could possibly bind at the interface under the densest arrangement possible.

The analysis above suggests that either the Au ions aggregate on the surface or they diffuse into the polymer matrix, so that the polymer functions as a reservoir for gold ions during in-situ
reduction at or near the interface. Support for the latter hypothesis can be found from the cross-sectional images of the samples, like that in Figure 5A, which show that most of the Au NPs produced by NaBH₄ reduction are not actually on the surface, but rather are buried within the polymer matrix at a depth as much as 20 nm below the interface. This in turn implies that both metal ions and the reducing agent can diffuse into the polymer matrix. It is well documented that solvents can swell cross-linked polymers, including SU-8, and this effect can be used to chemically modify polymeric surfaces. The provides support for the hypothesis that both the metal ion source and the reducing agent NaBH₄ appear to penetrate into the polymer matrix, leading to formation of Au NPs below the interface. The observations described above suggest that in-situ reduction does not always occur solely at the interface of a polymeric surface. Other types of surface chemistry conducted at polymeric surfaces may likewise involve diffusion of species into the polymeric matrix, and the matrix itself may be equally or more important to the progress of such reactions as the solution medium at the interface.

3.2.4 XPS analysis of surface-bound gold

At least three bonding modes (Figure 7) can be envisioned for chemisorption of gold ions onto an amine-functionalized polymer. These include neutral and charged Au(III) and Au(I) species. (1) Ion pairing of AuCl₄⁻ with a protonated amine could form a charged Au(III) species. (2) The amine could displace a chloride ligand and eliminate HCl, forming a covalently bound neutral Au(III) species. And by analogy with the known reaction of AuCl₄⁻ with alkylamines in solution, (3) the amine could partially reduce Au(III) to Au(I) with loss of HCl and formation of an Au(I)-imine complex. To identify the most likely bonding mode, XPS analysis was carried out
for SU-8 films aminated with EDA, AEP or TEPA, and then treated with HAuCl₄. These spectra were compared to XPS data in the literature for reference compounds containing Au(III), Au(I), and Au(0) species. Analysis of gold oxidation states via XPS is complicated by the fact that X-rays can induce reductive decomposition of Au(III). For this reason, XPS spectra were collected as a function of X-ray exposure time to obtain a time-dependent analysis of the Au oxidation state.

![Figure 7](image_url)

Figure 7. Possible modes for chemisorption of gold ions at the amine-functionalized polymer surface, both at and below the interface.

Figure 8A shows the first of a series of spectra obtained through time-resolved XPS analysis of an SU-8 polymer film that was aminated with EDA then treated with HAuCl₄. The dominant features at 87.7 eV and 91.4 eV correspond to Au(III), whereas the weaker peak at 85.3 eV and the shoulder at 88.9 eV correspond to Au(I). The Au(III) peaks were found to diminish progressively with each subsequent scan, whereas the Au(I) peaks increase concomitantly. Similar behavior was observed for samples prepared using the binding agents AEP and TEPA. The areas of the 4f_{7/2} peaks were measured for each oxidation state and plotted versus time, as shown in Figure 9, to quantify the atomic-percentage of gold in each oxidation state as a
function of X-ray exposure time. After a period of less than 20 min, the amount of Au(III) on all of the aminated samples had been reduced to less than 50%, and less than 20% after a period of 40 minutes. These time scales are long compared to the 120 seconds required to obtain an individual spectrum, so each data point may be regarded as an instantaneous snapshot of the gold oxidation states present at the sample. It is interesting to note that the rate at which X-ray exposure decomposes Au(III) to Au(I) differs with the binding agents. X-ray induced decomposition was fastest for EDA, which contains only primary amines, and slower for AEP and TEPA, which contain secondary and tertiary amines. This suggests that the binding group, depending upon its structure, can partially stabilize Au(III) against X-ray-induced decomposition.

These observations are similar to the findings of Buntine et al.\textsuperscript{55} with some key differences. In their report, soft X-ray exposure of Au(III) supported on silicon produced Au(I), which decomposed further to Au(0) within \textit{circa} 15 min, following first-order kinetics. The time constants found by Buntine et al. are shorter than that observed in the present work, perhaps because the synchrotron source they used provided high X-ray flux. But more intriguing is that under our conditions no Au(0) was observed, not even after 70 min of X-ray exposure. Au(0) was only detected when samples were subjected to chemical reduction, using NaBH\textsubscript{4}, citrate, or hydroquinone. For example, Figure 8B shows the XPS spectrum obtained for a sample having Au ions bound to the surface with EDA then chemically reduced using NaBH\textsubscript{4}. Only two peaks are observed. These are located at 87.6 eV and 83.9 eV and have integrated areas in a ratio of 3:4, as expected for the \textit{4f}\textsubscript{5/2} and \textit{4f}\textsubscript{7/2} peaks of Au(0).\textsuperscript{53-55} This shows that the NPs formed by chemical reduction consist of Au atoms in oxidation state zero.
Figure 8. XPS spectra of gold bound to SU-8 polymer films using ethylene diamine (A) after treatment with HAuCl$_4$ and (B) after chemical reduction using NaBH$_4$ to form Au NPs. The experimental data (blue curve) were fit (purple curve) by summing one or more Gaussian-Lorentzian doublets (remaining colors), which correspond to oxidation states Au(0), Au(I), and Au(III). The red vertical lines indicate the locations of the 4f$_{7/2}$ peaks for each oxidation state. Panel A is the first in a time-resolved sequence of XPS spectra that were recorded to assess how X-ray exposure affects the oxidation state of surface-bound gold. The time-resolved changes in the area of the Au(I) and Au(III) peaks are depicted in Figure 9.
Figure 9. Atomic percentage of Au(I) and Au(III) observed as a function of exposure time during XPS measurements of SU-8 polymer films bearing gold affixed using the binding agents EDA, AEP, or TEPA. Hollow markers represent Au(I) and filled markers represent Au(III). These data were obtained from time resolved spectra, like that in Figure 8A, by integrating the areas of the 4f\(7/2\) peaks used to represent Au(I) and Au(III) in the best fit of each spectrum.

Extrapolating the time-resolved data to the time-origin suggests that the gold ions bind primarily as Au(III), but approximately 20% binds as Au(I). The Au-Cl ratios were also examined, and were found for long exposure times to be nearly 1:1. This is consistent with the surface-bound gold evolving to the Au(I)-imine complex shown in Figure 7 (mode 3). It was not possible to distinguish whether Au(III) was present in the ionic or neutral complex form shown in Figure 7 (modes 1 and 2). Au(0) was only found when samples were chemically reduced using NaBH\(_4\), citrate, or hydroquinone, which resulted in formation of gold NPs as described above. It is noteworthy that secondary and tertiary amines have been reported to be capable of reducing AuCl\(_4^-\) to Au(0) in solution, forming Au NPs,\(^{30,56-58}\) whereas primary amines cannot.\(^{57-58}\) Yet no evidence for Au(0) was found – even when binding gold ions using agents like AEP and TEPA that contain
secondary and tertiary amines -- until a sample was forcibly reduced using NaBH₄, citrate, or hydroquinone.

3.3 Conclusion

This work shows that synthesizing Au NPs at a cross-linked polymer surface by \textit{in-situ} reduction of metal cations does not necessarily generate particles solely at the liquid-polymer interface. Reducing agents commonly used to synthesize NPs in solution, such as NaBH₄ and citrate, can generate particles within the cross-linked polymer SU-8 as much as 40 nm below the surface. In contrast, hydroquinone appears to generate NPs only at the interface. It is proposed that diffusion of the metal cation and the reducing agent through the polymer matrix affects the size of Au NPs formed and the depth at which they are generated, and that this can be controlled through the choice of reducing agent and the gold-ion binding agent. Conditions that restrict attachment of the binding agent at the interface likewise favor Au NP generation on the surface, even when NaBH₄ is used as the reducing agent. NPs generated at the interface by citrate and hydroquinone are much larger than those generated below the surface. This, too, can be controlled through choice of the reducing agent. When the strong reducing agent NaBH₄ is reacted with Au ions bound at the interface, the rapid reaction favors nucleation over growth yielding only small NPs, all bound at or very near the interface. Particles generated by \textit{in-situ} reduction with NaBH₄ on SU-8 are shown to be oblate spheroids.

These results suggest it may be possible to control synthesis of Au NPs below the interface of a polymer. This could be useful for several emerging applications in photonics. For example, it is well known that metal NPs can be used to achieve dramatic field enhancement of optical
effects \textsuperscript{59-61}. In the case of fluorescence, the overall emission enhancement is optimized at a certain distance from the NP, because absorption enhancement and NP-induced quenching are competing effects that exhibit different distance dependence \textsuperscript{62}. As such, controlling the depth at which Au NPs are created below a surface by the method reported here may be useful for creating material systems with controlled optical enhancement that are not compromised by fluorescence quenching.

3.4 References


4 NANOSCALE CHARACTERIZATION OF GOLD NANOPARTICLES CREATED BY IN SITU REDUCTION AT A POLYMERIC SURFACE

Work in this chapter was published as

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4.1 Introduction

Electroless deposition of metals onto nonconductive surfaces is a widely used process in electronics (e.g., metallizing printed wiring boards, magnetic recording), silvering of mirrors and decorative arts.¹ New applications are possible in the optical field for electroless silver deposition of three-dimensional metamaterials.² In ED, a reducing agent transfers electrons to metal ions at a catalytic surface of a material, while the rate of metal cluster formation within the solution is slower than at the surface. For ED of nanoparticles (NPs) and layers on nonconductive surfaces, the composition of the solution, temperature, stirring speed and pH value determine the speed of the deposition process.³ However, other parameters, such as the sample surface, can also influence the deposition process. Gold nanoparticles (Au NPs) have been used as nucleation sites for silver deposition,³-⁴ and we study here the arrangement, size and depth of Au NPs on a surface and their influence on the deposition of silver NPs on the surface. In this paper, we study initial Au NPs deposited by different methods onto films of the cross-linkable epoxide SU-8.⁵ The goal of the work presented here is to understand the correlation between processing and the Au NP distribution and size on the polymer surface. We also suggest a fast way for the quantitative
4.2 Theory of High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy

The HAADF technique has the advantage that the contrast is highly dependent on the atomic number of the material and not on the crystal orientation; it provides structural and chemical information with atomic resolution.\textsuperscript{6-7} The quantitative measurement of the thickness and volume of Au NPs from images of plan-view samples requires the intensity calibration of the HAADF detector intensity. To accomplish the contrast calibration, the HAADF detector intensity was measured in the direct imaging mode and the corresponding charge-coupled device (CCD) camera intensity was recorded in the diffraction mode. The beam intensities were measured for different spot sizes, gun lenses and condenser aperture sizes keeping the extraction voltage in the electron microscope constant. The HAADF detector shows some variability (about 10\%) of its sensitivity depending on where the electron beam hits the detector. The insert in Figure 10 shows an image of the HAADF detector. The background signal in the dark areas of the insert shows variations of less than 3\% and a linear interpolation of the background signal over the bright detector area was used. The background was subtracted and the intensities were averaged ($I_{\text{HAADF,avg}}$) over the HAADF detector for calibration of different incident electron beam probes (Figure 10). We found that the HAADF detector intensity scales with the linear CCD signal and can be best fitted as the following:

$$I_{\text{HAADF,avg}} = A I_{\text{CCD}}^B,$$  \hspace{1cm} (1)
where \( I_{HAADF,\text{avg}} \) is the intensity of the HAADF detector, \( I_{CCD} \) is the intensity (per second) of the CCD detector, \( A \) and \( B \) are constants.\(^8\) Taking the log of Equation (1),

\[
\log I_{HAADF,\text{avg}} = B \log I_{CCD} + \log A,
\]

Figure 10. Plot of the intensity of the HAADF detector versus CCD camera intensity for HAADF detector calibration.

