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Article

Electrochemical-Shock Synthesis of Nanoparticles from Sub-femtoliter Nanodroplets

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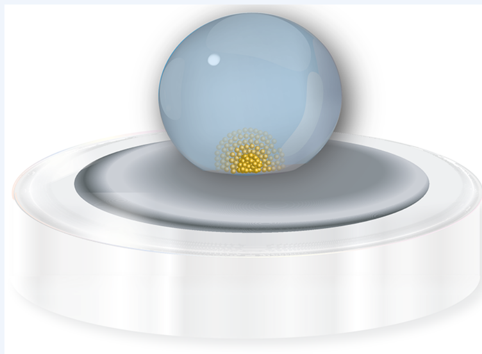

CONSPECTUS: Nanoparticles have witnessed immense development in the past several decades due to their intriguing physicochemical properties. The modern chemist is interested not only in methods of synthesizing nanoparticles with tunable properties but also in the chemistry that nanoparticles can drive. While several methods exist to synthesize nanoparticles, it is often advantageous to put nanoparticles on a variety of conductive substrates for multiple applications (such as energy storage and conversion). Despite enjoying over 200 years of development, electrodeposition of nanoparticles suffers from a lack of control over nanoparticle size and morphology. There have been heroic efforts to address these issues over time. With an understanding that structure−function studies are imperative to understand the chemistry of nanoparticles, new methods are necessary to electrodeposit a variety of nanoparticles with control over macromorphology and also microstructure.

This Account details our group's efforts in overcoming challenges of classical nanoparticle electrodeposition by electrodepositing nanoparticles from water nanodroplets. When a nanodroplet full of metal salt precursor is incident on the electrode biased sufficiently negative to drive electroplating, nanoparticles form at a fast rate (on the order of microseconds to milliseconds). We start with the general nuts-and-bolts of the experiment (nanodroplet formation and methods for electrodeposition). The deposition of new nanomaterials often requires one to develop new methods of measurement, and we detail new measurement tools for quantifying nanoparticle porosity and nanopore tortuosity within single nanoparticles. We achieve nanopore characterization by using Focused Ion Beam milling and Scanning Electron Microscopy. Owing to the small size of the nanodroplets and fast mass transfer (the contents of a femtoliter droplet can be electrolyzed in only a few milliseconds), the use of nanodroplets also allows the electrodeposition of high entropy alloy nanoparticles at room temperature.

We detail how a deep understanding of ion transfer mechanisms can be used to expand the library of possible metals that can be deposited. Furthermore, simple ion changes in the dispersed droplet phase can decrease the cost per experiment by orders of magnitude. Finally, electrodeposition in aqueous nanodroplets can also be combined with stochastic electrochemistry for a variety of interesting studies. We detail the quantification of the growth kinetics of single nanoparticles in single aqueous nanodroplets. Nanodroplets can also be used as tiny reactors to trap only a few molecules of a metal salt precursor. Upon reduction to the zerovalent metal, electrocatalysis at very small metal clusters can be probed and evaluated with time using steady-state electrochemical measurements. Overall, this burgeoning synthetic tool is providing unexpected avenues of tunability of metal nanoparticles on conductive substrates.

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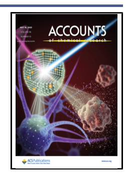

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2019, *13*, 4572−4581.[2] *Nanoparticle porosity was determined and fitting for nucleation and growth under electrokinetic/mass transfer conditions was performed. Porosity is controlled by changing the viscosity. Single nucleation and growth transients were observed when water droplets with chloroplatinate and glycerol collided with an electrode.*

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INTRODUCTION

Ever since Democritus (and likely before), humans have been interested in tiny fractions of matter. For instance, if you have a piece of silver, and you keep cutting it in half, what is the smallest unit piece of silver? This is what Democritus termed the *atom* (perhaps Democritus did not realize we could dig deeper inside the atom!). However, an even deeper question exists for the chemist: As you begin to decrease the size of silver, how do the chemical and physical properties of the silver change? This is an exciting question that Arnim Henglein devoted decades to understanding.[5] When Michael Faraday was working with optically transparent gold plates and noticed the solution turning a red color, he realized that he was making very tiny gold particles. This size-dependent color change has been taken advantage of for a variety of applications, and Faraday's nanoparticles are still suspended and on display at the Royal Institution.[6,7]

