Effect of Size, Coverage, and Dispersity on the Potential-Controlled Ostwald Ripening of Metal Nanoparticles

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ABSTRACT: Here, we describe the size-dependent, electrochemically controlled Ostwald ripening of 1.6, 4, and 15 nm-diameter Au nanoparticles (NPs) attached to (3-aminopropyl)triethoxysilane (APTES)-modified glass/indium-tin-oxide electrodes. Holding the Au NP-coated electrodes at a constant negative potential of the dissolution potential in a bromide-containing electrolyte led to electrochemical Ostwald ripening of the different-sized Au NPs. The relative increase in the diameter of the NPs (ΔD/NP) during electrochemical Ostwald ripening increases with decreasing NP size, increasing applied potential, increasing NP population size dispersity, and increasing NP coverage on the electrodes. Monitoring the average size of the Au NPs as a function of time at a controlled potential allows the measurement of the Ostwald ripening rate. Anodic stripping voltammetry and electrochemical determination of the surface area-to-volume ratio provide fast and convenient size analysis for many different samples and conditions, with consistent sizes from scanning electron microscopy images for some samples. It is important to better understand electrochemical Ostwald ripening, especially under potential control, since it is a major process that occurs during the synthesis of metal NPs and leads to detrimental size instability during electrochemical applications.

INTRODUCTION

Ultrasmall metallic nanoparticles (NPs) are widely used for catalytic and sensing applications due to their higher surface area-to-volume ratio (SA/V) and increased reactivity as compared to larger sizes and bulk counterpart. For different catalytic and sensing applications, NPs may be used at a relatively high temperature, at a high electrochemical potential, or under gaseous conditions. The structural stability of the metal NPs is critical to maintain their reactivity for their particular application. The main processes leading to NP instability during applications are dissolution, aggregation, and ripening (or coarsening). Ripening is an undesirable process that directly leads to an increase in average size, increase in size dispersity of NPs, and decrease in the number of NPs, resulting in loss of overall surface activity of the NPs. Three common types are known as Ostwald ripening, Smoluchowski ripening, and digestive ripening. They all lead to size instability of metal NPs, which has negative effects on their function for the application of interest. For example, Crooks and co-workers reported that the size of citrate-coated, 2 nm-diameter Au NPs increased to 6–7 nm by ripening after CO2 reduction based on STEM size measurements. However, they found that similar-sized, dendrimer-capped 2 nm Au NPs almost remained the same size after the same catalytic cycle. Ostwald ripening involves the growth of bigger metal NPs at the expense of smaller ones within a disperse population. This is distinguished from Smoluchowski ripening, which involves the coarsening of particles by diffusion, collision, and fusion of particles to form larger particles. Various methods, such as ozone treatment, thermal treatment, electrochemical treatment, and chemical treatment, have been used prior to applications of NPs in catalysis and sensing to increase activity by removing various stabilizers surrounding the NPs. These treatments also often lead to an increase in average NP diameter by ripening, which negatively affects their performance in various catalytic, sensing, or other electrochemical applications. Ostwald ripening is a major process that occurs during NP synthesis and even over time in a solution of metallic NPs. A better understanding of Ostwald ripening is needed to improve NP synthesis and size stability. It is not always clear whether Ostwald or Smoluchowski ripening is dominant as both can also occur at the same time. However, they usually can be distinguished from the kinetics or NP size histograms. Ostwald ripening can occur by thermal diffusion of metal atoms, which move from small NPs to join larger NPs to lower their overall surface energy. Electrochemical Ostwald ripening occurs by oxidation of small metal NPs to metal ions, which then deposit on larger NPs by reduction back to the metallic form. Ostwald ripening can be explained by NP curvature. The chemical potential (ΔμNP) of metal NPs is equal to 2VmY/r,
where \( V_m \) is the molar volume of the metal, \( Y \) is the surface energy, and \( r \) is the radius of curvature. \(^{23}\) Small metal NPs have higher chemical potential due to small \( r \) and higher surface energy. This drives the Ostwald ripening process, where small metal NPs readily oxidize and redeposit onto larger NPs with lower chemical potential. The critical radius \( \left( r_c \right) \) of NPs, \(^{27}\) which is the stable radius in equilibrium with the surrounding metal ions in solution, \(^{34}\) is \( r_c = (2 Y V_m/RT \ln S) \). Here, \( T \) is the temperature, \( R \) is the gas constant, and \( S \) is the supersaturation of the metal ions, which is the bulk metal ion concentration divided by the metal ion solubility at a flat surface. Although Ostwald ripening is driven by the chemical potential difference of different-sized metal NPs in a population, the closer the smaller NPs are to being below \( r_c \), the faster they will become eliminated through Ostwald ripening. Since \( S \) is a potential-dependent value, being larger at more negative potentials, the rate of Ostwald ripening should then be potential-dependent. Similarly, the thermodynamic NP oxidation potential decreases with decreasing NP size, \(^{35-38}\) as described by Plieth, \(^{39}\) which is another way of describing the electrochemical potential difference driving the oxidation/reduction processes in electrochemical Ostwald ripening.

There have been several studies on the electrochemical Ostwald ripening of metal NPs, both in the solution phase \(^{13}\) and on conductive substrates. \(^{31}\) In the solution phase, ripening of metal NPs can occur in a disperse size population of NPs with a redox molecule that controls the electrochemical potential in the solution. NPs of smaller size will dissolve and redeposit onto larger NPs through oxidation and reduction of the mediator. For example, Jang and co-workers reported the Ostwald ripening of cetyltrimethylammonium bromide (CTAB)-stabilized, 1.6 nm-diameter Au NPs in the presence of \( \text{H}_2\text{O}_2 \) in solution. \(^{40}\) Br\(^{-}\) ions from CTAB assisted in the formation of \( \text{AuBr}_3^- \) during Au oxidation from smaller NPs, leading to reduction of \( \text{AuBr}_3^- \) onto larger Au NPs, with \( \text{H}_2\text{O}_2 \) mediating both processes. Without a redox mediator, different-sized NPs would need to collide and directly transfer electrons and atoms between each other, which is more difficult due to surface stabilizers and slow kinetics.