The following values were found: slope \( B = 1.098 \pm 0.016 \), \( A = (4.48 \pm 0.14) \times 10^{-5} \) and the correlation coefficient \( R = 0.99981 \).

After the calibration of the detector signal to correctly account for nonlinear effects, the fraction of electrons scattered onto the HAADF detector for each scan position in an experiment is obtained. Before and after the HAADF-STEM measurement for an Au sample, a STEM image
of the detector (in imaging mode) is acquired. This measurement is done twice to ensure that the electron beam intensity did not change during the acquisition of HAADF-STEM images. Au NPs of diameter 50 nm - 60 nm were used to find the fraction of scattered electrons per nm of the Au sample. Among the NPs viewed without sample tilt and two sample tilts of 45° and −42°, several showed no change in diameter indicating a nearly spherical shape. In addition, the measured HAADF-STEM intensity of those selected NPs did not change significantly for the three viewing directions. The measured diameter \( D = 49.5 \text{ nm} \pm 0.2 \text{ nm} \) and the corresponding volume \( V = 6.34 \times 10^4 \text{ nm}^3 \) of the selected NP shown in Figure 11 remains the same when the sample is tilted in the microscope holder in the positive and negative direction thus confirming its spherical shape. In addition to HAADF-STEM micrographs, bright field-TEM images of the same NPs were taken to confirm the measured diameters and shapes at the three sample tilt angles.

![Figure 11. (a - c) STEM micrographs of Au NPs 50 nm – 60 nm in diameter at 0°, 45° and −42° tilt of the TEM holder. The tilt axis is vertical and the particle diameter along a line across the nanoparticle marked in (a) remained constant.](image-url)
Summation of the intensities of each pixel ($\sum I$) over the whole NP gives us 

$$\left(\frac{\sum I}{I_{\text{HAADF,avg}}}\right) \times \left(\frac{\text{pixel area}}{V}\right) = 0.213\%,$$

representing the fraction of the HAADF signal intensity per nm of Au thickness relative to the HAADF intensity for the incident beam directly on the detector. Taking the average of several Au NP measurements, this signal fraction is $0.207\% \pm 0.010\%$.

After correcting for the nonlinearity of the HAADF detector, the fraction of scattered electrons is $0.25\%$ per nm of Au thickness with the above detector brightness and contrast settings. The local thickness of the selected NP shown in Figure 11 is determined from the HAADF intensity of a cross section through the NPs’ center. This measured local thickness corresponds well to the local thickness assuming a spherical particle as shown in Figure 12.

![Graph](image)

Figure 12. Height of the selected nanoparticle in Figure 11 from HAADF intensity (solid grey line) and from local thickness (solid black line).
4.3 Results and Discussion

4.3.1 Morphology of Au NPs from bright field imaging

Direct evidence concerning the morphology, size and density comes from the TEM studies of colloidal Au bound to SU-8 polymer on the TEM grids. Figure 13A, B and C show the bright field-TEM micrograph of Au NPs formed on SU-8 polymer using three different reducing agents of varying standard reduction potential.

Figure 13. (a) Cross-sectional Bright Field (BF) TEM micrographs of Au NPs formed by reduction with hydroquinone (HQ). (b) Au NPs formed from reduction of Au\textsuperscript{3+} ions by sodium citrate. (c) NaBH\textsubscript{4} reduced Au NPs on the SU-8 polymer surface.
TEM images reveal crystalline NPs with typical \{111\} and \{200\} lattice plane spacing. For hydroquinone-reduced Au, the Au NPs form a band on or near the surface of the polymer, with particle sizes in the 5-10 nm range, as shown in Figure 13A. As hydroquinone is a bulky reducing agent, there is less penetration into the polymer matrix, so the NPs are mostly formed near the surface of the polymer confirming recent findings by Taleb et al.\textsuperscript{3} Figure 13B shows Au NPs that are 10 nm – 15 nm in diameter formed by citrate reduction of Au\textsuperscript{3+} ions. These Au NPs formed by citrate reduction are found on the surface as well as up to 20 nm below the surface of the polymer. Smaller NPs of 3 nm – 4 nm average diameter are formed 20 nm inside the polymer matrix, whereas larger Au NPs of 12 nm – 15 nm average diameter are found only on the surface. Au NPs are formed on or near the surface of the polymer by reduction of Au ions by NaBH\textsubscript{4} as can be seen in Figure 13C. The NPs are spherical in shape and they are of range 2 nm – 5 nm in diameter with almost no faceting. Moreover, the Au NPs are aligned along a straight line 10 nm - 20 nm below the polymer surface. NaBH\textsubscript{4} is a strong reducing agent which produces small Au NPs whereas hydroquinone, having a higher standard reduction potential, generates bigger NPs. Moreover, hydroquinone, being a bulky molecule, fails to penetrate the polymer matrix to act upon the Au\textsuperscript{3+} ions that have adsorbed into the polymer matrix. Bright-field TEM images in Figure 13A and B suggest that when hydroquinone acts as reducing agent the Au NPs have smaller height (4 nm – 5 nm in diameter) than when formed by sodium citrate, in which case they are 10 nm – 15 nm in height. The measurement of the height confirms that the NPs are spherical in shape and they are not faceted.
4.3.2 Quantitative analysis of HAADF-STEM images

Plan-view samples were studied in the STEM mode using the HAADF detector. Evaluation of the NP size, volume and distribution on the surface has been carried out in the past using HAADF images.\textsuperscript{9-12} A representative plan-view HAADF-STEM image of an Au deposited sample from reduction by NaBH₄ is shown in Figure 14. The Au NPs, which can be seen as bright contrast features on the dark contrast SU-8 polymer, can be thought of as isolated particles deposited on the SU-8 polymer. An integration time of 10 μs for each of the 2048 × 2048 pixels was used to acquire the HAADF-STEM images. In the STEM mode with a HAADF detector, atomic number contrast was used to identify the NPs and to measure their sizes. The intensity-calibrated HAADF-STEM image confirms that (1) the particles are isolated, evenly spaced and not aggregated in two dimensions; (2) the particle coverage is uniform over areas macroscopic compared to the particle size and (3) only about 25% of the surface is covered without much long-range ordering.
To obtain information about the heights of the NPs, quantification of the intensity distribution in the calibrated STEM image is necessary. For incoherent scattering conditions in HAADF, the final pixel intensity consists of the sum of the individual scattering contributions from Au atoms together with the background signal.\textsuperscript{13-14}

\[ I_{\text{Final}} = I_{\text{Au}} + I_{\text{B}}, \]  

(3)

where \( I_0 \) is the background signal of the image, which can be easily determined considering that the thickness of the polymer layer is either constant or linearly changing over the area of each NP. Polymer layers without NPs were used to test how thickness changes affect the HAADF-STEM signal. The image intensity modulations caused by thickness variations of the polymer appear on
a scale of significantly more than 2 nm. The amplitude variations of the signal due to the polymer are at most 20% of the intensity caused by Au NPs of 2 nm diameter. However, these small background intensity variations appear on a larger scale than the size of the NPs studied here. The background signal was therefore determined around each NP and a linear interpolation of this background signal was subtracted from the image intensities of each NP. A total of 150 NPs with observable intensity were manually evaluated from the images using the Digital Micrograph (Gatan, Inc.) software package. The volume of each NP was determined from the sum of the intensities over the total number of pixels considering the size of each pixel. From the intensity calibration, the volume of each NP was determined. A mean thickness was obtained for each NP, as well as the volume. The corresponding volume distribution is shown in Figure 15.

Figure 15. Volume distribution of 150 Au NPs.
It has to be noted that NaBH₄ is a strong reducing agent which produces small surface bound NPs.¹⁵-¹⁷ The average volume \( \langle V \rangle \) of the NPs was found to be 8 nm³ with a 56% relative standard deviation whereas the average area \( \langle A \rangle \) of the NPs was determined to be 6.5 nm² with a particle size distribution width of 0.7 nm. Considering the Au NPs to be circular in cross section, the height of each NP was calculated from geometry and is given by

\[
H_t = 1.5 \times \text{Average Thickness}
\]  \hspace{1cm} (4)

The height distribution of the Au NPs is shown in Figure 16. The NP height distribution shows that almost 60% of the particles have a height of 1 - 2 nm. A positive skewness value depicts the asymmetry of the distribution and that most NPs have heights below the average height of all the NPs.

The average Au NP height (\( \langle H_t \rangle \)) is calculated taking into consideration the nonlinearity of the HAADF detector. The NPs were considered to be circular in cross section and yield a value for \( \langle H_t \rangle \) of 1.97 nm for the 150 NPs. The standard deviation of the height of the NPs \( \sigma_H \) was found to be 0.74 nm from the measurements.
A further attempt was made to study the detailed morphology of the Au NPs if we consider the NPs as ellipsoidal. The in-plane projected shape of the NPs is found to be elliptic rather than circular with a long axis $x_n$ and a short axis $y_n$, giving an effective diameter of $D_n = \sqrt{x_n y_n}$. Independent of the first measurements where we assumed a circular projection, the long and the short diameter were now measured manually for each NP. The same NPs were analyzed again to determine the shape and size (volume) of each NP. This independent measurement of NP volumes was also performed to test if the criteria for background subtraction and determination of cross-sectional area can be consistently applied.

The effective diameter of the particles distribution is shown in Figure 17. The average effective diameter $D_n$ of Au NPs is 2.84 nm with a majority of NPs having a diameter between
2.5 and 3 nm. The in-plane aspect ratio \( \frac{y_n}{x_n} \) of less than 1 suggests that most of the Au NPs are oblate spheroids with \( < \left( \frac{y_n}{x_n} \right) > \) of 0.90. Only about 5% of the measured NPs show no deviation from circular projected shape. Further considering that the NPs are ellipsoids having height \( H_n \), the volume is given by \( V_n = \frac{\pi x_n y_n H_n}{6} \). The in-plane and out-of-plane aspect ratio \( \frac{y_n}{x_n} \) and \( \frac{H_n}{D_n} \) are shown in the histograms of Figure 18 and Figure 19, respectively. After measuring and evaluating the sizes of 150 NPs, the dimensions of each NP were determined again in a separate measurement. This was done to check if the data evaluation from the HAADF-STEM micrographs was consistent.

![Figure 17. Distribution of the effective diameter of Au NPs.](image-url)
Figure 18. In-plane aspect ratio of Au NPs distribution.

Figure 19. Out of plane aspect ratio of Au NPs distribution.
The mean out of plane aspect ratios $\langle \frac{H_n}{D_n} \rangle$ for both independent measurements (the first measurement is indexed as ‘n1’ and the second as ‘n2’ in the following) are 0.64 and 0.66, respectively. The mean value $\langle H \rangle$ and standard deviation $\sigma_H$ of the height distribution are smaller than the corresponding $\langle D_n \rangle$ and $\sigma_H$ values which prove the assumption that the NPs are ellipsoids.