While nanoparticles have a rich history, they play a significant role in the modern era because of their unique physicochemical properties.[8−10] Not only have nanoparticles found applications in sensing technologies[11−13] and energy storage[14] and conversion devices,[15] they are being used to treat diseases and drive unfavorable organic transformations.[16] Even emerging nanomaterials, like high entropy alloy nanoparticles, have been synthesized recently, highlighting the fact that exciting new avenues of inquiry exist in nanoparticle synthesis. Another particularly exciting area of interest that should be mentioned that is not the focus of this Account (*vide infra*, "Single Nanodroplet Techniques") is the ability to probe single nanoparticles, one at a time.[17,18] This is important because no matter what synthesis method one chooses to make nanoparticles, no two nanoparticles will be exactly the same. This heterogeneity and structure−property relationships must be rigorously measured.

Perhaps one of the most versatile and robust methods of synthesizing nanoparticles is the direct chemical reduction of metal salts in the presence of a reducing agent.[20,21] This method allows one to tune the nanoparticle size and morphology based on easily tunable parameters like concentration and temperature. Another method, the inverse emulsion synthesis, goes like this: water nanodroplets with metal salt precursors and reducing agents are suspended in an oil phase. The reducing agents will reduce the metal salts to metal nanoparticles. Both homogeneous methods generally leave a relatively monodisperse sample of nanoparticles that are stabilized by a capping agent.

There are many applications (e.g., fuel cells[22−24] and batteries[25,26]) that call for the direct contact of a metal nanoparticle with a conductive substrate, which can be accomplished by electrodeposition. While electrodeposition is readily able to generate nanoparticles on conductive materials by direct electroreduction of metal salt precursors to the zerovalent metal, the technique has many limitations. These limitations arise despite enhanced control with electrodeposition, where the nucleation of a new phase depends on not only concentration but also the applied potential. As nuclei form on the substrate and begin to grow, they will eventually compete with a neighboring nucleus for metal salt precursor (so-called diffusion layer overlap). Such overlap prohibits the control of nanoparticle size and morphology. There are several clever ways around this, such as nucleating at a high overpotential and stepping the potential less negative to electrokinetically grow nanoparticles. However, such methods are not easily translatable to other surfaces since nanoparticle nucleation is inherently an inner-sphere reaction.

Driven to overcome the limitations in electrodeposition, our group has developed a new method of electrodepositing nanoparticles. This method, which we have termed nanodroplet-mediated electrodeposition,[1] is able to electrodeposit nanoparticles due to the rapid mass transfer of metal salts in sub-femtoliter droplets. When an oil-suspended nanodroplet full of metal salt precursor (say, chloroplatinate) diffuses to the electrode surface biased sufficiently negative to drive electrodeposition, platinum nanoparticles will form (Figure 1). Central to this multiphase experiment is obeying electroneutrality during the electrodeposition.[27−30] For this to happen, ions should be transferred from one phase to another. This happens

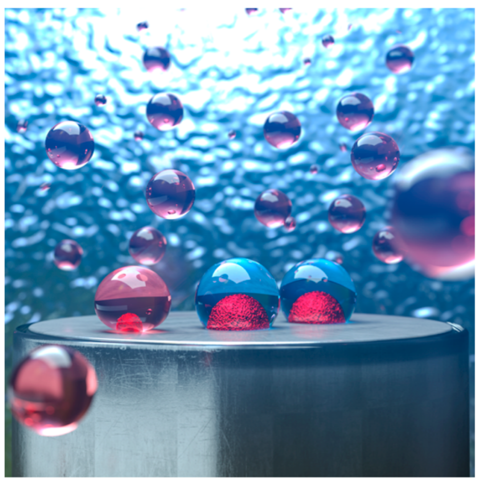

Figure 1. Artistic figure of water nanodroplets filled with a metal-salt precursor suspended in an organic phase. Droplets collide stochastically with the electrode surface. If enough energy is applied to the electrode surface, nucleation and growth of metal nanoparticles can occur. Nanoparticles generated at the electrode|water interface are represented in dark red. Adapted with permission from ref 19. Copyright 2020 American Chemical Society.