Electrochemical Ostwald ripening on a conductive electrode surface can occur with different-sized NPs on one electrode or on two different electrodes connected externally with a wire. In the case of different-sized NPs on a single conductive electrode surface, the NPs do not have to collide as they do in solution because they are electronically connected by the conductive support and act like a galvanic cell with two different half-cell potentials, driving oxidation of small NPs and reduction at the large NPs. For example, Brus and co-workers studied electrochemical Ostwald ripening of colloidal Ag NPs on a conductive surface using scanning electron microscopy (SEM). \(^{14}\) After exposing thin films of Ag metal on indium-tin-oxide (ITO) electrodes to water, bigger Ag NPs formed on ITO over time at the expense of smaller NPs, which they attributed to electrochemical Ostwald ripening. Lee and co-workers later used a similar approach to weld Ag nanowires (Ag NWs) that were dispersed onto ITO by performing electron beam evaporation of Ag NPs and adding a drop of water. \(^{41}\) Welding of the Ag NWs occurred by oxidation of smaller Ag NPs to form Ag\(^{+}\), which redeposited onto the Ag NWs. In the case of different-sized NPs on two different electrodes externally connected, the open-circuit potential can be measured during ripening. For example, Parthasarathy and co-workers reported the ripening of Pt or Ag NPs attached to one graphite electrode that was connected to a second graphite electrode containing bulk Pt or Ag, respectively, and placed in an electrolyte containing their corresponding metal ions. \(^{42}\) The open-circuit potential decreased with time due to electrochemical Ostwald ripening of the NPs, driven by the different electrochemical potentials of the NPs compared to that of the bulk metal.

To the best of our knowledge, there have not been any detailed studies on the potential-controlled electrochemical Ostwald ripening rate as a function of several different variables, including NP size, electrode potential, NP coverage, and NP size dispersity. Here, we use anodic stripping voltammetry (ASV) and electrochemically measured SA/V to determine the average size of 1.6, 4, 15, and mixed 4 nm/15 nm-sized Au NPs attached to amine-functionalized glass/ITO electrodes before and after electrochemical Ostwald ripening in Br\(^{-}\), which serves as a coordinating ligand to lower the Au oxidation potential. \(^{38,43}\) Our recent electrochemical NP size analysis methods are ideal for this study because it would be costly and tedious to measure NP sizes from multiple samples under multiple conditions by electron microscopy or scanning probe techniques. Our electrochemical approaches are fast, of low cost, and simple, allowing high throughput and statistical analysis of the results. Since the Ostwald ripening process is measured under potential control instead of an unknown open-circuit potential, \(^{14}\) the results are highly relevant to NP ripening and stability under conditions used in electrochemical applications involving catalysis, sensing, and energy devices.

## EXPERIMENTAL SECTION

### Chemicals and Reagents.
H\(\text{AuCl}_3\cdot3\text{H}_2\text{O}\) was synthesized from metallic Au (99.99\%) in our laboratory. (\(3\)-Aminopropyl)-triethoxysilane (\(3H_2O\)) was synthesized from Sigma-Aldrich. Ethyl alcohol and acetone (ACS/USP grade) were purchased from Pharmco-AAPER. Potassium perchlorate (99.0–100.5\%), trisodium citrate, potassium bromide (GR ACS), and perchloric acid (60\%) were purchased from Bio-Rad Laboratories, Beantown Chemical, EMD, and Merck, respectively. Tetrakis(hydroxymethyl)phosphonium chloride (80\% solution in water) was purchased from Acros Organics. Indium tin oxide (ITO)-coated glass slides (CG-50IN-CUV, \(R_f = 8–12 \Omega \)) were purchased from Delta Technologies Limited (Stillwater, MN).

### Synthesis of Tetrakis(hydroxymethyl)phosphonium Chloride-Stabilized, 1.6 nm-Diameter Au NPs.
We synthesized THPC-stabilized, 1.6 nm-diameter Au NPs as recently described, \(^{38}\) which was adapted from Duff and co-workers. \(^{44}\) First, 200 \(\mu\)L of 80\% THPC solution was diluted with 16.66 \(\mu\)L of nanopure water in a glass vial to produce a 0.95\% solution. Next, 500 \(\mu\)L of 0.2 M NaOH solution was added to a separate glass vial containing 15.16 \(\mu\)L of nanopure water. Then, 400 \(\mu\)L of the reducing 0.95\% THPC solution was added. Finally, 660 \(\mu\)L of 25 mM HAuCl\(_4\)-3H\(_2\)O was added to the vials with constant stirring. After the addition of HAuCl\(_4\)-3H\(_2\)O, an orange-brown color formed in solution, indicative of the formation of small Au NPs. These NPs were stable for a few days but were used immediately for our analysis.

### Synthesis of Citrate-Stabilized, 4 nm-Diameter Au NPs.
We synthesized 4 nm-average-diameter Au NPs as described by Murphy and co-workers. \(^{45}\) In this method, 0.5 mL of 10 mM HAuCl\(_4\)-3H\(_2\)O and 0.5 mL of 10 mM trisodium citrate were added to 18.4 mL of water followed by the addition of 0.6 mL of ice-cold 100 mM NaBH\(_4\) at once with rapid stirring for 2 h. After the addition of NaBH\(_4\), the solution turned red within 5 min, indicating the formation of Au NPs.

### Synthesis of Citrate-Stabilized, 15 nm-Diameter Au NPs.
Au NPs with an average diameter of 15 nm were synthesized by a modified Turkevich method. \(^{46}\) Briefly, 500 \(\mu\)L of 0.01 M HAuCl\(_4\)-
3H2O was added to 17.0 mL of nanopure water and heated to a rolling boil for 10 min. Immediately after, 2.5 mL of 0.01 M trisodium citrate was added, and the solution was stirred for another 10 min. After removing from heat, the solution was stirred for another 15 min and allowed to cool.

**Functionaization of Glass/ITO Electrodes with 3-Aminopropyltriethoxysilane (APTES).** Glass/ITO electrodes were cleaned by sonication in acetone, ethanol, and 2-propanol for 20 min in each solvent. The glass/ITO electrode was then functionalized with APTES by immersing into a solution containing 100 μL of APTES, 10 mL of 2-propanol, and two to three drops of nanopure water and heating at 70–75 °C for 30 min. The electrode was rinsed with 2-propanol and dried under N2.