The standard deviation in the height and volume of the NPs is given by

$$\sigma_H = \sqrt{\frac{\sum(H_{n1} + H_{n2} - 2 \langle H \rangle)^2}{4N}}$$

$$\sigma_V = \sqrt{\frac{\sum(V_{n1} + V_{n2} - 2 \langle V \rangle)^2}{4N}},$$

where $N$ is the total number of NPs, $V_{n1}$ and $V_{n2}$ are the volumes from calibrated HAADF-STEM images from the two separate measurements. Calculated $\varepsilon_H$ and $\varepsilon_V$ values from Equation (6) are 0.04 nm and 1.48 nm³. $\varepsilon_H$ is much smaller than $\sigma_H$, i.e. the measurement error in the height measurement is significantly smaller than the standard deviation in the size distribution.
4.4 Conclusion

This work presents data from the direct measurement of volumes of Au NPs using TEM. While several research papers have provided quantitative thickness and compositional data using the HAADF-STEM measurements,\textsuperscript{18-20} the above methods and analyses provide high accuracy in the determination of particle size distributions as well as three-dimensional volume data. From the statistical analysis, a better idea of the size distribution of NPs on or near the surface of the polymer is obtained. No significant faceting was observed and the assumption that the Au NPs are not exactly spherical in shape is valid. These Au NPs are oblate ellipsoids with the axis perpendicular to the surface being typically the shortest. The direct measurement of the mean thickness of NPs from the calibrated HAADF-STEM plan-view image renders more accurate data on the volume of Au NPs even if they are half buried in the polymer surface. The above method of formation of Au NPs by reduction of different reducing not only produced NPs on the surface but also below the surface inside the SU-8 polymer matrix. Au NPs formed by reduction using varying reducing agents differ in size according to the strength of reducing agent and range from 2 nm – 20 nm in diameter. The cross-sectional TEM micrograph in Figure 13A reveals that hydroquinone, being a bulky reducing agent, does not penetrate into the polymer matrix and the Au NPs are formed on the surface of the polymer. With NaBH\textsubscript{4} the Au NPs are much smaller 2 nm – 5 nm and are aligned in a band almost 10 nm – 20 nm below the polymer surface. SU-8 is used in fabrication of micro and nanoscale devices due to the small amount of shrinkage upon polymerization. The distribution of Au NPs should play an important role for the selective deposition of metal NPs for fabrication purposes.
Our technique measures the volume of Au NPs directly from the intensity-calibrated HAADF-STEM images rather than measuring the diameter. As a result, this technique reduces the experimental error in the measurement of the radius of the NP considerably. Statistical analysis identifies the dominant shape of the NPs when they are not exactly spherical. In this method the local background noise has been subtracted in the HAADF-STEM image for individual NPs to consider the small changes in height of the polymer layer beneath. For Au NPs, we show in Figure 12 that a thickness as high as 50 nm can be reliably determined from calibrated HAADF-STEM micrographs. Special care has to be taken that the NP is well focused to ensure that local thicknesses can be accurately determined from HAADF-STEM micrographs, especially at the NP edges where the thickness variation is large. However, if the integrated intensity is used to determine the volume of an NP, small defocusing effects do not significantly change the calculated volume as HAADF-STEM uses mostly incoherently scattered electrons. Defocusing merely blurs the outline of an NP making it more difficult to define its edge. Our method of analysis of Au NPs can be extended to other systems where we find a distribution of NPs on the surface of a substrate.

4.5 References


5 NANOSCALE MORPHOLOGY OF ELECTROLESSLY DEPOSITED SILVER METAL

5.1 Introduction

Electroless deposition is a means for forming colloidal metalized surfaces and continuous conducting metallized surfaces under ambient conditions.1-2 Unlike electroplating, ED can be achieved on a non-conducting surface because the metal is deposited from a bath that contains a source of the metal as a cation co-present with a chemical reducing agent. The ED bath is formulated to be metastable, so the reaction is thermodynamically spontaneous, but kinetically slow in solution. The ED reaction can be activated at a surface by attaching a nucleating species, typically a metal cation (e.g., Sn²⁺, Fe³⁺) or metal nano-particles.3-5 ED starts at the nucleation sites forming a layer of silver particles. Silver particles formed by initial ED serve as a self-activating surface that catalyze further deposition, so the process continues forming an increasingly thick layer of metal with time. Some investigators have reported ways to control the size of silver particles formed by ED.6-7 Yet to date there is little understanding of how the shape, size, and nanoscale morphology of the electrolessly deposited metal depends upon the constituents of an ED-bath and the deposition condition.

Here we report an investigation of ED of silver based on a formulation first proposed by Danscher et al.8 Figure 20 is a schematic of the processing parameters explored in this study. Polymeric surfaces were prepared by spin-coating the cross-linkable epoxide SU-8 onto glass substrates.9 The polymer samples were then treated with a bifunctional amine to which gold nanoparticles (NPs) could be attached to nucleate ED. The Au NP-seeded films were immersed in an ED bath and the resulting silvered polymer films were examined using a variety of analytical
techniques, including scanning electron microscopy (SEM), to characterize the nanoscale morphology. The procedure was repeated using a wide range of buffering agents, concentration of the silver ion, deposition times and two types of Au NP seeds. The findings reported here show that the nanoscale morphology of the deposited silver depends sensitively on the constituents of the bath, the nature of the surface-bound nucleation species, and the deposition time, and that these parameters could be used to control the nanoscale morphology and obtain metallized surfaces with targeted physical and chemical properties.

Figure 20. Steps of ED of silver and parameters that were varied to investigate their impact on the morphology of the resulting metal layer.

5.2 Results and Discussion

5.2.1 Electroless deposition of silver using the standard bath with gum arabic

Polymer surfaces seeded with in-situ synthesized AuNPs became reflective within 10 min. of immersion in the standard ED bath containing gum arabic and having [Ag⁺] = 33 mM. The
deposited metal had a yellow tint. The time required to obtain a completely reflective film is referred to hereafter as the "induction period." The length of the induction period provides insight into the activity of a given ED bath, although it cannot be simply related to the rate of the chemical reaction because the reflectivity of a metal film is a complex function of the metal thickness, morphology, and density.\textsuperscript{10-12} The deposition bath was light brown immediately after mixing due to the presence of gum arabic. After 60 min. the bath darkened due to slow formation of Ag NPs within the solution. As such, the standard bath can be used to deposit silver conformally onto a seeded polymeric surface for up to 60 min. The bath remains active toward deposition beyond 60 min., but then the surface morphology reflects the processes of both surface-catalyzed metallization and sedimentation of Ag NPs formed in solution.

SEM images were used to examine the nanoscale morphology of silver deposited over varying lengths of time. After 10 min. (Figure 21A) the silver layer consisted of spheroidal NPs having an average diameter of 22 nm ± 3 nm. The yellow tint of the metal layer can be attributed to scattering from the Ag NPs, which in air have a plasmon resonance that peaks at a wavelength near 400 nm.\textsuperscript{13} Most of the NPs were aggregated into a rice-grain shaped structures with an average length of a few NPs (71 nm ± 15 nm) but only one NP in width. At this early stage of deposition, surface coverage was incomplete, and the silver layer appeared to have a thickness of only one NP in most places. Films left in the bath for longer periods remained highly reflective with a yellow surface tint, but became more densely covered with aggregates. The size of individual NPs did not significantly increase, reaching a diameter of 26 nm ± 4 nm after 15 min., and 27 nm ± 4 nm after 20 min. Similarly, the length of the NP-aggregates did not change significantly, reaching 74 nm ± 19 nm after 15 min., and 79 nm ± 19 nm after 20 min. This suggests that with longer deposition times, individual aggregates and their constituent NPs reach
a maximum size, and additional metal adds to the surface by simply forming new aggregates, either nucleated at the surface or nucleated at existing aggregates.

Reducing the silver ion concentration of the ED bath to $[Ag^+] = 16.7$ mM increased the induction period to 20 min., but still yielded highly reflective films, also with a yellow tint. The metallized surfaces consisted mostly of spheroidal NPs and rice-grain shaped aggregates (Figure 21B). The NPs had an average width of $21 \text{ nm} \pm 2 \text{ nm}$ after 20 min. and $23 \text{ nm} \pm 2 \text{ nm}$ after 30 min., and the average length of the aggregates was $70 \text{ nm} \pm 16 \text{ nm}$ after 20 min. and $77 \text{ nm} \pm 17 \text{ nm}$ after 30 min. So, lowering the silver ion concentration by half significantly slows deposition but does not significantly alter the morphology of the deposited metal.

Reducing the silver concentration further to $[Ag^+] = 5.6$ mM dramatically increased the induction time and also significantly changed the morphology. A reflective surface (with yellow tint) was obtained only after approximately 2 hours of immersion in the bath. The surface consisted of spheroidal NPs and highly faceted NPs. After six hours of deposition, the average NP diameter was $65 \text{ nm} \pm 27 \text{ nm}$. Some of the faceted NPs had five-fold-symmetric surfaces (Figure 21C), very similar to the pentagonal bipyramidal particles that are known to form from twinned growth in colloidal suspensions$^{14-15}$ and via vapor deposition onto a surface.$^{16}$ Wiley et al. studied the effect of additives on colloid synthesis and found that poly(vinyl pyrrolidone) binds strongly to $\{100\}$ planes and allows other facets to grow faster, resulting in pentagonal bipyramidal NPs. Bögels et al. showed that multiply twinned structures form during vapor deposition when the temperature of the substrate is much lower than that of the source. Bögels claimed these conditions initially form unstable icosahedral nuclei, which lead to multiply twinned structures.$^{16}$ In each case, there was an external driving force causing the multiply twinned structures. With
ED, gum arabic may be acting to stabilize icosahedral nuclei, which are then able to grow into pentagonal bipyramids.

Figure 21. SEM images showing the morphology of silver formed using the standard ED bath, with gum arabic, having (A) $[\text{Ag}^+] = 33.3$ mM (after 10 min.); (B) $[\text{Ag}^+] = 16.7$ mM (after 30 min.); and (C) $[\text{Ag}^+] = 5.6$ mM (after six hours). In all cases deposition was nucleated by in-situ formed Au NPs.

5.2.2 Electroless deposition of silver using the standard bath without gum arabic

Upon mixing the standard bath without gum arabic, a gray-white precipitate of silver citrate formed when $[\text{Ag}^+] = 33.3$ mM, while for the standard bath with gum arabic when $[\text{Ag}^+] = 33.3$ mM, no precipitate was present. Trisilver citrate has a solubility in water at standard conditions of 0.56 mM in silver citrate, and 1.7 mM in silver. Thus, a precipitate should be observed at all conditions used in this study where citrate is used, as both the $\text{Ag}^+$ and citrate are above the solubility of the Ag/citrate species. The fact that no precipitate is observed in the standard bath in the presence of gum arabic suggests that the amine and carboxylate moieties contained within the glycoproteins of gum arabic are coordinating with $\text{Ag}^+$, bringing the free $\text{Ag}^+$ concentration below the solubility limit.
For ED baths without gum arabic when \([\text{Ag}^+] = 16.7 \text{ mM} \) or 5.6 mM, no precipitate is observed. These concentrations of \(\text{Ag}^+\) should also form a precipitate. However, the ED bath is prepared at a low pH, and thus, much of the citrate is protonated. At a pH of 3.8 and a total citrate concentration of 200 mM, it is found that the concentration of the completely unprotonated form of citrate that takes place in the Ag/citrate precipitation is 0.14 mM, giving a maximum allowable \(\text{Ag}^+\) concentration of 2.7 mM, which is still below the concentrations of \(\text{Ag}^+\) used in this study, meaning it is still expected that a precipitate would form in all ED baths that contain \(\text{Ag}^+\) and citrate. The only other aspect not being considered is the ability of the mono- and diprotonated forms of citrate forming soluble complexes with \(\text{Ag}^+\) in solution, thus reducing the free \(\text{Ag}^+\) concentration, and preventing the formation of a precipitate.