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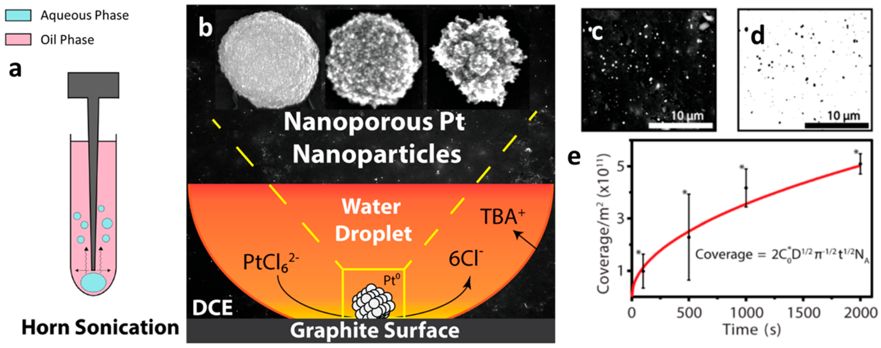

Figure 2. Electrodeposition from aqueous nanodroplets. (a) Schematic of the ultrasonication procedure, (b) nanoporous platinum nanoparticles electrodeposited using the nanodroplet method and a schematic representation of the ion transfer mechanism involved with a scale bar of 100 nm for each nanoparticle, (c) scanning electron microscopy micrograph of platinum nanoparticles, (d) high-contrast image of nanoparticles, and (e) nanoparticle coverage as a function of electrodeposition time. Data from ref 1.

due to the difference in the electrochemical potentials in both liquid phases, in which the ion transfer is dictated by the Gibbs free energy of ions transferring from one phase to the other.[31,32]

Throughout this Account, we refer to droplets as nanodroplets that have sub-femtoliter volumes. To calibrate the reader, mammalian cells are on the order of tens of micrometers in diameter and have volumes on the order of picoliter. Droplets that have diameters of about 1 μm qualify as sub-femtoliter.

■ ELECTRODEPOSITION OF NANOPARTICLES FROM WATER NANODROPLETS

Water nanodroplets can be easily made by dropping a small volume of water (10 μL) into a large volume of oil (10 mL 1,2-dichloroethane) followed by horn sonication. Dynamic light scattering is used to obtain the size distribution of the water nanodroplets (radii ∼100s of nanometers). Figure 2a shows a schematic representation of the horn sonication method. Figure 2b shows various platinum nanoparticle morphologies in the absence (far left) and presence (middle and far right) of surfactant.

The bottom portion of Figure 2b shows the electrodeposition mechanism. We chose 1,2-dichloroethane as the oil continuous phase because we had plenty to use in the lab. There are almost no special considerations for the oil continuous phase other than that it must be quite immiscible with water, and it is helpful to be able to dissolve nonaqueous electrolytes. The salts we most often use in the oil phase are alkylammonium salts, and we have grown fond of tetra-*n*-butylammonium perchlorate. As previously explained, the ion transfer is based on the Gibbs free energy of ion transferring from one phase to another. Therefore, upon the electroreduction of chloroplatinate to Pt^0 at the electrode|water interface, a negative anion must go out of the droplet, or a positive cation must go inside the droplet. The most favorable ion to transfer according to the Gibbs free energy is tetra-*n*-butylammonium (TBA^+).[33,34] For oxidation reactions (i.e., the electrodeposition of oxide nanoparticles), perchlorate (ClO_4^-) is the most favorable ion to transfer to obey electroneutrality. Because ions are required to traverse the liquid|liquid interface to obey electroneutrality, the overall electrodeposition potential will also include the ion transfer potential. Figure 2c shows a scanning electron micrograph of platinum nanoparticles on a graphite surface, and Figure 2d shows a high contrast image using ImageJ. The difference between Figure 2c and Figure 2d is the contrast. The difference in contrast was necessary to facilitate the coverage analysis with ImageJ. Figure 2e shows the nanoparticle coverage as a function of the electrodeposition time where C_0 is the concentration of droplets in solution, D is the diffusion coefficient of the water droplets, t is the time for the electrodeposition, and N_A is Avogadro's number. Diffusion coefficient can be obtained from the Stokes–Einstein equation,

$$D = \frac{k_B T}{6\pi\eta r}$$

where D is the diffusion coefficient of the droplets, k_B is the Boltzmann constant, T is the temperature, η is the kinematic viscosity, and r is the hydrodynamic radius of the droplets. To determine the droplet concentration in solution, the droplet size most be determined. After determining the droplet size, the number of droplets can be estimated from the total aqueous volume and then this value can be divided by the volume of the organic phase. We reasoned that the mass transport of water nanodroplets to the electrode surface would follow semi-infinite diffusion, and an integrated form of the Cottrell equation (plotted in red) can be used to predict the nanoparticle coverage as a function of deposition time.[35] Other variables that affect the coverage are the concentration of metal salt precursor, droplet stability, and the diffusion coefficient of the water droplets as observed in the equation in Figure 2e.