**Optical Characterization of Au NPs.** Ultraviolet-visible (UV–Vis) spectrophotometry was performed using a Varian Cary 50 Bio spectrophotometer. UV–Vis spectra were obtained in aqueous solutions of different-sized Au NPs from 350 to 850 nm at a fast scan rate of 80 nm/s using water as the blank. UV–Vis spectra of as-synthesized 1.6, 4, and 15 nm-diameter Au NPs are shown in Figure S1A. The UV–Vis spectra were normalized for absorbance of different-sized Au NPs. The localized surface plasmon resonance (LSPR) band of citrate-coated, 4 and 15 nm-diameter Au NPs appeared at 506 and 518 nm, respectively, which is consistent with the S1A. The UV

**Statistical analysis showed that the 15 nm Au NPs were divided into random areas of the electrode for the size evaluation to get a good representation of the entire electrode. Statistical analysis showed that the 15 nm Au NPs were 15.1 ± 1.6 nm in diameter. The 4 nm Au NPs were difficult to analyze accurately by SEM imaging but had previously been determined by our group to be 4.1 ± 0.7 nm in diameter by transmission electron microscopy (TEM) imaging.**

**Microscopic Characterization of Au NPs.** The as-synthesized Au NPs were attached to (3-aminopropyl)triethoxysilane (APTES)-functionalized glass/ITO (glass/ITO/APTES) electrodes by directly soaking the electrodes into solutions of NPs. We monitored the successful assembly of 4 and 15 nm Au NPs on the glass/ITO/APTES electrode by scanning electron microscopy (SEM) imaging (Figure S1C,D). SEM images of Au NPs before and after electrochemical Ostwald ripening were obtained with a Carl Zeiss SMT AG SUPRA 35VP field emission scanning electron microscopy (SEM) instrument at an accelerating voltage of 17.00 kV using an in-lens ion annular secondary electron detector. We generally obtained six to eight images from six to eight different random areas of the electrode for the size evaluation to get a good representation of the entire electrode. Statistical analysis showed that the 15 nm Au NPs were 15.1 ± 1.6 nm in diameter. The 4 nm Au NPs were difficult to analyze accurately by SEM imaging but had previously been determined by our group to be 4.1 ± 0.7 nm in diameter by transmission electron microscopy (TEM) imaging. TEM images of THPC-coated, 1.6 nm-diameter Au NPs were obtained with a 200 kV FEI Tecnai F20 operated in TEM mode. First, we functionalized silicon oxide-coated, 400-mesh Au grids (SPI Supplies, West Chester, PA) with APTES using the same procedure as we used for functionalization of the glass/ITO electrodes. NPs were attached to grids by directly soaking the functionalized grids into NP solutions for 4–5 min. After that, the grids were rinsed with water and dried gently under N2. TEM images of the 1.6 nm Au NPs showed them to be 1.6 ± 0.4 nm in diameter (Figure S1B), which is consistent with the results of Duff et al., who reported them to be 1.5 nm in diameter based on TEM.

**Size Analysis by Anodic Stripping Voltammetry (ASV).** A CH Instruments (Austin, TX) model CHI 660E electrochemical cell consisting of a three-electrode setup with Ag/AgCl (3 M KCl) as a reference electrode, a Pt wire as a counter electrode, and glass/ITO/APTES/Au NPs as the working electrode was used to perform ASV measurements. We measured the peak oxidation potential (Epa) of the Au NPs by scanning from −0.2 to 1.6 V (vs Ag/AgCl) in 10 mM KBr and 0.1 M KClO4 electrolyte at 0.01 V/s, as shown in Figure S1E. The downward anodic peaks in the scans are due to oxidation of Au by bromide mostly according to eq 1 below, with some possible contribution from eq 2 as well.

\[
\text{Au}^{0} + 4\text{Br}^{-} \rightarrow \text{AuBr}_{4}^{-} + 3e^{-} \quad (E^{0} = 0.85 \text{ V vs NHE}) \quad (1)
\]

\[
\text{Au}^{3+} + 2\text{Br}^{-} \rightarrow \text{AuBr}_{2}^{-} + e^{-} \quad (E^{0} = 0.96 \text{ V vs NHE}) \quad (2)
\]

The Epa of 1.6, 4, and 15 nm-diameter Au NPs decreased as the size of the NPs decreased in the order of 1.6 nm (Epa = 0.45 V) < 4 nm (Epa = 0.60 V) < 15 nm (Epa = 0.77 V). This is consistent with experimental works by us35,36,38 and others50 and theoretical works by Plieht39 and Henglein51 showing a negative shift in Epa (and E0) with decreasing NP size.

**Size Analysis by Electrochemical Surface Area-to-Volume (SA/V) Measurement.** Cyclic voltammetry was performed on Au NP-coated glass/ITO/APTES electrodes by scanning from −0.2 to 1.6 V and back in 0.1 M HClO4 at a scan rate of 0.1 V/s to measure the electroactive surface area (SA) of the Au NPs from the Au oxide reduction peak by peak, as described by our group previously. The oxidation/reduction reaction of the Au NP surface in 0.1 M HClO4 occurs by the following reversible reaction, as shown in eq 3.

\[
\text{Au}_{2}\text{O}_{3} + 6\text{H}^{+} + 6e^{-} \approx 2\text{Au} + 3\text{H}_{2}\text{O} \quad (3)
\]

The Au oxide layer only forms on the Au NP surface. The integrated charge of the oxide reduction peak corresponds to the electrochemical Au NP surface area (SA). The oxidation peak in the ASV from eqs 1 and 2 discussed earlier corresponds to the dissolution of all of the Au from the Au NPs and therefore reflects the total volume (V) of the sample of the Au NPs. SA/V is then determined by dividing the coulombs of charge from the reduction of Au oxide by those from full stripping of the Au NPs. SA/V was plotted versus 1/radius determined from SEM images of select Au NP triplets. This calibration curve was used to determine the average radius of unknown samples after different times of electrochemical Ostwald ripening from the electrochemically measured SA/V.

