Fine-Tuning Porosity and Time-Resolved Observation of the Nucleation and Growth of Single Platinum Nanoparticles

Matthew W. Glasscott and Jeffrey E. Dick

Department of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States

ABSTRACT: Porous metal nanoparticles (NPs) are important to a variety of applications; however, robust control over NP porosity is difficult to achieve. Here, we demonstrate control over NP porosity using nanodroplet-mediated electrodeposition by introducing glycerol into water droplets. Porosity approached 0 under viscous conditions (>6 cP), and intermediate viscosities allowed the fine-tuning of NP porosity between 0 and 15%. This method also allowed for control over average pore radius (1 to 5 nm) and pore density (2 to 6 × 10^{15} pores per square meter). Reduced mass transfer within water droplets was validated by studying single chloroplatinate-filled water droplet (droplet radius of ~450 nm) collisions on a platinum ultramicroelectrode (UME, r_{UME} = 5 μm). Collision transient lifetimes in the i–t response increased with increasing viscosity, and the total charge per event was conserved. The change in shape was consistent with the nucleation and growth of a platinum NP within the droplet, which was confirmed by fitting transients to classical nucleation and growth theory for single centers as a function of over-potential. This analysis allowed electrokinetic growth and diffusion-controlled growth to be distinguished and semi-quantified at the single NP level.

KEYWORDS: electrocrystallization, electrodeposition, nanodroplet, nanoparticle, nucleation and growth, porosity

The economical production of fuel-cell technologies necessitates maximizing the surface area of the catalyst of interest,1,2 which can be achieved by using porous nanomaterials. Unfortunately, only a few examples for the preparation of porous metal NPs exist in the literature,3−6 and the average pore size and density have proven difficult to control. We recently reported the electrodeposition of Pt NPs from water nanodroplets.7 In this experiment, droplets are loaded with a known concentration of hexachloroplatinic acid and suspended in a 0.1 M tetrabutylammonium perchlorate (TBAP) and 1,2-dichloroethane (DCE) in the continuous phase by ultrasonication. When water droplets are incident on an electrode biased sufficiently negative to drive the reduction of chloroplatinate to platinum metal, porous Pt NPs form. We were able to quantify porosity and nanopore tortuosity using focused ion beam nanoSlice Tomography (FIB-nST), an advanced characterization technique developed by our laboratory.8 Breugelmans and co-workers reported the electrodeposition of porous Pt NPs using a double-pulse technique.5,6 In that paper, the authors operated under high mass-transfer conditions with a rotating disc electrode. These results led us to hypothesize that Pt NPs electrodeposited from water droplets are porous because of the increased mass transfer in atto- to zeptoliter volumes. This arises due to the dependence of the mass transfer coefficient, m_{eff}, on the radius of the electrode, a, which has been estimated at <10 nm for sub-femtoliter droplets.9 Mass transfer can be controlled by modulating the viscosity of the solution, in which a higher viscosity decreases diffusional mass transfer. Exploiting this principle, Gonzolaz and Marshall have previously shown that the addition of glycerol to solutions of zinc sulfate causes more dense and uniform deposits to form under cathodic conditions,10 and they have developed simulations to model electrodeposition under viscous conditions.11,12