Another important aspect of the nanodroplet-mediated electrodeposition method is that because metal salts are confined to a sub-femtoliter volume, diffusion layer overlap does not occur between neighboring nanoparticles. Because diffusion layers do not overlap, we are able to achieve greater homogeneity in the nanoparticle morphology during electrodeposition.

One rather exciting and unexpected tunable parameter that we discovered was the porosity of platinum nanoparticles. As we were electrodepositing nanoparticles onto various conductive substrates, we realized that the nanoparticle sizes were much larger than what we expected. One can readily derive a nanoparticle radius by assuming a unit cell structure and volume, and the number of platinum atoms deposited can be derived from coulometry. This disparity caused us to hypothesize that the nanoparticles were porous; however, porosity at the time was difficult to visualize. While Transmission Electron Microscopy (TEM) is the best way to study nanoparticle porosity, such experiments require one to electrodeposit on a TEM grid. We showed that nanoparticle morphologies vary based on the conductive substrates on

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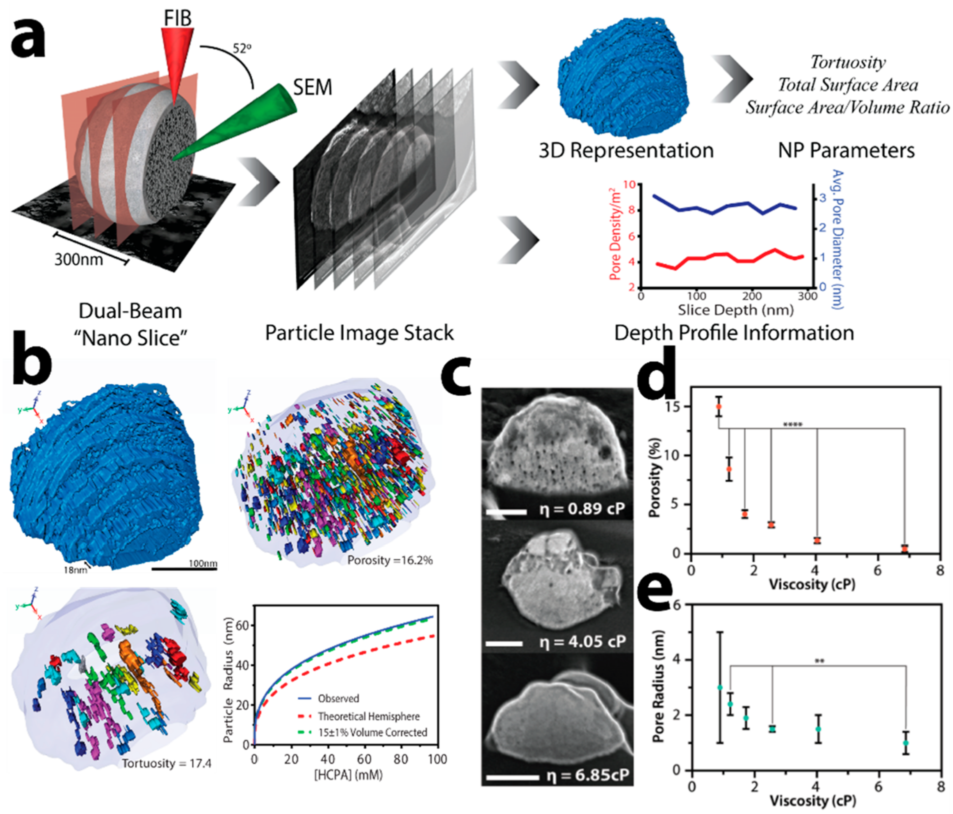

Figure 3. Images of analyzing nanoparticle porosity with FIB. (a) Schematic of the nanoslice process. (b) 3D rendering of the porosity and tortuosity in a single nanoparticle with the observed and theoretical particle radii plotted as a function of chloroplatinic acid concentration. (c) Different images of nanoparticle morphology as a function of water droplet viscosity. (d) Graphic data showing the porosity percentage in a nanoparticle as a function of viscosity. (e) Graphic data showing the pore radius in a nanoparticle as a function of viscosity. Data from refs 2 and 36. HCPA is hexachloroplatinic acid.

which we were electrodepositing. Thus, it would be convenient to develop a method to quantify nanoparticle porosity (and perhaps nanopore tortuosity) that could be used on a variety of conductive substrates.