When gum arabic was left out of the standard ED bath, deposition was very rapid, but the bath was highly unstable toward spontaneous formation of NPs in the liquid phase. The induction period for deposition was only 3 min. when \([\text{Ag}^+] = 5.6 \text{ mM}\), and it decreased to 2 min. when \([\text{Ag}^+] = 16.7 \text{ mM}\) and 33.3 mM. When \([\text{Ag}^+] = 5.6 \text{ mM}\), the bath turned gray after 7 min. due to formation of Ag NPs in solution. The more reactive baths having \([\text{Ag}^+] = 16.7 \text{ mM}\) and 33.3 mM became brown after only 4 min. and 2 min., respectively. As a result, long deposition times could not be performed using a standard ED bath lacking gum arabic. Danscher and co-workers\(^8\) described gum arabic as a “stabilizing colloid” that prevents \(\text{Ag}^+\) reduction in solution. The observations reported here underscore the importance of gum arabic in stabilizing the bath and prolonging its lifetime, although this occurs at the expense of rapid deposition.

Figure 22 shows the morphology of silver deposited from a standard bath having no gum arabic as a function of \(\text{Ag}^+\) concentration, after 5 min. of immersion. The metallized surface consists primarily of rice-shaped or fan-shaped aggregates comprised of smaller spheroidal NPs.
This morphology is similar to that obtained when gum arabic is present and \([\text{Ag}^+]\) is high (compare to Figure 21A), except that the aggregates and the constituent Ag NPs are larger. The fan-shaped morphology is particularly apparent for deposition at \([\text{Ag}^+] = 5.6 \text{ mM}\) (Figure 22C), for which growth appears to extend from a common nucleation point at the surface. At the lowest concentration, where deposition is slowest, growth is favored over nucleation, as evidenced by the smaller number of spheroidal features per aggregate. At higher concentrations, where deposition is faster, nucleation is favored over growth, as evidenced by the greater number of spheroidal particles per aggregate. For all concentrations, the orientation of individual fan-shaped features is not correlated, indicating that the aggregates nucleate and grow independently. The overall morphology is similar to fractal structures that dominate when the kinetics of growth is mass-transport limited and nucleated at regions of a structure that are most accessible to free ions within the medium. Similar fractal morphologies have been predicted by slippery ballistic deposition models.¹⁹
Figure 22. SEM images showing the morphology and feature size of silver deposited after 5 min. of immersion in a standard bath having no gum arabic and Ag\(^+\) concentrations of (A) 33.3 mM, (B) 16.7 mM, and (C) 5.6 mM.

Figure 23 is a series of histograms which shows how the length and width of the aggregates vary as a function of silver-ion concentration and deposition time. The average length and width of the aggregates are summarized in Table 1 and Table 2. Figure 24 is a representative set of SEM images which illustrate how the surface morphology varied with deposition time when \([\text{Ag}^+] = 16.7 \text{ mM}\). These data show that silver aggregates grow with deposition time, primarily by adding new particles and extending the overall length of the aggregate, whereas the width of individual silver NPs comprising the aggregates remains constant within uncertainty.
Figure 23. Histograms showing aggregate width (top row) and length (bottom row) of Ag NP aggregates comprising metallized surfaces generated by ED versus concentration of silver (columns) and deposition time. ED was performed using the standard bath with no gum arabic and \([\text{Ag}^+] = 5.6 \text{ mM}\) (left), 16.7 mM (center), and 33.3 mM (right).

Table 1. Average length of aggregates formed by ED of silver using a standard bath containing no gum arabic as a function of \([\text{Ag}^+]\) and the deposition time.

<table>
<thead>
<tr>
<th>Ag(^+) concentration</th>
<th>Deposition time</th>
<th>5.6 mM</th>
<th>16.7 mM</th>
<th>33 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min.</td>
<td>91 nm ± 19 nm</td>
<td>132 nm ± 23 nm</td>
<td>168 nm ± 35 nm</td>
<td></td>
</tr>
<tr>
<td>10 min.</td>
<td>118 nm ± 22 nm</td>
<td>179 nm ± 37 nm</td>
<td>211 nm ± 51 nm</td>
<td></td>
</tr>
<tr>
<td>15 min.</td>
<td>162 nm ± 30 nm</td>
<td>206 nm ± 41 nm</td>
<td>233 nm ± 56 nm</td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Average width of nanoparticles comprising the aggregates formed by ED of silver using a standard bath containing no gum arabic, as a function of $[\text{Ag}^+]$ and the deposition time.

<table>
<thead>
<tr>
<th>Deposition time</th>
<th>$5.6 \text{ mM}$</th>
<th>$16.7 \text{ mM}$</th>
<th>$33 \text{ mM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min.</td>
<td>$22 \text{ nm} \pm 2 \text{ nm}$</td>
<td>$20 \text{ nm} \pm 2 \text{ nm}$</td>
<td>$17 \text{ nm} \pm 2 \text{ nm}$</td>
</tr>
<tr>
<td>10 min.</td>
<td>$24 \text{ nm} \pm 2 \text{ nm}$</td>
<td>$20 \text{ nm} \pm 2 \text{ nm}$</td>
<td>$22 \text{ nm} \pm 3 \text{ nm}$</td>
</tr>
<tr>
<td>15 min.</td>
<td>$25 \text{ nm} \pm 2 \text{ nm}$</td>
<td>$21 \text{ nm} \pm 2 \text{ nm}$</td>
<td>$20 \text{ nm} \pm 2 \text{ nm}$</td>
</tr>
</tbody>
</table>

Figure 24. SEM images showing the morphology and feature sizes for silver deposited using a standard bath having no gum arabic and $[\text{Ag}^+] = 16.7 \text{ mM}$ after an immersion time of (A) 5 min., (B) 10 min., and (C) 15 min.

5.2.3 Seeding deposition using colloidal gold nanoparticles

The effect of using either in-situ Au NPs or colloidal Au NPs as seeds for ED was explored by comparing the morphologies of silver deposited in both cases. The two types of seeds could be expected to yield different outcomes because of differences in their size and surface functionalization. Figure 25 shows atomic force microscopy (AFM) images of polymer films at different stages of seed-particle functionalization. The AuNPs are bound to the polymer films
using amine groups. From Figure 25A, it can be seen that the amine-functionalized polymer films themselves are relatively smooth, exhibiting surface roughness of less than 2 nm. When in-situ AuNPs are synthesized on this surface, the roughness increases to 4 nm ± 3 nm. This is consistent with TEM cross-sectional measurements which show that the average diameter of in-situ formed Au NPs is 3.6 nm ± 0.8 nm. When colloidal AuNPs are bound to amine-functionalized polymer films, the surface roughness increases to 13 nm ± 3 nm. This agrees with values of 15 nm - 20 nm reported for the diameter of colloidal AuNPs synthesized in solution. It is also noteworthy that the density of coverage is higher for surfaces functionalized with the in situ Au NPs.
Figure 25. AFM images of amine-functionalized polymer surfaces (A) prior to Au NP binding; (B) after binding in-situ formed Au NPs; (C) after binding citrated Au NPs.

Figure 26 shows the morphology of silver seeded using colloidal Au NPs and deposited using the standard bath, with gum arabic. These images can be compared to Fig. 3, which shows the morphology obtained when deposition was seeded with in-situ generated Au NPs. The induction period lengthened when deposition was seeded with colloidal Au NPs. Films deposited at [Ag⁺] = 33 mM became reflective only after 30 min. The induction period was approximately 1 hour when [Ag⁺] = 5.6 mM. At all concentrations, the morphology of metal deposited using colloidal Au NP seeds was similar to that obtained when initiated by in-situ Au NPs. At [Ag⁺] = 5.6 mM, the metal layer consisted primarily of spheroidal NPs having an average particle
of 69 nm ± 13 nm. After 30 min. of deposition at [Ag+] = 33.3 mM, the metal layer consisted again of spheroidal particles, as well as some small rice-shaped aggregates having an average length of 114 nm ± 28 nm and average width of 21 nm ± 2 nm. After 60 min., larger rice-shaped aggregates were obtained, with an average width of 170 nm ± 45 nm and average width of 21 nm ± 2 nm. Although reflective films were obtained when deposition was seeded with colloidal Au NPs, voids in the films were clearly visible (see Figure 26A and Figure 26B). This is consistent with the fact that initial growth is seeded at the Au NPs, but the surface coverage was less dense with colloidal Au NPs were used.

![Figure 26. SEM images showing the morphology of electrolessly deposited silver seeded using surface-bound colloidal Au NPs (standard bath, with gum arabic). (A) [Ag+] = 33.3 mM, 30 min. deposition. (B) [Ag+] = 33.3 mM, 60 min. deposition. (C) [Ag+] = 5.6 mM, six hour deposition.](image)

Depositing silver from a standard bath without gum arabic also yielded a similar morphology whether seeded by colloidal Au NPs or in-situ Au NPs. As before, the primary difference observed was that seeding deposition with colloidal Au NPs increased the induction period. When [Ag+] = 5.6 mM, deposition seeded with colloidal Au NPs was only apparent after 7 min., when the films began to turn gray, and a completely reflective film was not obtained until approximately 10 min. This is nearly twice as long as the induction period observed when ED was
seeded with *in situ*-reduced Au NPs. The colloidal Au NPs produced using the Turkevich method yield NPs capped by citrate. The increased induction period indicates the citrate capping groups on the colloidal Au NPs must first be removed in order for deposition to occur. At some points on the surface, larger-scale flower-like features, having a width of 300 nm - 500 nm and slightly raised from the surface, could be found when ED was seeded with colloidal Au NPs (Figure 27). These may result from ED onto agglomerated colloidal Au NPs, which were also observed by AFM at some points on the colloidal Au NP functionalized polymer surface.

Figure 27. SEM images at two magnifications showing the morphology of electrolessly deposited silver seeded by colloidal Au NPs (standard bath, no gum arabic, [Ag⁺] = 33.3 mM, after 10 min.).

### 5.2.4 Effect of varying carboxylate buffer species

While the citrate buffered ED bath gave mainly small, spherical NPs that agglomerated into larger structures, solution-based Ag NPs with a wide variety of shapes and sizes have been synthesized through addition of different surfactants. These surfactants not only interact with the metal ion in solution, but also interact with the forming NPs, capping certain facets and directing NP growth. We hypothesize that the citrate buffer is acting as the growth directing
surfactant and that changing the identity of carboxylate buffer will alter the morphology of the deposited metal.