In this article, we explore the origins of the Pt NP porosity generated from nanodroplet-mediated electrodeposition by adding glycerol to the water droplets to reduce mass transfer. When the viscosity was over 6 cP, porosity vanished, and intermediate values of viscosity allowed control over the porosity of NPs. To study the effect of glycerol in the water droplet, experiments involving the collisions of chloroplatinate-
filled water droplets onto ultramicroelectrodes (UMEs) were performed. We demonstrate that the addition of glycerol allows for the time-resolved observation of the NP nucleation and growth process within the water droplet, which can be semi-quantitatively modeled based on classical nucleation and growth theory. Scheme 1 provides a graphical representation of the experiment. Chloroplatinate-filled water droplets were suspended in DCE with 0.1 M TBAP. TBAP acts as a non-aqueous supporting electrolyte and is used to maintain charge balance during the electrodeposition process. Under low-viscosity conditions (pure water, 0.89 cP), the usual blip (or peak) in the amperometric $i-t$ response was observed. This blip has been previously reported by many groups for organic and aqueous droplets, and the decay coincides with the electrolysis of the contents within the droplet. The SEM image associated with this experiment after being sliced by the FIB-nST cross-sectioning indicated a porous tomography. In contrast, by increasing the viscosity to 6.85 cP, the $i-t$ response for the collision of single droplets changed drastically, taking on a parabolic or instantaneous shape at the onset of the collision transient. Because outer-sphere redox reactions such as the reduction of potassium ferricyanide maintained a blip shape in both high- and low-viscosity droplets, our results suggested that parabolic and instantaneous responses were due to the nucleation and growth of a single NP (vide infra). The SEM image associated with this high-viscosity experiment is given in the bottom right, which indicates a denser tomography.

RESULTS AND DISCUSSION

Effect of Glycerol on Mass Transfer. To probe the effects of glycerol on mass transfer, we studied the reduction of ferricyanide on a 10 μm diameter Pt UME. The results are given in Figure 1a. In the absence of glycerol, the voltammogram for ferricyanide reduction exhibits a lower steady-state current in the absence of supporting electrolyte. This can be explained by electrophoretic migration, which repels negatively charged ferricyanide from the electrode surface, ultimately decreasing the limiting current level. The limiting current for ferricyanide reduction in the presence of 250 mM sodium perchlorate is what one would predict with diffusion control. The effects of electrophoretic migration decrease as the viscosity increases. Migration effects are directly related to the current density; therefore, the decrease in overall current while the electrode size remains constant indicates that as solutions become more viscous, migration plays less of a role in...
As viscosity increases, the percent difference between limiting current values for the voltammograms decreases, which can be observed in Figure 1a. Figure 1b gives similar data for the reduction of chloroplatinate acid to Pt, which is a four-electron reduction:

$$\text{PtCl}_6^{2-} + 4e^- \rightarrow \text{Pt}^0 + 6\text{Cl}^- \quad E^{\circ} = 0.25V \text{ vs } \text{Ag/AgCl} \quad (1)$$

where $E^{\circ}$ is the experimentally obtained formal potential. A similar overall trend is observed: as the solution becomes more viscous, voltammograms for chloroplatinate acid reduction deviate less in the presence or absence of supporting electrolyte. It is also interesting to note the rather sluggish kinetics inherent after increasing the viscosity. While this is observed in the ferricyanide reduction results, the observation is accentuated in the chloroplatinate reduction results. This is most likely due to the inner-sphere nature and complicated four-electron reduction process of chloroplatinate compared to the simple, one-electron reduction of ferricyanide to a freely diffusing product (ferrocyanide). These data indicate that under viscous conditions, mass transfer is reduced, and migration does not play a large role. This is also the case for systems that pass very small amounts of charge, which is most relevant to electrochemistry in nanodroplets. As stated previously, migration effects are directly related to current density, which would be enhanced on NPs growing in a droplet. Thus, we cannot completely rule out the effects of electrophoretic migration, which may play a role in nanodroplet-mediated electrodeposition (vide infra).