Such a need caused us to develop focused ion beam nanotomography, schematically depicted in Figure 3a. A gallium focused ion beam (FIB) is used to slice nanoparticles every 5 to 15 nm, and scanning electron micrographs of the resultant nanoparticles can be observed after slicing. Slices can then be recapitulated into 3D, where one can study nanopores as they twist and wind throughout the nanoparticle. Figure 3b shows data from slicing a single platinum nanoparticle. This technique confirmed our hypothesis that the platinum nanoparticles created from the nanodroplet-mediated electrodeposition method were indeed porous. Pores could then be tracked using a 3D model, as shown in the upper right panel in Figure 3b, and the bottom left panel in Figure 3b shows larger pores, which allowed the calculation of nanoparticle tortuosity. As stated above, the discrepancy between the nanoparticle size and the calculated size was because the nanoparticles were porous. By using the 3D rendering, porosity can be rigorously accounted for, and the bottom right panel in Figure 3b shows that the porosity correction rectifies the expectation.

A question that follows the previous discussion is why platinum nanoparticles are porous. Because nanodroplets are on the order of 100s of nanometers, a small molecule can diffuse from one side to another in a matter of microseconds. We were curious if this rapid mixing had anything to do with the nanopore formation. To probe this further, we added glycerol to the nanodroplets to slow down mass transfer.[2,36,37] There are other factors that could influence the metal deposition, such as adsorption to the liquid‖liquid interface, potential drop in the electrochemical double layer, and the electric field at the complex interface.[34,38] The viscosity of glycerol solutions is easily measurable using the limiting current in steady-state voltammetry. Figure 3c shows sliced platinum nanoparticles and pores as a function of viscosity, and Figure 3d,e shows the quantitative output of the image analysis. The nanoslice method allowed us to study nanoparticle porosity, and we were able to tune the porosity of platinum nanoparticles by slowing down mass transfer.

■ ELECTRODEPOSITION OF HIGH ENTROPY ALLOY NANOPARTICLES FROM WATER NANODROPLETS

In the previous section, we commented on the importance of mass transfer within a nanodroplet, especially as it pertains to the electrodeposition of nanoparticles. This short electrolysis time is an incredibly useful property. To illustrate this further, take the familiar bulk electrolysis equation given below,

$$i(t) = i_0\, e^{-(mA/V)t}$$

where $i(t)$ is the time-dependent current for bulk electrolysis, i_0 is the initial current (not the exchange current), m is the mass transfer coefficient, A is the area of the electrode that is covered by a single droplet, V is the volume of the reactor, and t is time. The equation assumes that the concentration is homogeneous inside the reactor, and so the solution must be well mixed.