**Ostwald Ripening Studies.** We kept a similar total volume (total amount of Au) of different-sized Au NPs on the glass/ITO/APTES surface for the size-dependent Ostwald ripening studies to relate the Ostwald ripening rate to size as opposed to Au coverage effects. To keep the coverage the same, we obtained CVs of the glass/ITO/APTES/Au NPs in 0.1 M HClO4 to determine their electroactive surface area (SA) from the Au oxide reduction peak. Since we now know the Au NP size, we then estimated the volume (V) as V = (SA × r) / 3. The Au oxide reduction peak integration was (2.0–2.7) × 10–5 C and (0.7–1.0) × 10–5 C for 4 and 15 nm Au NPs, respectively, which gave a total volume of Au in the range of (3.25–4.25) × 10–5 C for both sizes. We unfortunately could not directly measure the electroactive surface area of 1.6 nm Au NPs because they are unstable and convert to 4 nm Au NPs in just one CV cycle. In this case, we obtained a similar coverage as 4 and 15 nm Au NPs, as determined by ASV, by soaking the glass/ITO/APTES/Au NP electrode in a solution of 10-fold-diluted, THPC-coated, 1.6 nm-diameter Au NPs for 3 min. The reproducibility of the soaking conditions was sufficient to obtain good statistics on the Ostwald ripening rate of different-sized Au NPs, independent of the Au coverage. Coverage was adjusted in the coverage studies by altering the Au NP soaking time and measuring the CV. Disparity was varied by co-attaching 4 and 15 nm Au NPs by soaking in a mixed NP solution.

Electrochemical Ostwald ripening was performed by holding the potential of various Au NP-coated electrodes at 0.0, 0.30, and 0.45 V (Ag/AgCl reference and Pt counter electrodes) for 35, 70, 105, or 140 min in 10 mM KBr and 0.1 M HClO4 electrolyte solution. We skipped 0.45 and 0.0 V for the 1.6 nm Au NPs for reasons discussed later. Then, we removed the electrode from the cell, rinsed it with nanopure water, and dried it under N2 before ASV or SA/V size analysis.

**RESULTS AND DISCUSSION**

**Monitoring Ostwald Ripening as a Function of Electrode Potential for Different NP Sizes by Anodic Stripping Voltammetry (ASV).** We monitored the effect of potential and NP size on the electrochemically controlled Ostwald ripening by using ASV size analysis. ASV is a powerful technique to monitor NP size changes on the electrode surface.
due to the dependence of the peak oxidation potential \( (E_p) \) on the NP size (Figure S1E). Figure 1 shows ASVs of glass/ITO/APTES/15 nm Au NP electrodes after holding these electrodes at 0.0 V (Figure 1A), 0.30 V (Figure 1B), and 0.45 V (Figure 1C) for 0, 35, 70, 105, and 140 min in 10 mM KBr and 0.1 M KClO₄ electrolyte. There is no shift in the initial \( E_p \) value of \( \sim 0.77 \) V when these electrodes were held for up to 105 min at 0.0 V (vs Ag/AgCl), but a small shift of \( \sim 40-50 \) mV occurred after holding for 140 min (Figure 1A). The \( E_p \) starts to show more significant changes after holding for 35 min at 0.30 V (Figure 1B, blue plot). We observed a new shoulder peak at 0.95 V after holding the potential for 70 min at 0.30 V, indicating a significant increase in NP size. The shoulder peak at 0.95 V increased with the holding time, becoming a clearly distinct peak after 140 min (Figure 1B, brown plot). Based on the theoretical work by Pleith and experimental work by our group, the new peak at 0.95 V indicates that some of the NPs increased to sizes larger than 20 nm during ripening. Also, the peak at 0.76 V indicates that some particles remained at \( \sim 15 \) nm in size. There are also some very small peaks at potentials between 0.0 and 0.4 V, which we attribute to tiny NPs that did not fully dissolve during ripening. The presence of these small Au NPs indicates an electrochemical Ostwald ripening mechanism.

To confirm our findings, we obtained SEM images of 15 nm Au NPs after 140 min of ripening at 0.30 V (Figure 1E) and compared them to those for no ripening (Figure 1D). The average NP size increased from \( 15 \pm 2 \) to \( 22 \pm 8 \) nm. The larger average diameter and larger relative standard deviation after ripening are due to the inhomogeneous size distribution of the NPs, consistent with the ASV and electrochemical Ostwald ripening. The size histogram of 15 nm Au NPs before (Figure S2A) and after 140 min of ripening at 0.30 V (Figure S2B) further supports the ASV results.

Next, we held the potential at 0.45 V for various times. In this case, we found that the shoulder peak at 0.95 V appeared within 35 min (Figure 1C, blue plot), which is faster than at 0.30 V. After 140 min, we observed two very distinct oxidation peaks for Au at 0.76 and 0.95 V, representing two different size populations. This clearly indicates that the ripening rate increased with increasing potential. The final average size of the Au NPs was found to be \( 26 \pm 7 \) nm based on SEM images. The full size histogram of the Au NPs after 140 min at 0.45 V is shown in Figure S2C of the Supporting Information.

As the NPs dissolve during electrochemical Ostwald ripening, it is common to observe NPs smaller than the original population in Ostwald ripening studies. As mentioned above, we did observe peaks at lower oxidation potentials in the ASV of 15 nm Au NPs in the potential range of 0.0–0.55 V after ripening at 0.30 V (Figure 1B). Figure S3A (Supporting Information) also shows three ASVs after ripening at 0.30 V for 105 min with evidence of smaller Au NPs. They all display peaks with \( E_p \) at 0.75 V and a small shoulder at 0.95 V, as discussed previously. Figure S3B (Supporting Information) also shows the ASVs zoomed in from 0.0 to 0.65 V, where it is clear that there is a series of small peaks in the 0.10–0.55 V range, which correspond to the oxidation of 1–2 nm-diameter Au NPs based on Pleith’s prediction and earlier reports by our group. These small Au NPs, not visible by SEM, come from larger Au NPs that did not fully dissolve during ripening. It is typically difficult to catch these smaller Au NPs, but they occasionally appear in the ASV (25–30% frequency), as shown in Figure 1B and Figure S3.