In addition to affecting the NP size and morphology, it is also evident that the identity of species in the ED bath affect the bath itself. An ideal ED bath would be one that does not form a precipitate upon mixing of chemicals, does not form a significant number of NPs in solution and does not contain chemicals that can be difficult to work with, such as highly viscous gum arabic. The citrate-buffered ED baths described above either form a precipitate upon mixing, generate NPs in solution, or contain difficult chemicals to work with (gum arabic). Additional carboxylate-based buffers were explored based on carboxylate solubility, Ag⁺-carboxylate solubility, and carboxylate denticity. All other components of the bath were held constant so that any changes observed in the ED could be ascribed to the nature of the carboxylate. All depictions were seeded with in situ-reduced Au NPs, [Ag⁺] = 33.3 mM, no gum arabic present, and pH adjusted 3.8, as was used for the standard bath.

5.2.5 Monocarboxylates as buffering agents

5.2.5.1 Lactate buffer

An ED bath buffered with lactate generated dull, but reflective films within 3 min., and NPs began to form within the solution itself after 5 min. These observations indicate that lactate stabilizes the ED against spontaneous reduction better than citrate, used in the standard bath. SEM images in Figure 28 show that the lactate-buffered bath generated a different morphology, consisting primarily of spheroidal particles 50 nm – 75 nm in diameter, interspersed with large platelets, having a width that averaged 200 nm – 300 nm, but as large as 500 nm in some cases.
These larger features will scatter light, contributing to the dull appearance of the films. Fan-shaped features were also observed (white arrow in Figure 28B), similar to those produced by the standard bath at [Ag⁺] = 5.6 mM, although at much lower surface density.

![SEM images of silver deposited using a lactate buffered bath (after 5 min., no gum arabic, seeded by in situ-reduced Au NPs) at magnifications of (A) ×25,000 and (B) ×100,000.](image)

Figure 28. SEM images of silver deposited using a lactate buffered bath (after 5 min., no gum arabic, seeded by in situ-reduced Au NPs) at magnifications of (A) ×25,000 and (B) ×100,000.

5.2.5.2 Acetate buffer

The acetate-buffered bath produced a nontransparent, reflective film with a blue tint after only 45 s – the shortest induction time observed for any bath reported – but NPs developed in solution within 2 min. of preparation. These observations suggest the bath is highly unstable toward spontaneous reduction in solution. The bath could deposit silver onto films for as long as 6 min. after mixing, but the reflectivity diminished with increasing deposition time.

Figure 29 shows the nanoscale morphology of silver deposited by the acetate-buffered bath. The silver layer consisted exclusively of highly faceted particles having a width that increases with deposition time and exceeds 100 nm. The produced films were tinted blue, which is due to scattering at the plasmon resonance of the highly faceted Ag NPs. Mock, et al. showed that as the faceting of a Ag NP increases, the plasmon resonance shifts to longer wavelength.13
Because these films are blue, yellow/orange light is being scattered, which is at a much longer wavelength than the typical ~410 nm light scattered by spherical Ag NPs. Multiply twinned pentagonal bipyramids are also formed, like those produced by the standard bath at low [Ag\(^+\)]. Another feature that was present at all deposition times was a thin plate-like feature, such as the feature seen in Figure 29B. This plate-like morphology is typically approximately 25 nm wide and of varying length, but appears to grow longer as deposition time increases. As the time in the ED media increased to 5 min., evolution of a four-fold symmetry also became apparent, as shown in Figure 29D. This morphology is indicative of a single crystal of Ag, which assumes an FCC lattice. Though single crystals may be present at earlier deposition times, it is difficult to determine due the random orientation of the highly faceted structures apparent throughout the deposition.

![Figure 29. SEM images of silver deposited using an acetate-buffered bath (no gum arabic, seeded by in situ-reduced Au NPs) after (A) 45 s, (B) 90 s, (C) 135 s and (D) 300 s, respectively.](image-url)
5.2.5.3 Formate buffer

When formate was used as the buffer, the ED bath became cloudy and gray within 3 min. of mixing, and filled with flocculent gray solid after 15 min. The bath deposited silver onto polymeric films, making them nontransparent grey within 2 min, but they never became reflective. SEM imaging (Figure 30) shows that the surface of the films was incompletely covered by highly faceted spheroidal particles having a bimodal distribution of widths. The larger NPs appear to lie on top of smaller NPs immediately at the surface. The larger NPs grew with time, reaching an average width of 849 nm ± 198 nm after 15 min. The smaller NPs did not grow significantly, possibly because mass transport to the surface was restricted by the larger NPs above. The low reflectivity of these surfaces is likely due to the large size of the particles and uneven surface coverage, which generates significant scattering.
5.2.5.4 Benzoic acid

The benzoate-buffered ED bath remained clear and only turned slightly yellow after 20 min. due to slow spontaneous formation of Ag NPs in solution. Nontransparent, reflective films were obtained after 5 min. Films treated for as long as 15 min. became gray and non-reflective. The deposited silver consisted of highly faceted NPs (Figure 31), including some pentagonal bipyramids (see structure encircled in Figure 31D) having widths on the order of 100 nm. Gaps visible between the particles indicate that the surface coverage is incomplete. Some smaller NPs are visible within these gaps (< 15 nm) may have remained small due to reduced mass transport around the larger particles above.
Figure 31. SEM images of silver deposited using a benzoate-buffered bath (no gum arabic, seeded by in situ-reduced Au NPs) after (A, C) 10 min. and (B, D) 20 min., respectively. The structure circled in (D) shows a pentagonal bipyramid, which is evidence of twinned growth.

5.2.5.5 Salicylic acid

The bath buffered with salicylate provided thin and uneven deposition. Films treated up to 20 min. became grey, with only patches of metallic reflectivity. The bath itself was not stable against reduction of silver in solution, turning brown within 30 s of mixing and becoming completely opaque after 2 min. The rapid reduction of silver in solution implies salicylate does not strongly coordinate Ag⁺, leaving it free to be reduced rapidly by hydroquinone. The rapid formation of reduced silver in solution depletes Ag⁺ so deposition at the film is poor. SEM images of nonreflective portions of the silvered film (Figure 32A) show that surface coverage was sparse. In the reflective regions, (Figure 32B) the surface coverage was more dense and consisted of faceted and multi-domain particles with an averaged width of 55 nm ± 15 nm.
5.2.5.6 Summary of monocarboxylic buffering agents

Table 3 summarizes the results and key points of ED utilizing monocarboxylates. The acetate-buffered bath generated a nontransparent, reflective film in the shortest time, whereas the salicylate-buffered bath did not produce a nontransparent film, even after 20 min, showing that the length of the induction period correlates strongly with the solubility of the silver carboxylate salt. Additionally, it is known that Ag⁺/carboxylate complexes form in solution, reducing the effective concentration of free Ag⁺ and slowing deposition. Furthermore, Bjerrum showed that for complexes of Ag⁺ and amine containing molecules, a correlation between the metal/ligand formation constant (Kᵢ),

\[ Kᵢ = \frac{[AgL]}{[Ag^+][L^-]} \]  \hspace{1cm} (7)

and the proton/ligand formation constant (K_{H+}),

\[ K_{H+} = \frac{[HL]}{[H^+][L^-]} \]  \hspace{1cm} (8)
can be found, and that these constants scale approximately linearly.\textsuperscript{27} As such, comparison of various proton/ligand binding constants for carboxylic acids coupled with the metal/ligand solubility should give a general trend of the strength of silver/carboxylate binding in solution. Indeed, Table 3 shows that as log($K_{H^+}$) increases for the soluble Ag$^+$ complexes of acetate, formate and lactate, so does the time required to obtain a completely reflective film. This indicates a slower deposition, reduced free Ag$^+$, and greater binding between Ag$^+$ and the carboxylate.

To further test the hypothesis that an Ag$^+$/carboxylate complex is forming, an ED bath was prepared using fluoride as the buffer. Since silver fluoride completely dissociates in solution, the effect of possible complexation between Ag$^+$ and the buffer was removed. When silver nitrate was added to the reductant solution containing the fluoride buffer (pH = 3.8) and hydroquinone, immediate reduction of Ag$^+$ was evident by generation of a black solution, which is due to aggregation of Ag NPs.\textsuperscript{28} This shows that the carboxylate buffer plays an important role in coordinating free Ag$^+$ in solution and preventing, or at least delaying, unwanted Ag$^+$ reduction in solution.

All monocarboxylate buffers used provided faceted, multidomain NPs. Deposition baths containing benzoate, lactate and acetate provided twinned structures, as determined by the presence of five-fold symmetric pentagonal bipyramids, as previously discussed. For depositions that gave bimodal particle size distributions, the underlying NPs appear to be amorphous, while the larger particles retain a high degree of faceting.
Table 3. Summary of various constants, NP sizes and morphologies for different monocarboxylates used to buffer the standard bath.

<table>
<thead>
<tr>
<th>Buffer species</th>
<th>Reflective, nontransparent film obtained / min</th>
<th>log($K_{H+}$)</th>
<th>Solubility / M</th>
<th>Particle size / nm (Deposition time)</th>
<th>Nanoscale morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate</td>
<td>&lt; 1</td>
<td>−4.76</td>
<td>0.611</td>
<td>75 nm (45 s) - 300 nm (6 min.)</td>
<td>Faceted Twinning No plate features</td>
</tr>
<tr>
<td>Formate</td>
<td>&lt; 2</td>
<td>−3.77</td>
<td>Soluble</td>
<td>Bimodal: 110 nm (all times); 500 nm (2 min.) - 850 nm (15 min.)</td>
<td>Faceted Multidomain Small NPs are amorphous</td>
</tr>
<tr>
<td>Lactate</td>
<td>3</td>
<td>−3.86</td>
<td>0.391</td>
<td>Bimodal: 20 nm - 50 nm (all times); 300 nm (5 min.) - 2 μm (15 min.)</td>
<td>Faceted Fewer multidomain particles Twinning Plates features</td>
</tr>
<tr>
<td>Benzoate</td>
<td>8</td>
<td>−4.20</td>
<td>0.0114</td>
<td>50 nm (5 min.) - 100 nm (20 min.)</td>
<td>Faceted Multidomain Twinning Plate features</td>
</tr>
<tr>
<td>Salicylate</td>
<td>None</td>
<td>−2.97</td>
<td>0.00418</td>
<td>55 (15 min.)</td>
<td>Sparse metal coverage Faceted Multidomain</td>
</tr>
</tbody>
</table>

5.2.6 Dicarboxylates as buffering agents

Like the studies on monocarboxylates, several dicarboxylic acids were chosen to increase bath longevity and to determine what factors affect the morphology of the deposited metal. The dicarboxylates included maleic, fumaric and oxalic acids. These dicarboxylates were chosen due
to their order of magnitude difference in solubilities of the silver salt, with solubilities of 5.43 mM, 0.588 mM and 0.0672 mM for the silver salt of maleate, fumarate and oxalate, respectively. ED conditions were the same as the studies on monocarboxylates, where films were deposited in the absence of gum arabic, onto in situ-reduced Au NPs and with \([\text{Ag}^+] = 33.3 \text{ mM}\). In each case, the pH was adjusted to match that of the standard bath (pH = 3.8), so effects due to differences in pH could be avoided.