Quantification of Nanoparticle Porosity by Focused Ion Beam nanoSlice Tomography. We previously introduced FIB-nST to characterize the porosity and nanopore tortuosity of single NPs electrodeposited onto different substrates, and details of this procedure are given in the Methods section below. In the current experiments, Pt NPs were electrodeposited onto HOPG and studied. The gallium ion beam sliced the NPs orthogonal to the HOPG plane, and follow-up scanning electron microscopy (SEM) imaging was carried out at a 52° angle. Representative SEM results of these slices are given in Figure 3a, and more results are given in Figure S2. Image processing using ImageJ was then used to quantify the porosity of these NPs as a function of viscosity. In each case, three representative NPs were sliced and analyzed. Figure 2b shows the porosity as a function of viscosity. For all statistics, an analysis of variance (ANOVA) was performed to elucidate whether or not the results were statistically significant and quantify the confidence. From Figure 2b, it is obvious that porosity of single NPs can be tuned with high precision. We also investigated the pore density, which is shown in Figure 2c. The overall trend indicates that as viscosity increases, pore density decreases. This trend is also apparent for pore radius, shown in Figure 2d. For pore radius in particular, the image processing analysis relies on contrast differences. For the SEM technique, pore sizes less than 1 nm in radius begin to approach the limit of the imaging technique. Despite these limitations, we are able to conclude that average pore size can also be tuned by varying the viscosity of the droplets. Figure 2e shows the NP radius as a function of viscosity. Even though there is significant overlap between neighboring measurements, the ANOVA analysis predicts statistical significance, which is largely due to the sample size measured (hundreds of NPs). The blue dotted line is the calculated size of a theoretical hemispherical NP, which assumes a closest-packed, face-centered-cubic Pt crystal structure. The volume of the unit cell is used in conjunction with the number of platinum atoms that have been deposited, which is directly related to the concentration of chloroplatinate in the water droplet. The robustness of this estimation has been demonstrated previously to show that pore volume in porous NPs accounts for the increase in observed particle radius over the theoretical radius.
In these experiments, the convergence of the observed NP radius to the calculated NP radius at higher droplet viscosities suggests that the particles are becoming more dense. From these data, we conclude the porosity of single Pt NPs can be controlled. Furthermore, these data indicate that the reason for porous NP growth has to do with the mass transfer within the droplets. Collisions of Chloroplatinate-Filled Water Droplets on Ultramicroelectrodes. To further characterize the effects of glycerol on nanodroplet-mediated electrodeposition, we chose to study the collision of single water droplets on UMEs. Bard and co-workers spearheaded the study of droplet collisions on UMEs by investigating the oxidation of ferrocene in toluene droplets suspended in water, and this method was extended to other analyte species and systems. We initially chose to suspend water droplets in oil, such as DCE, so that we could study the electrodeposition of aqueous metal salts from within water droplets and the electrocatalysis of metallic clusters as small as 10 atoms. Because the irreversible reduction of chloroplatinate to platinum is a complicated process, we chose to first study the effect of glycerol addition to the droplets on ferricyanide, a well-characterized, reversible, outer-sphere oxidant with a negative charge-state similar to chloroplatinate. Figure 3 shows representative collisions of water droplets filled with 35 mM ferricyanide in the absence of glycerol, and Figure 3b shows the results in the presence of glycerol. It is clear from these results that the shape of the transient is conserved under conditions of low and high viscosity.

This observation is in striking contrast to collision results in the presence and absence of glycerol for chloroplatinate reduction, which is presented in Figure 4. Figure 4a shows a representative i-t blip for chloroplatinate without glycerol, and Figure 4b shows a representative i-t response for the reduction of chloroplatinate within a water droplet in the presence of glycerol. It is important to note that the charge is conserved in each of these scenarios, indicating the same amount of chloroplatinate is reacted in each response. Figure 4c shows the amperometric event length as a function of viscosity. As viscosity increases, the time for nucleation and growth and subsequent exhaustion of chloroplatinate within the droplet should increase, and this plot shows that this is indeed the case. Finally, integration under the i-t response can give the charge (Q) passed when a droplet collides with the UME surface. One can then use Faraday’s Law to calculate the diameter of the droplet (d_
onsense

\[ d_{\text{drop}} = 2 \sqrt{\frac{0.75Q}{nFCA}} \]  

(2)

where n is the number of electrons transferred, F is Faraday’s Constant, and C is the concentration of chloroplatinate in the droplet. The bars in Figure 4d indicate a histogram of the sizes calculated by 340 collision events of water droplets filled with chloroplatinate. The normalized frequency is proportional to the droplet concentration. The electrochemical results overlay well with nanoparticle tracking analysis (NTA). Importantly, one can observe from this plot that dynamic light scattering (DLS) only gives a broad distribution, whereas the electrochemical calculation and NTA both give discrete modalities that cannot be readily resolved in DLS. The agreement between NTA and the calculated results from Faraday’s law is significant in that it suggests complete electrolysis of the chloroplatinate contained within the droplets.