Figure 2 shows the electrochemical Ostwald ripening of 4 nm-diameter Au NPs at the same potentials and times shown for the 15 nm-diameter Au NPs in Figure 1 to understand the effect of size on the ripening rate. At 0.0 V, the \( E_p \) does not show any significant change up to 105 min. However, after 140 min, we observe the main peak shifting positive and becoming a doublet, and a small peak appeared around 0.95 V (Figure 2A, brown plot), indicating a size increase.

After holding at 0.30 V, the peak at 0.95 V became much more distinct, and the main peak at 0.70 V shifted close to 0.80 V after 140 min of ripening compared to the same time at 0.0 V (Figure 2B, brown plot). We obtained SEM images after 140 min of ripening at 0.30 V (Figure 2E) and found that the average diameter increased to 14 ± 6 nm. The average size of the NPs is larger, and there is also greater size dispersity. The size histogram in Figure S4A of the Supporting Information shows that most of the NPs were larger than 8 nm in diameter. We do not have size histograms of 4 nm Au NPs without ripening to directly compare our results because this is near the resolution of our SEM instrument. Previous transmission electron microscopy (TEM) images found them to originally be 4.1 ± 0.7 nm. While we were not able to detect Au NPs smaller than the original population by ASV or SEM size histograms (Figure S4), the results from the 15 nm Au NPs and potential dependence on the ripening rate lead us to believe that they are also growing by electrochemical Ostwald ripening.

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ASV obtained in 10 mM KBr and 0.1 M KClO₄ electrolyte with a scan rate of 0.01 V/s. SEM images of 4 nm Au NPs (D) at 0 min of ripening, (E) after 140 min of ripening at 0.30 V, and (F) after 140 min of ripening at 0.45 V.

Figure 2. ASV of citrate-coated, 4 nm Au NPs after Ostwald ripening at (A) 0.0 V, (B) 0.30 V, and (C) 0.45 V for 0, 35, 70, 105, and 140 min of ripening each in Br⁻-containing acidic electrolyte solution. ASV obtained in 10 mM KBr and 0.1 M KClO₄ electrolyte at a scan rate of 0.01 V/s. SEM images of 4 nm Au NPs after Ostwald ripening at 0.30 V for 0, 35, 70, 105, and 140 min of ripening at 0.45 V. (E) after 140 min of ripening at 0.30 V, and (F) after 140 min of ripening at 0.45 V.

The ripening of 4 nm Au NPs at 0.45 V was even faster compared to that at 0.30 V (Figure 2C). At this potential, the oxidation peak at 0.95 V was more prominent than the peak at 0.70 V, which shifted to near 0.80 V. The average size after 140 min at 0.45 V was 27 ± 14 nm based on the SEM images. The size range was 5 to 60 nm in the histograms (Figure 2F and Figure S4B).

The ripening of 1.6 nm-diameter Au NPs under the same reaction conditions at 0.30 V occurred very fast, as reported in our recent article. In our previous work, we did not determine the rate of ripening and only showed the data for 35 min. Figure 3A shows the ASVs of 1.6 nm Au NPs before (0 min) and after ripening at 0.30 V for different times. The Eₚ shifted completely from 0.45 to 0.70 V after 35 min, which indicates that all of the 1.6 nm Au NPs transformed to 4–5 nm-diameter Au NPs. Some of those particles ripened further to form even larger NPs with time based on the distinct peak at 0.95 V after 105 and 140 min (Figure 3A). SEM images (Figure 3B) showed the Au NPs to be 13 ± 5 nm. The size histogram (Figure S5) after 140 min shows particle sizes ranging from 6 to 40 nm. We were not able to study the ripening at 0.45 V for the 1.6 nm Au NPs since that is at the dissolution potential. The ASVs at different potentials and times qualitatively show that smaller-sized Au NPs ripen faster at lower potentials compared to larger NPs, presumably due to the lower oxidation potential of the smaller Au NPs.

**Monitoring Ostwald Ripening as a Function of Size Dispersity by ASV.** To study the effect of size dispersity on the rate of Ostwald ripening, we attached a mixture of 4 and 15 nm Au NPs to the glass/ITO/APTES electrode. We expected that the ripening rate would be higher for the mixture of two different size NPs due to the higher electrochemical potential difference (ΔEₚ or ΔE₁₅) between the NPs, which helps drive the ripening process. The glass/ITO/APTES was soaked in a 1:3 mixture of 4 and 15 nm Au NPs, and we held the potential of the electrode at 0.30 V for 0, 35, 70, 105, and 140 min. Figure 3C shows the ASVs of the mixture of NPs with no ripening (0 min) and after ripening for the different times. The ASV at 0 min has a dominant peak at 0.75 V, near the Eₚ of the 15 nm Au NPs. This is due to the larger fraction of 15 nm Au NPs in the sample. In this case, we found that 140 min of ripening completely shifted the Eₚ to 0.95 V with very little shoulder at 0.75 V. This is dramatically different than the 15 nm Au NPs without 4 nm Au NPs at 0.30 V after 140 min (Figure 1B), where there was only a very small peak at 0.95 V. This result clearly shows that the ripening rate is significantly higher when there is a large size distribution of the NPs. In this case, the ripening rate of the 15 nm Au NPs increased dramatically by adding a small fraction of 4 nm Au NPs to the electrode. A similar effect of NP size dispersity on Ostwald ripening in solution has been reported by others, but our studies show direct evidence of the effect of size dispersity on Ostwald ripening of electrode surface-attached NPs under potential control. SEM images (Figure 3D) found the NPs to be 45 ± 9 nm in size, which is about twice as large as the 22 nm size at this potential without 4 nm Au NPs (Figure 1E). The size histogram (Figure S6) shows that most NPs remain in the size range of 40–50 nm in diameter.