5.2.6.1 Maleic acid

The ED bath utilizing maleic acid had the highest longevity in terms of a lack of initial precipitate and lack of reduction of silver in solution. After a period of 20 min., the bath was completely transparent, though a slight yellow tint was present, which is indicative of Ag NPs, and after a period of one hour, the bath was still transparent, though a brown precipitate had begun to form, indicative of larger, Ag NPs. The first macroscopically visible flocculant solid in solution was noted after two hours and the number of visible solids had increased significantly after a period of 5.5 hours. Since very little silver is reduced in solution and/or deposited relative to the amount of \(\text{Ag}^+\) in solution, this ED bath could potentially support multiple batches of films.

The nanoscale morphology obtained from the maleic acid buffer is initially somewhat rounded features, with some faceting present, as seen in Figure 33A. At short deposition times, deposited NPs do not form a complete monolayer on the substrate and complete surface coverage of the film occurs after approximately 20 min. At deposition times less than 20 min. (Figure 33B), it is difficult to determine if the NPs are single crystals or multidomained. As deposition time increases, faceting becomes more apparent, though faceting is weaker than all monocarboxylate
buffers used. After a deposition time of one hour, plate-like NPs appear, which have a definitive single crystal structure (Figure 33C). This is a small plate growing vertically from the substrate showing six-fold symmetry, indicative of the silver FCC lattice. After a period of 5.5 hours, the number of plate features has greatly increased, and most of the NPs are now larger than 500 nm (Figure 33D). Some twinned structures were found, and the rest of the NPs appear to be large, single domain crystals.

Figure 33. SEM images of the nanoscale morphology of the silver film deposited using the standard bath with maleic acid used as the buffer. (A) 5 min. of deposition. (B) 20 min. of deposition. (C) One hour of deposition. (D) 5.5 hours of deposition.

5.2.6.2 Fumaric acid

When fumaric acid was used as the buffer, a white precipitate formed. As time proceeded, the bath became increasingly gray in color and eventually obtained a slight brown tint at
approximately 20 min., indicating growth of Ag NPs in solution. The films were initially reflective silver, yet transparent after a period of 5 min. and eventually became a nontransparent, nonreflective gray color with a slight blue tint after about 15 min.

After 5 min. of deposition, Ag NPs have not formed a complete monolayer and the NP morphology is round with relatively small, yet strong, faceting, as seen in Figure 34A. As deposition time increases, the nanoscale morphology remains unchanged, with NPs only growing in size and maintaining the relatively small facets, as seen in Figure 34B. Additionally, there remains an incomplete coverage of the substrate with the NPs and it was noted that only some of the NPs appear to grow. After 20 min., some of the NPs have grown to larger than 400 nm, while some particles remain smaller than 50 nm, showing that growth is favored over nucleation when using fumarate. Rather than a bimodal distribution found in some monocarboxylate depositions, formic acid generates a continuum of NP sizes.
There was another feature, that had also been noted in depositions using other buffer systems, which is the presence of large triangular plates and large multiply twinned structures, each being greater than a micron in size, such as in Figure 34C, and long, rod features, such as those seen in Figure 34D. Energy dispersive x-ray (EDX) analysis showed these large features are an alloy of gold and silver, with the triangular feature seen in Figure 34C containing an Ag:Au ratio of 4.9:1 and the multiply twinned structure containing an Ag:Au ratio of ~1:1. To ensure EDX measurements were not simply penetrating the Ag NP layer and sampling the underlying Au NP layer, an EDX spectrum of an *in situ*-reduced Au film was obtained, and no Au peak was found. The long, rod feature in Figure 34D is approximately 3 µm long and does not contain any Au or any other elements, according to EDX spectra, that might give a clue as to why this feature has grown. Clukay *et al.* discussed that the SU-8 polymer matrix, onto which Ag films are being
deposited, acts as a reservoir for Au$^{3+}$ ions, which may not be completely reduced by NaBH$_4$ during the Au NP formation step.$^{21}$ During subsequent ED, Au$^{3+}$ ions may leech out of the SU-8 polymer matrix and be co-deposited onto the film. Silver and gold can form alloyed NPs at all proportions, though a given Ag:Au ratio does not necessarily predict a certain NP shape.$^{31}$

5.2.6.3 Oxalic acid

A milky white precipitate formed immediately upon addition of silver to the ED bath. No silver deposited onto the polymer film, even after a total of 60 min. Within 30 min., the precipitate had settled to the bottom of the deposition vessel, even with stirring. After a period of one hour, there was still no deposition onto the substrates and there was no apparent color change of the solution that would indicate any reduction of Ag$^+$ had occurred. This lack of deposition as well as reduction in solution is due to the fact that the solubility of silver oxalate is so low, meaning there is very little free Ag$^+$ to take place in deposition and proves that only free Ag$^+$ takes place in the reduction process.

5.2.6.4 Summary of dicarboxylate buffering agents

Table 4 summarizes the results and some of key points of ED carried out with dicarboxylic acids. The overall morphology obtained using dicarboxylate buffers at relatively short times (<20 min) is that of spheroidal particles with visible faceting. At much longer deposition times when using the maleate buffer, strong faceting and large single crystals and singly twinned structures are apparent. Maleic and fumaric acids were also chosen because they are geometric
isomers and the maleate ion can chelate Ag\(^+\), while fumarate cannot. This chelation effect helps explain the high longevity of the ED bath containing maleate.

Table 4. Summary of various constants, NP sizes and NP morphologies for different dicarboxylate buffers used in the standard bath.

<table>
<thead>
<tr>
<th>Buffer species</th>
<th>Reflective, nontransparent film obtained / min</th>
<th>log((K_{H^+}))</th>
<th>Solubility / mM</th>
<th>Particle size / nm (Deposition time)</th>
<th>Nanoscale morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maleate</td>
<td>5</td>
<td>-1.90, -6.07</td>
<td>5.43</td>
<td>65 (5 min) – 250 (20 min), 500+ (5.5 hr)</td>
<td>Spheroidal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Faceting increases as deposition time increases Highly faceted after 5.5 hrs</td>
<td></td>
</tr>
<tr>
<td>Fumarate</td>
<td>7</td>
<td>-3.03, -4.44</td>
<td>0.588</td>
<td>50 (5 min) – 200 (20 min)</td>
<td>Spheroidal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>particles Faceted, many facets present Large dispersion in particle size</td>
<td></td>
</tr>
<tr>
<td>Oxalate</td>
<td>None</td>
<td>-1.25, -4.14</td>
<td>0.0672</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>

5.2.7 Comparison of depositions using variations of standard bath

In general, three distinct deposition modalities are present at deposition times less than 20 min.: large, highly faceted NPs, spheroidal NPs with apparent faceting, and small spheroidal NPs, which can be part of rice-shaped aggregates. The large, highly faceted NPs were produced using monocarboxylate buffers and contain NPs consisting mostly of large domains and clearly defined faces. Dicarboxylate buffers produced more spherical NPs with some faceting, however, these facets are smaller than the facets produced using monocarboxylate buffers. Citric acid-based
depositions at short times (< 20 min.) produce spherical NPs with no apparent faceting, and these spherical NPs eventually form rice-grain aggregates. These observations show that as chelating ability of the ligand increases, the faceting of the deposited NPs decreases, which indicates that ligands may be binding to the deposited NPs and directing growth. Several groups have shown that changing the identity of an organic capping group in solution-based NP synthesis changes the shape of the NP.25,32-33

In terms of deposition rate, the most significant factor that affects deposition rate is a combination of the solubility of the Ag+/carboxylate salt and $K_{H^+}$ of the carboxylate. As both the solubility of the Ag+/carboxylate salt and $K_{H^+}$ decreases, so too does the deposition rate. Additionally, we found that the rate of deposition does not necessarily affect deposited NP morphology. Instead, the identity of the carboxylate appears to have a greater effect on the NP morphology, by binding certain facets of the deposited Ag and directing growth, giving different NP morphologies, which has been demonstrated in colloidal syntheses.25,32-33

The chelation effect plays a key role in bath longevity, as evidenced by monocarboxylic and dicarboxylic acids that cannot chelate Ag⁺ having shorter bath longevities than carboxylates that can chelate Ag⁺. Both citric and maleic acids can chelate Ag⁺, but citric acid has a much shorter bath longevity than maleate, which can be explained by the first protonation constant ($K_{H^+}$) of each acid. The first protonation constant of maleate is two orders of magnitude higher than that of citrate ($K_{H^+} = -1.09$ vs. -3.13), so we can expect the $K_f$ of the Ag⁺/maleate complex to be approximately two orders of magnitude higher than that of Ag⁺/citrate complex, according to the work of Bjerrum.27
5.2.8 Other properties of electrolessly deposited silver

5.2.8.1 Optical properties in the visible region

The UV-Vis absorption spectrum of various silvered films is shown in Figure 35. Films were removed from the ED bath before a nontransparent film was obtained, so a transmission absorption spectrum could be taken. Figure 35A and Figure 35B correspond to the rice-grain like aggregate, that can be approximated by ellipsoids, while Figure 35C and Figure 35D correspond to spherical grain morphology. Figure 35E is an absorption spectrum of an *in situ*-reduced Au NP surface. The sharp rise in absorbance at 350 nm is caused by the presence of a photoacid generator contained in the SU-8 layer and the baseline absorbance of 0.5 is caused by reflection at the front and rear interfaces of the supporting glass substrate.

The rice-grain like aggregates show a broad absorption across the visible spectrum (Figure 35A and Figure 35B). This broad absorption spectra of the rice-grain like aggregates is due to the random orientation of the aggregates on the sample surface, and the mixing of the transverse and longitudinal plasmon resonances.\(^{34}\) Spherical NPs show a peak between 450 nm and 500 nm (Figure 35C and Figure 35D). The slight red-shift of absorption maxima between Figure 35C and Figure 35D is due to an increase in average particle size.\(^{35-37}\)
Figure 35. UV-Vis absorption spectra of deposited silver under various conditions. (A) \([\text{Ag}^+] = 16.7 \text{ mM}\) in the presence of gum arabic onto in situ-reduced Au NPs. (B) \([\text{Ag}^+] = 5.6 \text{ mM}\) in the absence of gum arabic onto in situ-reduced Au NPs. (C) \([\text{Ag}^+] = 5.6 \text{ mM}\) in the presence of gum arabic onto in situ-reduced Au NPs. (D) \([\text{Ag}^+] = 5.6 \text{ mM}\) in the presence of gum arabic onto colloidal Au NPs. (E) \textit{in situ}-reduced Au NP film.

5.2.8.2 Optical properties in the infrared region

Figure 36 shows the reflectance spectrum of silver in the near-infrared to mid-infrared region. Figure 36 shows silver that was deposited in the presence (gray) and absence (black) of gum arabic. The two silver films have a similar thickness, 95 nm ± 10 nm and 110 nm ± 3 nm, and both films were reflective and nontransparent, as evidenced by the high reflectivity of both samples. The vibrational absorption peaks in the range of 500 cm\(^{-1}\) - 2500 cm\(^{-1}\) of silver deposited in the presence of gum arabic could possibly indicate the co-deposition of gum arabic onto the surface of the silver film.
5.2.8.3 **Conductivity**

Four-point probe measurements on films produced using the standard bath, both in the presence and absence of gum arabic, generated films whose conductivity varied between $4.1 \times 10^4 \, \Omega^{-1} \, \text{cm}^{-1}$ to as low as $0.58 \, \Omega^{-1} \, \text{cm}^{-1}$, which is 6.5 % and $9.2 \times 10^{-5} \%$ that of bulk silver ($\sigma = 6.3 \times 10^5 \, \Omega^{-1} \, \text{cm}^{-1}$). On average, the conductivity of the as-deposited films is about $1 \times 10^4 \, \Omega^{-1} \, \text{cm}^{-1}$ for films deposited in the absence of gum arabic and about $1 \, \Omega^{-1} \, \text{cm}^{-1}$ for films deposited in the presence of gum arabic. This provides further evidence that gum arabic is co-deposited onto the silver film, as gum arabic is a nonconductive organic glycoprotein that would act as an insulating layer and interrupt electron flow between Ag NPs.