Given the significant difference between the collision response for ferricyanide-filled droplets and that of chloroplatinate-filled droplets, we hypothesize that the observation can be attributed to the nucleation and growth of Pt NPs in the water droplets. The addition of glycerol slows down mass transfer such that the nucleation and growth of a single NP can be observed in the real-time amperometric trace and can be explained at least semi-quantitatively with classical nucleation and growth theory for single NPs (vide infra). A hallmark of nucleation and growth is that the process is highly dependent on the applied potential. Here, we define a parameter ΔE, which is the difference between the applied potential and the formal potential, E^0, of hexachloroplatinic acid reduction. Figure 5a shows representative current transients that were observed over a range of potentials. In Figure 5a, the parabolic growth can be observed at the foot of the event, where electokinetic growth would dominate the nucleation and growth response in a parabolic fashion. Instantaneous growth would be expected at higher ΔE, where the current—time transient would resemble the expected t^2/3 growth response for the growth of a single center. The final, blip-type of response was rarely observed at large ΔE, and we hypothesize that proton reduction from the chloroplatinic acid salt could be playing a role in this type of transient. It is important to note that we focus on the beginning of the rising edge to determine a parabolic or instantaneous classification to avoid convolution.

Figure 3. (a) Representative amperometry results showing collisions of attoliter water droplets loaded with 35 mM ferricyanide on a 10 μm Pt UME at 0 V vs Ag/AgCl. (b) Representative amperometry results of attoliter droplets loaded with 35 mM ferricyanide and 50% v/v glycerol to give an internal droplet viscosity of 6.85 cP. The peak width at half the height of the current spike (t_{1/2}) was used to evaluate the effect of droplet viscosity on the event length. The counter-electrode was a glassy carbon rod, and a double junction Ag/AgCl was used as a reference.
Figure 4. (a) Representative event shows typical blip shape for the reduction of 50 mM chloroplatinate as a single attoliter droplet with no added glycerol collides with a 10 μm Pt UME at 0 V vs Ag/AgCl. (b) Representative event presents a parabolic shape for chloroplatinate reduction under the same conditions but with 50% v/v glycerol, giving droplets an internal viscosity of 6.85 cP. (c) Amperometric event length for chloroplatinate reduction at various viscosities shows increasing trend with statistical significance (p < 0.0001) indicated by a one-way ANOVA. N = 60. (d) Comparable droplet size analyses by dynamic light scattering (DLS, blue trace), nanoparticle tracking analysis (NTA, orange trace), and amperometric analysis using Faraday’s law (histogram, N = 340) showing various modes of droplet diameters.

Figure 5. (a) Common current responses observed for chloroplatinate reduction under varying conditions of viscosity and applied potential. (b) Statistical analysis of specific event occurrence as a function of applied potential for a 6.85 cP droplet system shows high occurrence of parabolic events at low over-potentials shifting to a high occurrence of instantaneous events at high over-potentials. N = 164. (c) Representative current trace for 50 mM chloroplatinate reduction from 6.85 cP droplets at 0.2 V vs Ag/AgCl demonstrating commonality of parabolic growth. (d) Representative current trace for the same droplet system at 0 V vs Ag/AgCl highlighting shift to instantaneous transients. All experiments were performed on 10 μm Pt UME with a glassy carbon counter and double-junction Ag/AgCl reference electrode.