**Monitoring Electrochemical Ostwald Ripening as a Function of NP Size by Electrochemical SA/V Measurements.** The surface area-to-volume ratio (SA/V) is equal to 3/radius for spherical-shaped NPs. It is therefore a good method to measure the average NP size (radius = 3V/SA). Measuring SA/V as a function of time at a given Ostwald
Table 1. Calculated Size of NPs Based on Electrochemically Measured SA/V after Ostwald Ripening for 0.0, 35, 70 and 140 min for 1.6, 4, 15 and 1:3 mixture of 4 and 15 nm Au NPs at Different Ripening Potential (0.0 V, 0.30 V, and 0.45 V)

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<th>diameter (final)/diameter (initial)</th>
<th>calculated sizes of NPs after ripening at 0.30 V</th>
<th>diameter (final)/diameter (initial)</th>
<th>calculated sizes of NPs after ripening at 0.45 V</th>
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<td>2.1 ± 0.4</td>
<td>27.8 ± 2.0</td>
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<tr>
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<tr>
<td>140</td>
<td>32.5 ± 2.0</td>
<td>2.9 ± 0.3</td>
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</table>

The ripening potential allowed us to determine the average NP size as a function of ripening time. This allowed us to measure the average rate of ripening at different electrode potentials for different Au NP sizes, dispersity, and coverage to better understand Ostwald ripening. Recently, the electrochemical stability of Pt NPs was determined by measuring the SA through hydrogen adsorption and correlating it to microscopy images. However, the size was not known electrochemically because the volume was unknown. We did not use $E_p$ values from ASV to determine the average NP size (and rate) for these kinetic studies because $E_p$ values cannot accurately determine the size when there are multiple peaks and it does not distinguish sizes very well above ~30 nm in diameter. We therefore used the electrochemically measured SA/V to determine the average size of Au NPs as a function of ripening time. Since ASV provides the size populations present on the surface and SA/V provides the average size of the Au NPs, these techniques are complementary.

Figure S7A shows a CV obtained in 0.1 M HClO₄ of glass/ITO/APTES coated with 15 nm Au NPs before (0 min) and after (105 min) Ostwald ripening at 0.30 V. The electroactive surface area, as determined by the integrated area of the reduction peak at 0.8 V, decreased from 7.65 × 10⁻⁶ to 5.76 × 10⁻⁶ C during that time. The decrease in SA is consistent with an increasing size of the Au NPs due to Ostwald ripening. A similar trend was observed for all sizes of Au NPs studied in this work. The volume (V) of the same sample was measured by performing ASV in a Br⁻-containing electrolyte, which gave the total intergrated charge of 3.96 × 10⁻⁵ C (Figure S7B). The SA/V value for this sample was 0.145, determined by dividing the charge for the peak at 0.8 V from the CV by the charge for the stripping peak in ASV (5.76 × 10⁻⁶/3.96 × 10⁻⁵ = 0.145). We measured the SA/V ratios for all the samples studied to determine the NP sizes after Ostwald ripening under various conditions. The SA/V was converted to radius by comparing to a calibration curve of the measured SA/V versus 1/radius for known sizes determined by SEM imaging. The calibration curve was chosen over the direct measurement (SA/V = 3/radius) reported by our group recently because we were not able to clean the NPs with ozone due to it causing size changes for smaller NPs. The SA/V values for different-sized Au NP standards are shown in Table S1. Figure S8 shows the SA/V as a function of 1/radius for 1.6, 4, 15, 30, and 70 nm-diameter Au NPs. The size measured by the SA/V values generally matched well with the SEM-measured size of NPs after ripening. For example, the SA/V-measured sizes of 1.6, 4, and 15 nm-diameter Au NPs after 140 min of ripening at 0.30 V were 9.6 ± 0.8, 10.8 ± 1.8, and 21.3 ± 1.6 nm, which were reasonably close to the SEM-measured sizes of 13.4 ± 4.5, 14.4 ± 6.0, and 22.0 ± 7.5 nm, respectively (Tables S3, S6, S8, and S12). The size changes for smaller NPs are shown in Table S2—S9, Supporting Information.

Figure 4 shows the NP diameter and relative diameter, respectively, as a function of ripening time at 0.0 V (Figure 4A,D), 0.30 V (Figure 4B,E), and 0.45 V (Figure 4C,F) for 4 and 15 nm Au NPs. At 0.0 V, 4 nm Au NPs showed about a 25% increase in size after 140 min, while the 15 nm Au NPs showed ~17% size increase. At 0.30 V (Figure 4B,E), all samples changed more significantly with increasing ripening time. Au NPs with diameters of 4 and 15 nm increased by about a factor of 1.7 to 2.1. The final diameter was larger for the 15 nm diameter due to the initially larger size, but the 4 nm-diameter Au NPs increased by a higher percentage. The 1.6 nm-diameter Au NPs increased to a similar final diameter as 4 nm Au NPs but had a larger factor of 6.4 increase due to the initially smaller size. Figure 4C,F shows the NP diameter as a function of ripening time at a potential of 0.45 V for 4 and 15 nm Au NPs. Both sizes grew to a final diameter of 25–30 nm, while the 4 nm Au NPs showed a higher relative change,
growing by a factor of 5.4 as compared to 2.0 for the 15 nm Au NPs.

The Lifshitz–Slyozov and Wagner model (LSW) is popular for describing the Ostwald ripening kinetics of particles.\textsuperscript{29} Based on the LSW model, the mean particle radius ($r$) will be $r = Kt^{\beta}$, where $K$ is a constant, $t$ is the ripening time, and $\beta$ is 1/3 for a diffusion-controlled process and 1/2 for an interface-controlled process. Different researchers determined the $\beta$ value experimentally and found it to be $\sim 0.33$ for the diffusion-controlled growth of metal NPs.\textsuperscript{28,30} We attempted to determine the $\beta$ value from plots of NP radius versus ripening time and found that our data provided variable $\beta$ values using the classical LSW model. Others also found these models to be inadequate, especially for very small size NPs.\textsuperscript{57} This could be due to the fact that the LSW model assumes a single concentration of metal ions in solution, where, in reality, there are different metal ion concentrations around different-sized NPs.