In an effort to increase the conductivity of the gum arabic deposited films, the films were annealed at temperatures much lower than the melting point of bulk silver (961 °C) for short times.

Figure 36. Reflection IR spectra of silver deposited using the standard bath in the absence and presence of gum arabic.
(<2 min.). Figure 37 shows the conductivity of deposited silver films as a function of annealing time (Figure 37A) and temperature (Figure 37B) for nominally 100 nm thick films deposited in the presence of gum arabic. Temperature-dependent annealing showed a gradual change, following a logarithmic increase in conductivity with temperature. For this study, all films were annealed for 60 s at varying temperatures. In exploring the time-dependent aspect of annealing, films were annealed for various times at 250 °C. We found that there is a significant increase in conductivity in a short amount of time, with films obtaining their maximum conductivity in 10 sec. After this time, all films yielded similar conductivities, averaging $7.0 \times 10^4 \, \Omega^{-1} \, \text{cm}^{-1}$ and varying by less than a factor of two from minimum to maximum values. Temperatures above 250°C were not explored because the SU-8 resin onto which the silver was deposited decomposes at 385°C.

![Figure 37. Plot showing conductivity as a function of (A) temperature and (B) time for silver films deposited using the Danscher method in the presence of gum arabic for 20 min. For time-dependent study, all films were annealed at 250 °C. For temperature dependent study, all films were annealed for 60 s.](image)

Visual observations as well as SEM images have shown that the appearance of the deposited silver particles does not appreciably change at either the macro- or nanoscale upon
thermal annealing. Moon et al. showed that sintering of Ag NPs at temperatures similar to the current study and well below the melting point of bulk silver increased conductivity by melting the NP surface. This surface melting would allow neighboring particles to come into contact at a greater surface area lowering resistance, and thus, increase the conductivity. Additionally, the presence of IR absorption peaks in the reflection spectrum of the as-deposited silver film in the presence of gum arabic (Figure 36) helps support the idea that gum arabic is present on the silver film and may act as an insulator lying between neighboring particles. The addition of heat may be enough to drive the loosely bound organic molecules from between particles, allowing for better contact of NPs.

5.3 Conclusion

The size and shape of silver nanoparticles generated by ED depends strongly on numerous chemical and physical parameters, including the concentration of the silver ion, the deposition time, the carboxylate comprising the buffer, the presence or absence of gum arabic, and the nature of the underlying Au NP seed layer. By varying these conditions, particle shapes from small spherical NPs, to highly faceted and large single crystal NPs, to long, fan-like aggregates can be obtained having sizes that range from circa 20 nm for the semi-spherical particles to nearly a micron in length for highly faceted single crystal NPs. The different ED conditions also affect the optical properties of the deposited metal layer. The electrical conductivity of ED-silvered films can be significantly increased by annealing. Low temperature annealing increases reflectivity as well as conductivity of the films. These improvements may result because annealing removes
organic residues that co-deposit between adjacent NPs and/or partial fusing of adjacent NPs at the interface, which improved ohmic contact between particles.

5.4 References


6 KINETICS OF ELECTROLESS DEPOSITION

6.1 Introduction

In order to more fully understand the process of ED, we would like to understand the reaction mechanism of this process. Insight into the mechanism can generate a greater understanding of ways to control the reaction, and possibly the morphology of the deposited silver. One way to determine the reaction mechanism is through chemical kinetics. By determining how the concentrations of various species affect the rate of the overall reaction, which in this case relates to the amount of silver deposited over a given time, the rate of the ED reaction can be determined.

To determine the reaction mechanism, the order of the reaction with respect to each reactant must be determined. This can be done by the method of initial rates.\(^1\) In this method, the rate of the reaction being studied is determined when the reaction has just begun, so the concentration of all reactants can be considered constant and equal to their initial value. The concentration of a single reactant is then varied, while the concentrations of all other constituents in the bath are held constant, and the reaction rate is determined for each concentration. This allows for determination of the order with respect to the species being varied. This is done in the following way. The overall reaction being considered is

\[
2\text{Ag}^+(aq) + C_6H_6O_2(aq) \xrightarrow{\text{Citric Acid, } pH=3.8} 2\text{Ag(s)} + C_6H_4O_2(aq) + 2H^+(aq),
\]

where \(C_6H_6O_2(aq)\) is hydroquinone (HQ) with a generalized rate expression
\[ v = k [\text{Ag}^+]^a [\text{H}_2\text{Q}]^b [\text{Cit}]^c [\text{H}^+]^d, \]  

(10)

where \([\text{Cit}]\) is the concentration of the citric acid buffer, \(v\) is the rate of the reaction in units of mg cm\(^{-2}\) s\(^{-1}\), \(k\) is the rate constant, and \(a, b, c,\) and \(d\) is the order with respect to each reactant. If the concentrations of all reactants but silver are held constant, then Equation (10) simplifies to

\[ v = k' [\text{Ag}^+]^a, \]  

(11)

for example, where \(k'\) is a pseudo rate constant. Taking the log of this equation leads to

\[ \log v = \log k' + a \log[\text{Ag}^+]. \]  

(12)

By varying \([\text{Ag}^+]\) and obtaining different rates, the order of the reaction can be obtained from the slope of line obtained by plotting \(\log[\text{rate}]\) against \(\log[\text{Ag}^+]\). This technique can be methodically repeated for each reactant, determining orders for each reactant.

Once the orders for each reactant are determined, we can begin to elucidate the reaction mechanism. Most reactions occur as a sequence of elementary reactions or steps, each involving one or more molecules. The series of elementary reactions can be summed to give the overall reaction. Although the reaction rate is determined by the slowest elementary reaction, reaction orders calculated from the above rate equations can still give clues to preceding or subsequent fast elementary reactions.\(^1\) Generally, a first order reaction, where \(a\) from Equation (11) is equal to 1, involves a single molecule, a second order reaction \((a = 2)\) involves the collision of two
molecules, etc. Reaction orders can also be zero, as well as fractional, with the latter being caused by either formation of an intermediate, or a chemical equilibria occurring before the slow step of the reaction.\textsuperscript{2}

In this chapter, the kinetics of the standard bath in the absence of gum arabic will be studied. The order with respect to Ag\textsuperscript{+}, hydroquinone, citric acid and pH will all be determined, and a proposed mechanism will be discussed.

6.2 Results and Discussion

To confirm that there are no background interferences from the sample preparation, several Ag\textsuperscript{+} standards were created. These standards were prepared by making films in a similar manner to those that underwent ED. Films of SU-8 were spin-coated and cross-linked, aminated, followed by gold deposition and reduction. These gold-deposited films were then exposed to trace metal grade nitric acid, as though the films were being digested, and a known amount of AgNO\textsubscript{3} was added. The hypothesis here is that by adding a known amount of Ag\textsuperscript{+} to a sample that has undergone all the processing steps of ED, without the final silver layer deposition, the signal from silver in the ICP-MS should only be from the Ag\textsuperscript{+} that was added. If the concentration of silver determined using ICP-MS is different than the amount of silver that has been added, there is some sort of interference that is introduced by the sample preparation. Samples prepared and analyzed using ICP-MS had target Ag\textsuperscript{+} concentrations of 7.9, 79 and 790 ppb in 2\% HNO\textsubscript{3} and the ICP-MS determined concentrations of 7.75, 81.2 and 795 ppb, confirming the ICP-MS there is no background interference from the sample.
There are several errors reported throughout this section whose origin require clarification. The error bars on each point used to determine the rate comes from the standard deviation of averaging several separate trials of ED at a given concentration. The error given in the rate is the standard deviation that arises from the least squares fitting of the individual points. The errors of the individual points are not factored into the fitting because in general, the error associated with the fitting is larger in magnitude than the errors associated with individual points. The error reported in the order is also from the error generated from least squares fitting of the log/log plot, which is also larger in magnitude than any error reported for any given order.

6.2.1 Reaction order with respect to Ag⁺

The rates of each Ag⁺ concentration studied, as well as the log/log plot used to determine the order is shown in Figure 38. The rate of each reaction decreases as [Ag⁺] decreases, giving an order with respect to Ag⁺ of 0.231 ± 0.010. This fractional order indicates that Ag⁺ may be part of an equilibrium reaction that occurs before the rate determining step. Djokic showed that Ag⁺/citrate complexes form in solution, and we previously discussed how mono- and diprotonated citrate are likely forming soluble Ag⁺ complexes in solution. To further illustrate how an equilibrium reaction before the rate determining step can produce a fractional reaction order, consider the following. Suppose a reaction occurs as two elementary steps,

\[ A_2 \rightleftharpoons 2A \quad K = \frac{[A]^2}{[A_2]} \quad (13) \]

\[ A + B \rightarrow C \quad rate = k[A][B]. \quad (14) \]
Here, the first step is an equilibrium reaction that is considered fast compared to the second step, which is the rate limiting step. Since reactant $A$ is an intermediate, we need to substitute, giving

$$\text{rate} = k \sqrt{K[A_2]} = k'[A_2]^{\frac{1}{2}}$$  \hspace{1cm} (15)$$

which gives a fractional order with respect to $A_2$.

Figure 38. Time vs. mass of Ag deposited per unit area at different starting Ag$^+$ concentrations. The slope of each curve gives the rate of that deposition. The blue points on each plot represent points within the linear portion of the data, and the points used to determine the rate. The orange points represent additional collected data not part of the rate determination. (Lower right) Log/log plot used to determine the order with respect to Ag$^+$. 
6.2.2 Reaction order with respect to citrate

The rates of each citrate concentration studied, as well as the log/log plot used to determine the order is shown in Figure 39. The order with respect to the citrate buffer was found to be 0.186 ± 0.012, which indicates the citrate buffer is likely part of an equilibrium reaction before the ED reaction. This which agrees with the fractional rate of Ag⁺ and the hypothesis that Ag⁺ and citrate are forming a soluble complex in solution. The positive order of citrate in this reaction is initially counterintuitive. One would expect that as citrate concentration decreases, the rate of ED would increase because more Ag⁺ is now free and uncoordinated, which would lead to a negative reaction order. The positive reaction order can be explained in one of two possible ways: 1) The Ag⁺/citrate complex is the species that transports and binds to the film surface immediately before reduction by hydroquinone, or 2) citrate not only binds to Ag⁺ in solution, but also binds to the Ag NPs that have been deposited onto the film, which has already been hypothesized. The process of citrate binding to the surface film surface would have an associated equilibrium constant, so decreasing the citrate concentration in solution would also decrease the amount of citrate bound to the deposited Ag NPs on the film surface. With fewer citrate molecules bound to the surface, there are more sites for the catalytic ED reaction to occur, increasing the reaction rate and leading to a positive reaction order.
6.2.3 Reaction order with respect to hydroquinone

The order with respect to HQ was found to be $1.100 \pm 0.095$ and the rates of each HQ concentration studied, as well as the log/log plot used to determine the order is shown in Figure 40. This agrees well with theory of HQ reduction, where HQ undergoes a two proton, two electron reduction in two successive steps, with the first oxidation of the hydroquinone to a semiquinone via a single electron oxidation being the rate determining step. The first oxidation is a unimolecular reaction, governed by first order kinetics. The second oxidation step is also unimolecular and first order, and takes place at a much faster rate because of the higher oxidation potential of the semiquinone. Thus, the overall rate of the reaction is first order.
Figure 40. Time vs. mass of Ag deposited per unit area at different starting HQ concentrations. The slope of each curve gives the rate of that deposition. The blue points on each plot represent points within the linear portion of the data, and the points used to determine the rate. The orange points represent additional collected data not part of the rate determination. (Lower right) Log/log plot used to determine the order with respect to the HQ.