with the bulk electrolysis of the droplet contents. Figure 5b shows the quantification of these results. One can see an obvious trend: at lower ΔE, the parabolic-type of growth is observed most often. At higher ΔE, the instantaneous nucleation and growth response is observed most often. Figure 5c shows a representative amperometric i–t response for lower ΔE, and Figure 5d shows a representative amperometric i–t response for high ΔE. These results indicate that our observations are the nucleation and growth of single Pt NPs. The peak of each response represents the interplay between the growth of the particle and the exhaustion of chloroplatinate in the water droplet. Additional data showing the observed transient response as a function of droplet viscosity and further amperometric traces with parabolic and instantaneous transients are given in Figures S3 and S4, respectively. The background current in these experiments is oxygen reduction occurring on the underlying Pt UME. We sometimes observed step-like responses, which we attribute to droplets coming off of the UME, providing a rapid increase in current if oxygen reduction is being driven at the UME surface. At higher over-
potential, where proton reduction can occur on the platinum deposits, we observed elongated nucleation and growth events.

To highlight the importance of slowing down mass transfer via glycerol to observe nucleation and growth of single NPs, we were interested in whether or not it would be possible to resolve the nucleation and growth simply by performing amperometry at much higher sampling frequencies. In our attempts, we devised an experiment to measure at 100 kHz (1 point every 10 μs) using an AxoPatch two-electrode potentiostat. We were not able to resolve the nucleation and growth event; however, we did observe nucleation and growth events in the presence of glycerol using the high-frequency measurement technique. These results are given in Figure S5.

The faster sampling permits the resolution of smaller droplets colliding with the UME but does not allow the resolution of NP nucleation and growth without the addition of glycerol.

Semi-Quantitative Treatment of Nucleation and Growth of Single Pt NPs. To further test our hypothesis that collision transients in the presence of glycerol were indicative of the nucleation and growth of single NPs, we used classical nucleation and growth theory to fit collision transients as a function of potential. Previously, Kucernak and co-worker provided a model to predict the i−t response for the nucleation and growth of a single NP under electrokinetic and diffusion-limited growth, given by:27

\[ i(t) = \frac{nHFDC^* \left( e^{2 \alpha n \Delta E} - e^{(2\alpha n-1) \Delta E} \right) \sqrt{(C^*DFn)^2 + 8DC^*J_0^2 \left( e^{2 \alpha n \Delta E} - e^{(2\alpha n-1) \Delta E} \right) V_n t - C^*DFn}^2}{2J_0 e^{2aN \Delta E} \sqrt{(C^*DFn)^2 + 8DC^*J_0^2 \left( e^{2 \alpha n \Delta E} - e^{(2\alpha n-1) \Delta E} \right) V_n t}} \]  

(3)

where \( H \) is a shaping factor (\( 2\pi \) for a growing hemisphere), \( n \) is the number of electrons, \( C^* \) is the bulk concentration, \( D \) is the diffusion coefficient, \( \Delta E \) is the difference between the applied potential and the formal potential, \( E' \) (we have chosen to use \( \Delta E \) in place of \( \eta \), over-potential, given the complexity in quantifying the equilibrium potential, \( E_{eq} \) vide infra), \( V_n \) is molar volume, \( J_0 \) is the exchange current density, \( \alpha \) is the transfer coefficient, and \( f = F/RT \), where \( F \) is Faraday’s constant, \( R \) is the universal gas constant, and \( T \) is temperature. This equation predicts the limiting responses for the nucleation and growth of single NPs: For small \( \Delta E \), a gradual (parabolic) growth occurs, and for large values of \( \Delta E \), an instantaneous growth occurs that follows \( t^{1/2} \). The panels in Figure 6 show representative collision transients as a function of potential for chloroplatinate reduction in the water droplets. From these data, it can be seen that a large fraction of the responses follows the gradual, parabolic response at lower \( \Delta E \) and an instantaneous nucleation and growth response at larger \( \Delta E \). Figure 6 gives the equation fits for representative collision responses under electrokinetic control (Figure 6a, parabolic growth) and diffusion control (Figure 6b, instantaneous growth). The parameters for the fits, which were generated manually, are given in the figure caption, and \( \alpha = 0.5 \) and \( J_0 = 8 \times 10^{-6} \) A/cm² in all cases.27 We chose to tune only two variables: the diffusion coefficient, which stayed mostly constant throughout the fitting process, and the value of \( \Delta E \). Though these values are typically considered constants, the data acquired over multiple experiments likely contain slight variability. For example, we have previously shown using finite element simulations that the curvature of the droplet reduces mass transfer to the contact radius,7 which may manifest experimentally as decreased mass transfer. Because the droplets...
are not perfectly monodisperse, size and curvature differences between droplets may introduce variation between individual transient events.