Parthasarathy and co-workers\textsuperscript{42} observed a deviation from the LSW model for the Ostwald ripening of Ag and Pt NPs under an open-circuit potential. They fit their data to a linear regression. We also found reasonable linear fits to our data, and although we did not use a specific model, we were able to approximate the ripening rates for the different situations in terms of diameter increase per minute and percent diameter increase per minute. The $R^2$ value of the fits was higher than 0.92, indicating a reasonably good fit. Table 2 shows the slopes for the NP diameter versus time plots (Table 2, column 3) and slope of $D_{\text{final}}/D_{\text{initial}}$ versus time plots (Table 2, column 4). We multiplied the slope of $D_{\text{final}}/D_{\text{initial}}$ versus time by 100 to calculate the rate of percent diameter increase.

Table 2. Electrochemically Measured NP Ripening Rate in Terms of Increase in Diameter (nm/min) and % Increase in Diameter (% Increase/min) as a Function of Ripening Potential for 1.6, 4, and 15 nm Au NPs at 0.0, 0.30 and 0.45 V

<table>
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<tr>
<th>NPs size (nm)</th>
<th>ripening potential (V)</th>
<th>rate of increase in diameter (nm/min)</th>
<th>ripening rate (% increase in diameter/min)</th>
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<td>0.01</td>
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</tr>
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<td>0.30</td>
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<td>0.79</td>
</tr>
<tr>
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<td>0.45</td>
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<td>3.0</td>
</tr>
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<td>0.00</td>
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</table>

Figure 5 (A) Electrochemically measured NP diameter per minute and (B) percent increase of NP diameter per minute as a function of ripening potential for 1.6, 4, and 15 nm Au NPs at 0.0, 0.30, and 0.45 V.

We measured the size of Au NPs at different times of ripening at 0.30 and 0.45 V by SEM, as shown in Table S12 of the Supporting Information. We made the same plots (Figure S9, Supporting Information), and the results were reasonably close to the electrochemically determined plots. For example, 1.6 nm diameter Au NPs increased by a factor of 6.4 based on SA/V and 8.4 based on SEM at 0.30 V. The 4 nm diameter Au NPs increased by a factor of 2.0 and 5.4 based on SA/V and
3.5 and 6.5 based on SEM at 0.30 and 0.45 V, respectively. The 15 nm diameter Au NPs increased by a factor of 1.7 and 2.0 based on SA/V and 1.5 and 1.7 based on SEM imaging. This indicates that our electrochemically measured sizes match reasonably well with the SEM measured size of NPs, leading to the same trends and conclusions. The possible reason for the bigger mismatch with smaller-sized NPs, where the SA/V was consistently smaller than SEM, could be that the electron microscopy is biased toward larger NPs as it may not detect all of the smallest Au NPs.

**Monitoring Ostwald Ripening as a Function of NP Size Dispersity and Coverage by Electrochemical SA/V.** We next monitored the effect of NP size dispersity and coverage on the electrochemical Ostwald ripening rate of the Au NPs. Figure 6A,B shows the NP diameter and relative diameter, respectively, as a function of ripening time at 0.3 V for the 1:3 mixture of 4 and 15 nm Au NPs. The sample showed an extremely large ripening rate in terms of total final diameter (~32.5 nm) and size increase relative to the initial ~11 nm average diameter of the mixed NPs (~300% increase). The size increased to 45 nm based on SEM images, which is ~400% increase (Figure S10, Supporting Information). The slopes of the Figure 6 plots gave rates of 0.15 nm/min and 1.33% diameter increase/min, as shown in Table 2. The rate is significantly higher than 15 nm Au NPs alone, indicating that increased size dispersity significantly increases the electrochemical Ostwald ripening rate. Also, the coverage of NPs on the electrode surface played a significant role in the rate of Ostwald ripening since the AuBr₅⁻ ions from a smaller dissolving Au NP have to diffuse to a larger Au NP before deposition. Close proximity of the Au NPs should cause a larger concentration gradient between two NPs and allow greater collection of the AuBr₅⁻ ions at the larger NPs. The coverage values were determined from the ASV of the 15 nm Au NPs, which were (5.0–6.5) × 10⁻⁶ C and (2.0–2.6) × 10⁻⁴ C for low and high coverage values, respectively. This corresponds to ~1 and 45 NPs/μm², respectively. The Eₚ and SA/V ratio of 15 nm Au NPs at low coverage did not show any significant change with ripening time, as shown in Figure S11A and Table S10. However, the Eₚ and overall SA/V ratio increased significantly for higher coverage, as shown in Figure S11B and Table S11. We plotted the NP diameter versus ripening time and D_final/D_initial versus ripening time for coverage ranges of (5.0–6.5) × 10⁻⁶ C, (3.5–4.2) × 10⁻⁵ C, and (2.0–2.6) × 10⁻⁴ C using a ripening potential of 0.30 V, as shown in Figure 7A,B. For higher coverage, D_final/D_initial versus ripening time showed an increase in NP diameter by ~2.2 times, but for the lower two coverage values, it showed an increase of only 1.7 and 1.4 times, respectively. These results clearly confirm that the rate of Ostwald ripening increases with an increase in NP coverage on the electrode surface. Table 3 shows the rates in terms of increase in diameter per minute and percent increase in diameter per minute for the three different coverage values. Figure 7C,D shows the plot of rate in diameter increase per minute (Figure 7C) and percent increase per minute (Figure 7D) as a function of NP coverage for the 15 nm-diameter Au NPs ripened at 0.30 V. The ripening rate increased linearly with an increase in NP coverage.

**Discussion of Ostwald Ripening.** Ostwald ripening of Au NPs occurs in multiple steps. Oxidation is the first step of Ostwald ripening (Scheme 1, step 1), where the smaller Au NPs dissolve at a lower electrochemical potential and with faster rates. At potentials below the Eₚ value, the particles are not completely dissolved, but a small amount of dissolution from the NPs whose sizes are much smaller than the average

![Figure 6](image1.png)

**Figure 6.** (A) Electrochemically determined NP diameter versus ripening time and (B) D_final/D_initial versus ripening time at 0.30 V for glass/ITO/APTES coated with 1:3 mixture of 4 and 15 nm Au NPs.

![Figure 7](image2.png)

**Figure 7.** (A) NP diameter versus ripening time and (B) D_final/D_initial versus ripening time for 15 nm-diameter Au NPs at 0.30 V for various coverage values of NPs on the electrode surface, as indicated. (C) NP diameter per minute and (D) percent increase of NP diameter per minute as a function of NP coverage.