6.2.4 Reaction order with respect to H⁺

The rates of each H⁺ concentration studied, as well as the log/log plot used to determine the order is shown in Figure 41. The order with respect to H⁺ was found to be -0.286 ± 0.127. It should also be noted that the fit of the regression line in the log/log plot is quite poor, signifying there may be a more complicated mechanism occurring. A negative order was also unexpected because as the hydrogen ion concentration increases, more of the buffer becomes protonated, so the amount of free Ag⁺ in solution should increase, increasing the rate of the reaction. The opposite is found to be the case, where an increase in hydrogen ion concentration showed a decrease in reaction rate.
Figure 41. Time vs. mass of Ag deposited per unit area at different starting H\(^+\) concentrations. The slope of each curve gives the rate of that deposition. The blue points on each plot represent points within the linear portion of the data, and the points used to determine the rate. The orange points represent additional collected data not part of the rate determination. (Lower right) Log/log plot used to determine the order with respect to the H\(^+\).

Upon further investigation it was found that the reduction potential of hydroquinone depends heavily on the pH of the solution. Marcus developed a theory that shows the relationship between the Gibbs free energy of a reaction, which is related to reduction potential of the reaction, and the rate constant:

\[
k_{ET} = k_{ET}(0) \exp \left[ \frac{-(\lambda + \Delta G^\circ)^2}{4\lambda RT} \right]
\]

(16)

where \(k_{ET}\) is the rate constant of the electron transfer reaction, \(k_{ET}(0)\) is activationless rate constant, \(\lambda\) is the energy required to reorganize the nuclei from the equilibrium positions of the
reactants to the equilibrium position of the products, $\Delta G^\circ$ is the Gibbs free energy, or driving force, of the reaction, $R$ is the gas constant, and $T$ is the temperature of the reaction. Equation (16) shows that with all other factors held constant, as $\Delta G^\circ$ becomes more negative, the rate constant becomes larger, thus increasing the rate of the reaction. As $H^+$ increases, the reduction potential of hydroquinone also increases, making $\Delta G^\circ$ more negative, which increases $k_{ET}$. So, it is not that the order with respect to $H^+$ changes as $[H^+]$ changes, but rather the rate constant increases as $[H^+]$ increases.

6.2.5 Induction period

One remaining piece of data from kinetics experiments that has not yet been discussed, but that is present in the data, is the so-called induction period. The induction period is the amount of time required for the ED reaction to reach a linear rate. Initially, the deposition of metal is slow, until sufficient metal is deposited so that autocatalytic deposition can occur. Additionally, before Ag is deposited, the coverage of the Au NP seeds required to catalyze the initial reaction does not completely cover the film surface and the reaction likely does not reach a constant velocity until a completely metallized surface is achieved. In general, as the rate of the reaction increases, the induction time of the deposition decreases.

6.2.6 Reaction mechanism

Having estimates for the order of the reaction in terms of each species, we can now propose a reaction mechanism. The order of the reaction with respect to $Ag^+$ suggests that it and citrate ion form a complex, the identity of which remains unknown. The investigations of the morphology
of the metal versus choice of buffering species indicate that citrate ion coordinates with deposited Ag NPs, altering the nanoscale morphology and slowing growth. The order of the reaction with respect to hydroquinone is unity, indicating that the rate determining step involves oxidation of hydroquinone. The rate of formation/dissociation of the complex of Ag⁺ and citrate must be faster than the oxidation of hydroquinone. If this were not the case, the order with respect to hydroquinone would not be unity. Given that the order of the reaction with respect to H⁺ is non-constant and negative, the rate limiting step does not involve a proton transfer. This is not surprising in that proton transfer in aqueous media is typically very rapid. However, the dependence of the rate on H⁺ may result from the pH dependence of the reduction potential of hydroquinone, as well as shifts in the equilibrium between protonated forms of citrate.

One possibility for the ED mechanism can be eliminated based on the determined orders. The first proposed mechanism is that HQ first reduces the metal surface and the metal surface reduces Ag⁺ from solution. This possibility can be eliminated because Ag⁺, citrate, and HQ all appear in the rate equation. Given that reduction of HQ is the rate limiting step, Ag⁺ would not appear in the rate equation if it adsorbed onto the film surface after HQ oxidation. Another mechanism that can be eliminated is the simultaneous adsorption of Ag⁺ and HQ onto the film, followed by reduction of Ag⁺. This possibility can be eliminated because it would exhibit an order with respect to Ag⁺ of unity, which is not observed. Given this information, the likely step by step reaction mechanism is as follows:

1)  Citrate bound to the ED Ag film desorbs.

2)  Free Ag⁺ adsorbs onto the ED metal surface.

3)  HQ reduces adsorbed Ag⁺ to Ag⁰.

4)  Citrate re-adsorbs onto the ED Ag film.
There is an additional possibility that instead of free Ag\(^+\) binding to the surface, the Ag\(^+\)/citrate complex could bind to the surface, followed by dissolution of citrate and reduction by HQ. This possibility is also consistent with the observed orders because as both the Ag\(^+\) and citrate concentrations increase, the concentration of the complex increases, which would increase the rate of the reaction. The fractional order of both Ag\(^+\) and citrate could then arise from the adsorption/desorption of the complex onto and off of the film surface and it would be expected that the fractional orders would be similar, which was experimentally found. Both mechanisms are plausible, and additional experiments are needed to eliminate one of these possibilities.

6.3 Conclusion

This work demonstrates a method to measure the amount of Ag deposited through ED, to extract the rate of the reaction, and to determine the order of the reaction with respect to each species, so a mechanism for the ED reaction can be hypothesized. The order of the reaction with respect to silver is 0.231 ± 0.010, and the order of the reaction with respect to citrate is 0.186 ± 0.012. These non-integer reaction orders suggest that both Ag\(^+\) and citrate are involved in a fast equilibrium reaction before reduction by HQ. The order with respect to HQ is 1.100 ± 0.095, which is consistent with theory that HQ undergoes two successive one electron oxidations, both governed by first order kinetics. The order of the reaction with respect to H\(^+\) was found to be non-constant, which may result because of two competing pH-dependent factors. First, lowering the pH decreases the reduction potential of HQ, which would inhibit the ED reaction. Yet, decreasing pH will protonate citrate, freeing Ag\(^+\) in solution and favoring ED. The proposed ED reaction mechanism involves diffusion of either free Ag\(^+\) or the Ag\(^+\)/citrate complex to the film surface,
followed by reduction of Ag\(^+\) by HQ. Additionally, further evidence that citrate adsorbs onto the film surface was provided, which would account for the very different Ag NP morphology seen when changing the identity of the buffer in ED.

6.4 References


7 SUMMARY AND OUTLOOK

This dissertation explores several aspects of ED, including (1) how various amines and reducing agents affect the size and distribution of Au NPs generated in situ at a polymeric surface, (2) detailed characterization of these Au NPs, (3) the how the morphology of Ag-ED is affected by various chemical parameters, and (4) what the reaction mechanism may be for ED based on deposition system first reported by Danscher. Using small diamines, like EDA, with a small reducing agent, like NaBH₄, generated small (< 2 nm) Au NPs not only at the polymer surface, but up to 20 nm into the polymer matrix. Using HQ as the reducing agent produced a combination of small Au NPs below the polymer surface and larger (~10 nm) Au NPs at the polymer surface. Using either bulky amine groups, like AEP or TEPA, or bulky reducing agents, like citrate, produced large Au NPs only at the polymer surface. Using HAADF-STEM allowed for more detailed characterization and analysis of these Au NP-decorated polymer films. Using this technique, it was found that the Au NPs are spherical and that (1) the particles are isolated, evenly spaced and not aggregated in two dimensions; (2) the particle coverage is uniform over areas macroscopic compared to the particle size and (3) only about 25% of the surface is covered without much long-range ordering.

The size and shape of silver nanoparticles generated by ED depends strongly on numerous chemical and physical parameters, including the concentration of the silver ion, the deposition time, the carboxylate comprising the buffer, the presence or absence of gum arabic, and the nature of the underlying Au NP seed layer. By varying these conditions, particle shapes from small spherical NPs, to highly faceted and large single crystal NPs, to long, fan-like aggregates can be obtained having sizes that range from circa 20 nm for the semi-spherical particles to nearly a
micron in length for highly faceted single crystal NPs. The longevity of ED baths can be altered by judicious selection of the buffering species, with maleic acid giving the highest longevity of any bath studied. The different ED conditions also affect the optical properties of the deposited metal layer. The electrical conductivity of ED-silvered films can be significantly increased by annealing. Low temperature annealing increases reflectivity as well as conductivity of the films. These improvements may result because annealing removes organic residues that co-deposit between adjacent NPs and/or partial fusing of adjacent NPs at the interface, which improved ohmic contact between particles.

Kinetics studies of the ED bath showed non-integer orders for both Ag⁺ and citrate, indicating that these species partake in an equilibrium reaction before the rate determining step. HQ was found to have an order of approximately one, in agreement with the kinetics known for HQ reduction. The order with respect to H⁺ is non-constant, caused by H⁺ competing in the Ag⁺/citrate equilibrium as well as H⁺ altering the reduction potential of HQ. The proposed ED reaction mechanism involves diffusion of either free Ag⁺ or the Ag⁺/citrate complex to the film surface, followed by reduction of Ag⁺ by HQ. Additionally, further evidence that citrate adsorbs to the film surface was provided, which would account for the very different Ag NP morphology seen when changing the identity of the buffer in ED.

The findings reported here can be leveraged to extend studies of ED. First, it is known that carboxylates coordinate Ag⁺ in solution, but the formation constant (Kᵢ) of these complexes remains unknown. Knowledge of Kᵢ values could lead to engineering ED baths with high longevity that can be potentially be used for multiple coatings, thus improving throughput and decreasing generated waste. Additionally, if the Kᵢ is known, a more precise mechanism can be elucidated by decoupling the Ag⁺ and citrate ion concentrations and allow for discrimination
between the free Ag\(^+\) and the Ag\(^+\)/citrate mechanisms. Second, the nature of the carboxylate absorption to the ED metal surface is not known. It was shown that different carboxylate buffers lead to very different ED metal morphology on the nanoscale, but the precise mechanism by which this happens remains unknown. If this can be determined, further control over the NSM of the ED surface can be achieved, so these surfaces could be used in fields where a specific NP shape is required.