In this section, it is not our intent to be quantitative regarding parameters involved in the nucleation and growth of single NPs. However, it is our hope to show that the results presented here provide a platform on which the study of nucleation and growth of single NPs can be built. There are several ambiguities that require further experimentation. For instance, the over-potential for nucleation and growth is difficult to define. As shown by Plieth theoretically27 and Henglein experimentally,29–35 the potential of a NP changes with the NP size, implying the over-potential for nucleation and growth may depend on NP size.36,37 In our experiments, we use a homemade salt bridge to an aqueous Ag/AgCl reference electrode. For these studies, we have found the liquid junction potential to be <5 mV. In our experiments, we add TBAP to the DCE continuous phase and hypothesize that the transfer of TBA+ into the droplet maintains charge balance during the reduction of chloroplatinate to Pt0. To begin to understand the effect of the TBA+ ion-transfer potential on our applied potential, we loaded droplets with ruthenium hexamine chloride (Ruhex). The reduction potential of Ruhex was shifted 35 mV more negative in the droplet system with TBA+ chloride (Ruhex). The reduction potential of Ruhex was more negative in the droplet than in pure water, indicating the energy cost for transferring electrons to Ruhex with the TBA+ ion-transfer potential is ca. 35 mV. More details of this experiment are given in Supporting Information Figure S6. There are also large discrepancies in the diffusion coefficient of chloroplatinate in the literature.27,38–40 In our experiments, no supporting electrolyte was used; therefore, we cannot completely rule out electrophoretic migration. Electrophoretic migration is directly related to the current density, which is likely high considering the small (<10 nm) contact radius of the droplet and, during growth, the radius of the growing NP. Very small amounts of charge are passed during the collision transients, and even smaller current densities are apparent in droplets with higher viscosity, which decreases the effect of electrophoretic migration. Furthermore, during the deposition of platinum, TBA+ transfers into the droplet, and chloride is a product of chloroplatinate reduction. This means that over time, electrolyte builds up in the droplet. We have attempted to perform control experiments with large salt concentrations in the droplets; however, droplet stability limited the observation of collisions on UMEs. The model used above to fit collision transients does not take into account electrophoretic migration, which may manifest itself in the small diffusion coefficient necessary to fit experimental results. The effects of migration on the collision transients will be a topic of future investigation. Despite these uncertainties, the values of ΔE and D used to make the fits are given in the caption in Figure 6.

CONCLUSIONS

We have demonstrated that porosity of Pt NPs synthesized using nanodroplet-mediated electrodeposition can be precisely tuned by controlling the viscosity within the droplet. FIB-nST revealed pore size, density, and overall porosity decreased as viscosity increased. We have also demonstrated that one can observe time-resolved nucleation and growth of single Pt NPs when collisions of single glycerol/chloroplatinate-filled water droplets are studied on Pt UMEs. Importantly, the shape of the current transient for ferricyanide reduction in water droplets did not depend on the viscosity of the droplet (i.e., the blip-type shape was conserved independent of viscosity), but this shape changed drastically for chloroplatinate reduction, indicating a nucleation and growth process. The current transients for chloroplatinate reduction changed as a function of applied potential, and the shape of the current transients could be modeled semi-quantitatively by classical nucleation and growth theory.