<table>
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<th>NPs coverage (NPs/μm²)</th>
<th>NPs diameter (% increase/min)</th>
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<td>1.1–1.3</td>
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<tr>
<td>40–51</td>
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</table>
Scheme 1. Mechanism of Electrochemically Induced Ostwald Ripening of Au NPs Attached to Glass/ITO Electrode

size occurs based on the following Nernst equation, assuming that eq 1 is the dominant electrochemical reaction

\[ E = E^0 + \frac{0.0592}{3} \log\left(\frac{[\text{AuBr}_4^-]}{[\text{Br}^\text{-}]}\right) \]  

Solving for the concentration of dissolved Au in terms of \([\text{AuBr}_4^-]\) in the Nernst equation gives

\[ [\text{AuBr}_4^-] = [\text{Br}^\text{-}] \times 10^{3(E-E^0)/0.0592} \]  

where \(E\) is the applied potential, and \(E^0\) is the size-dependent standard potential for the chemical half-reaction of Au dissolution in Br\(^-\). Since \([\text{Br}^-]\) is constant (in excess), \([\text{AuBr}_4^-]\) next to the Au NPs depends exponentially on how large \(E\) is relative to \(E^0\), or the magnitude of \(E - E^0\). Since \(E\) is constant but \(E^0\) is smaller for smaller Au NPs, there will be a larger \([\text{AuBr}_4^-]\) next to smaller Au NPs and smaller \([\text{AuBr}_4^-]\) next to larger Au NPs, as shown in Scheme 1, steps 1 and 2. The unequal dissolution leads to a concentration gradient and diffusion of \(\text{AuBr}_4^-\) from the small NPs to the large NPs (step 2). This causes \([\text{AuBr}_4^-]\) to become too large according to the Nernst equation at the larger Au NPs, leading to Au deposition at the larger Au NPs (Scheme 1, step 3). As the larger Au NPs become even larger, their \(E^0\) value shifts more positive, which further drives reduction of \(\text{AuBr}_4^-\) in solution by deposition onto the large Au NPs. This causes those NPs to grow larger until equilibrium is established with \(\text{AuBr}_4^-\) in solution (Scheme 1, step 4). In contrast, the \(E^0\) shifts more negative as the smaller Au NPs dissolve. The combination of this and diffusion of \(\text{AuBr}_4^-\) away from the small NPs leads to further dissolution of those Au NPs until they eventually fully dissolve (Scheme 1, step 4). The variation of the \(E^0\) values for different-sized Au NPs leads to different local \([\text{AuBr}_4^-]\) at the different-sized Au NPs, and then diffusion and the changing \(E^0\) values as large NPs grow and small NPs dissolve lead to the electrochemical Ostwald ripening process.

Based on this description, the ripening rate depends on the value of \(E\) relative to the average \(E^0\) of the sample since this controls the amount of \(\text{AuBr}_4^-\) that dissolves (step 1). The closer \(E\) is to \(E^0\), the greater dissolution there is. This is the reason why the rate is larger for smaller Au NPs (they have smaller \(E^0\)) and the rate grows exponentially as \(E\) increases due to the log dependence in the Nernst equation. Large size dispersity causes larger differences in \(E^0\) for different NPs, which causes higher potential and concentration gradients between NPs, leading to higher ripening rates as observed for mixtures of 4 and 15 nm Au NPs. The decreased distance between the Au NPs increases the concentration gradient and flux of \(\text{AuBr}_4^-\) ions between small and large NPs, explaining the reason for the larger rates for higher NP coverage. Our data on potential, size, size dispersity, and coverage are therefore consistent with the electrochemical Ostwald ripening model described in Scheme 1.

CONCLUSIONS

We report the potential-controlled, size-dependent Ostwald ripening reactivity of 1.6, 4, and 15 nm-diameter Au NPs. The size changes before and after ripening at different potentials and times were monitored by both electrochemical ASV and SA/V measurements and SEM. Our results show that smaller-sized Au NPs display a higher rate of Ostwald ripening, based on the relative increase in diameter, as compared to larger-sized Au NPs under similar electrochemical conditions. The rate of Ostwald ripening also depends on the dispersity of NPs. A mixture of two very different-sized NPs displayed a higher rate of ripening as compared to a single NP size population under the same reaction conditions due to the larger variation in \(E - E^0\) at the different NPs, leading to higher potential and concentration gradients between neighboring NPs. The mechanism of Ostwald ripening was confirmed from the SEM-measured size and size histogram of NPs before and after ripening. The size histograms show Au NPs that are smaller than the original size population for 15 nm Au NPs, which is a clear indicator of Ostwald ripening. The ASVs showed two distinct oxidation peaks at 0.75 and 0.95 V, attributed to two different NP size populations after ripening, but also showed multiple small oxidation peaks in the potential range of 0.0–0.45 V. These peaks represent small Au NPs, which were formed during the dissolution of bigger-sized Au NPs, a clear sign of Ostwald ripening. The rate of Ostwald ripening increased dramatically with increasing NP coverage, showing the importance of diffusion of \(\text{AuBr}_4^-\) species from small to larger NPs. The rate of Ostwald ripening determined from the electrochemically measured SA/V of Au NPs was comparable to the rate measured by SEM but is a much faster and lower-cost technique. While our data are consistent with Ostwald ripening, we cannot rule out the fact that electrochemically induced migration, transformation, and coalescence could also occur to some extent as well, as recently shown by TEM.58,59

Our work clearly shows the importance of electrochemical methods as an analytical tool to understand the fundamental reactivity and size stability of metals on the nanoscale. This work provides important fundamental knowledge general to all metals that may lead to methods for preventing size instability from Ostwald ripening during applications and is also potentially important for using electrochemical methods to manipulate metal NP sizes directly on electrode surfaces.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.9b02421.

Figures showing UV–Vis spectra, TEM and SEM images, ASVs, size histograms, and CV coverage values
of different-sized Au NPs; and tables showing microscopy-measured radii and electrochemically measured surface area-to-total volume ratios of different-sized Au NPs (PDF)

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**Notes**

The authors declare no competing financial interest.

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