Historically, experiments involving the nucleation and growth of single NPs have been difficult to achieve.41–46 In these previously published experiments, very small (radius <100 nm) electrodes are fabricated such that the probability of nucleating and growing on more than one surface site on the electrode is minimized and the growth of single NPs can be observed. Kucernak and co-workers developed carbon nano-electrodes to study the electrodeposition of platinum onto the nanoelectrodes.27 Mirkin and co-workers also studied the electrodeposition of metals on nanoelectrodes.37,48 Thus, a direction in the field, beginning with Fleischmann’s studies of nucleation and growth on microelectrodes,42–44 has been minimizing electrode size such that the nucleation and growth of single NPs can be studied under various conditions. Here, we demonstrated that electrochemistry via attoliter water droplets also fulfills this requirement due to the small contact radius, effectively a nanoelectrode, which forms when a droplet collides with an electrode surface.9,26 Furthermore, the nucleation and growth of several NPs can be observed over the duration of a single experiment, which is not possible using nanoelectrodes. The results presented here not only set a foundation to gain control over NP porosity using nanodroplet-mediated electrodeposition but also provide a powerful method with which to study nucleation and growth of single Pt NPs without the use of nanoelectrodes.

METHODS

Reagents and Materials. All chemicals were of analytical grade unless noted otherwise and used as received. Dichloroethane (DCE, 99.8%), tetrabutylammonium perchlorate (99%), hexachloroplatinate acid hydrate (99.99%), glycerol (99%), potassium ferricyanide (99.98%), hexaammineruthenium chloride (98%), hydrogen peroxide, sulfuric acid, nitric acid, and hydrochloric acid were purchased from Sigma-Aldrich and used without further purification for experiments, electrode characterization, and cleaning. Stock solutions (100–300 mM) of chloroplatinate were made in Milli-Q water (>18 MΩ·cm) and diluted as necessary to be used in the emulsion preparation. Metal salts were stored in a dark refrigerator (4 °C) to avoid photodecomposition. Platinum ultramicroelectrodes were obtained from CHI instruments and polished before experiments iteratively with 0.3 μm, 0.1 μm, and 0.05 μm alumina powder. Highly oriented pyrolytic graphite (HOPG) was obtained from Sigma-Aldrich and exfoliated with adhesive tape before experiments to ensure a clean surface. The salt bridge employed to create a double-junction Ag/AgCl reference electrode was a borosilicate U-tube filled with 1 M KCl and 4% w/v agarose, which forms a conductive gel. No obvious junction potential or other deleterious effects could be observed in the cyclic voltammogram of 1 mM ferrocene methanol in a 0.1 M KCl aqueous solution as a result of the salt bridge double-junction reference. Additionally, we have found this material to be stable in DCE for over 2 months.

Instrumentation. The electrodeposition experiments were performed using a CHI model 601E potentiostat (CH Instruments, Austin, TX). All experiments were conducted in a grounded Faraday cage and utilized a glassy carbon rod (Alfa Aesar) and a double-junction Ag/AgCl electrode (CH Instruments) as the counter and reference electrode, respectively. The emulsion was prepared using a Q500 ultrasonic processor (Qsonica, Newtown, CT) with a 1” microtip probe. SEM imaging and FIB cross-sectioning were
completed using a Helios 600 Nanolab Dual Beam System (FEI, Hillsboro, OR) at 30 keV and 0.69 nA unless otherwise noted. DLS and NTA utilized a Zetasizer Nano ZS and NanoSight NS300 (Malvern Panalytical, Westborough, MA), respectively. High-frequency measurements were obtained using anAxopatch 200B with a Digidata 1320A digitizer (Molecular Devices, San Jose, CA).

**Non-hydrophilic Mediated Electodeposition Procedure.** A water-in-oil emulsion was prepared from a 30 μL aqueous droplet containing 50 mM chloroplatinate and varying amounts of glycerol in an organic phase of 5 mL of DCE. TBAP (0.1 M) was added to the DCE phase as a non-aqueous supporting electrolyte and charge balance mediator by the transfer of ‘TA’ across the oil—water interface during electrodeposition. The resulting two-phase solution was then ultrasonicated (500 W, amplitude 40%) using a pulse mode method (5 s on, 5 s off, 6 total cycles) to form the emulsion. After ultrasonication, the three-electrode setup was inserted into the emulsion and biased at a potential sufficient to reduce chloroplatinate to platinum in a four-electron process. Current transients were recorded as attoliter droplets stochastically diffused to and collided with the electrode surface, where their contents were reduced to form single Pt NPs. For SEM/FIB imaging experiments, the electrodeposition was carried out on a 3 mm HOPG disc electrode secured in a Teflon cell with a Viton O-ring. The substrate was thoroughly rinsed with neat DCE, ethanol, and water prior to analysis to remove excess glycerol. The viscosity of the droplet was determined by a previously reported density model based on the water-to-glycerol ratio, and these values matched well the diffusion-limited currents for ferricyanide reduction on UMEs.30

**Water-in-Oil Emulsion Characterization via Nanoparticle Tracking Analysis.** The corrosive nature of DCE, the oil phase in our emulsion experiments, generally precludes analysis by instruments that incorporate plastics and polymers susceptible to degradation. Additionally, attempts to analyze a water-in-DCE emulsion optically should use more hydrophobic materials such that water droplets do not wet the surface and impede the optical path. Though the use of quartz cuvettes allows water-in-DCE emulsion analysis by DLS, resolving individual modes of droplet sizes in a polydispersed system is difficult due to the ensemble measurement strategy employed. Nanoparticle tracking analysis uses a microscope with a laser light source to obtain the diffusion coefficient of individual nanoparticles by tracking the darkfield scattering pattern, allowing the quantification of size on a particle-by-particle basis. To apply this technique to our emulsion system, we integrated PTFE tubing and a sampler with a particle of interest to minimize potential alignment shifts. Initiation of slicing with the FIB at 30 keV and 1.5 pA allowed the slicing of NPs. After each slice, SEM was used to image porosity within each NP. We previously used this technique to slice single NPs with 10 nm resolution, obtaining detailed tomographic information. This allowed the pore structure to be reconstructed in 3D. Importantly, we found the pore density and size to remain relatively constant throughout each NP, meaning that any given slice provides porosity, average pore size, and pore density representative of the entire NP. Therefore, in this work, we cross-sectioned Pt NPs to obtain a single image instead of slicing multiple times. NP images were then processed with open-source software ImageJ using the “Particle Analysis” tool to quantify porosity, pore size, and pore density.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.9b00546.

Additional details on measurement of droplet diameter via nanoparticle tracking analysis, cross-section NP tomography, transient response as a function of droplet viscosity, examples of current traces for parabolic and instantaneous events, Axsopatch high-frequency amperometry of blip and instantaneous transients, and quantification of ion-transfer potential and liquid junction potential (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: jedick@email.unc.edu.

**ORCID**

Matthew W. Glasscott: 0000-0001-5743-7738

Jeffrey E. Dick: 0000-0002-4538-9705

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We gratefully acknowledge the University of North Carolina at Chapel Hill for start-up funds, which supported this work. This work was performed in part at the Chapel Hill Analytical and Nanofabrication Laboratory, CHANL, a member of the North Carolina Research Triangle Nanotechnology Network, RTNN, which is supported by the National Science Foundation, grant no. ECCS-1542015, as part of the National Nanotechnology Coordinated Infrastructure, NNCI.

**REFERENCES**


(6) Glasscott, M. W.; Pendergast, A. D.; Dick, J. E. A Universal Platform for the Electrodeposition of Ligand-Free Metal Nano-