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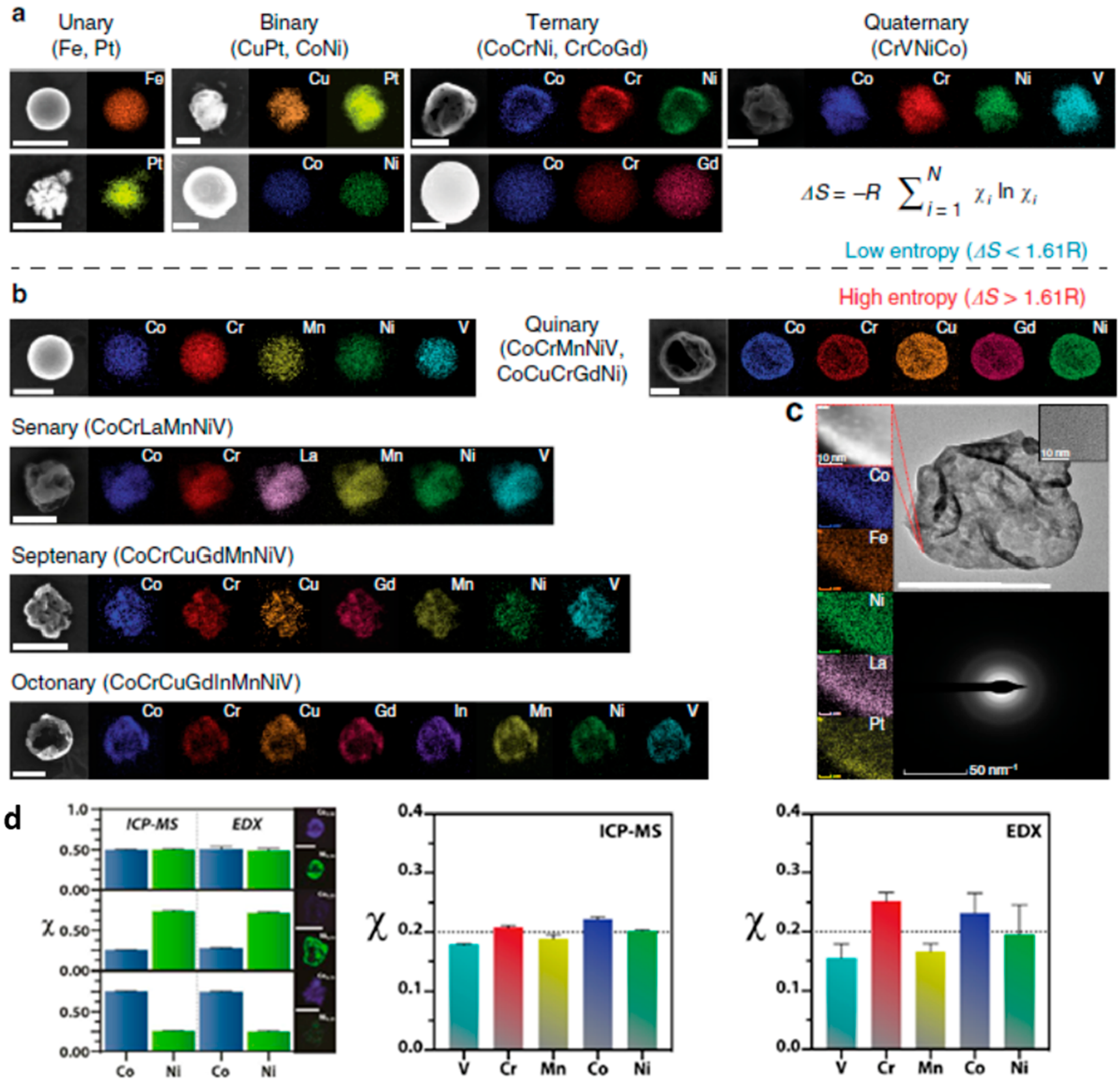

Figure 4. (a) Electrodeposition of low to medium entropy alloy nanoparticles. (b) Synthesis of high entropy alloy nanoparticles. (c) Representative high entropy alloy nanoparticle with the diffraction pattern showing the particle to have an amorphous structure. (d) Evidence that controlling initial metal stoichiometry in the droplet can control the amount of metal deposited in the single nanoparticle. Scale bars are 500 nm, except for the images that indicate the scale bar number. Data from ref 3.

Furthermore, the equation is intuitive: the electrolysis time can be diminished by a large electrode area compared to the volume. From this equation, the bulk electrolysis time for sub-femtoliter volumes is on the order of a few milliseconds, as we have observed previously.[3]

In 2018, Hu and co-workers published the carbothermal shock synthesis of high entropy alloy nanoparticles.[39] The term "shock" refers to a process going to completion within several 10s to 100s of milliseconds. In their experiment, vaporized metals were heated and cooled within milliseconds, causing the metals to deposit in their zerovalent state with no time to phase-separate. They were thus frozen in a high entropy state. Given this experiment, we were interested in whether or not the electrodeposition method could be used to electrodeposit high entropy alloy nanoparticles. There are several definitions for high entropy alloys. Historically, it has been known to be materials with five or more metals in equimolar ratio.[40] Others defined it as 5 or more metals with 5 to 35 atomic percentage, while other groups define them to be materials that have a configurational entropy bigger than 1.6R, where R is the gas constant.[40,41]

We had success in easily creating bimetallic nanoparticles with our nanodroplet-mediated electrodeposition method.[42] From the arguments given above, the electrodeposition of a nanoparticle at the mass-transfer limitation in a sub-femtoliter volume is on the order of a few milliseconds, and so we were interested in whether or not we could develop an electrochemical-shock synthesis method for high entropy alloys. Figure 4a shows detailed results of the electrodeposition of several metal salts that do not meet the high entropy requirement (5 or more metals randomly distributed in the nanoparticle). Figure 4b shows high entropy alloys all the way up to an 8-component alloy.[3] Figure 4c shows a high angle annular dark field scanning tunneling electron microscopy image and single atom electron dispersive X-ray (EDX) analysis, suggesting an amorphous structure that is further confirmed with selected area electron

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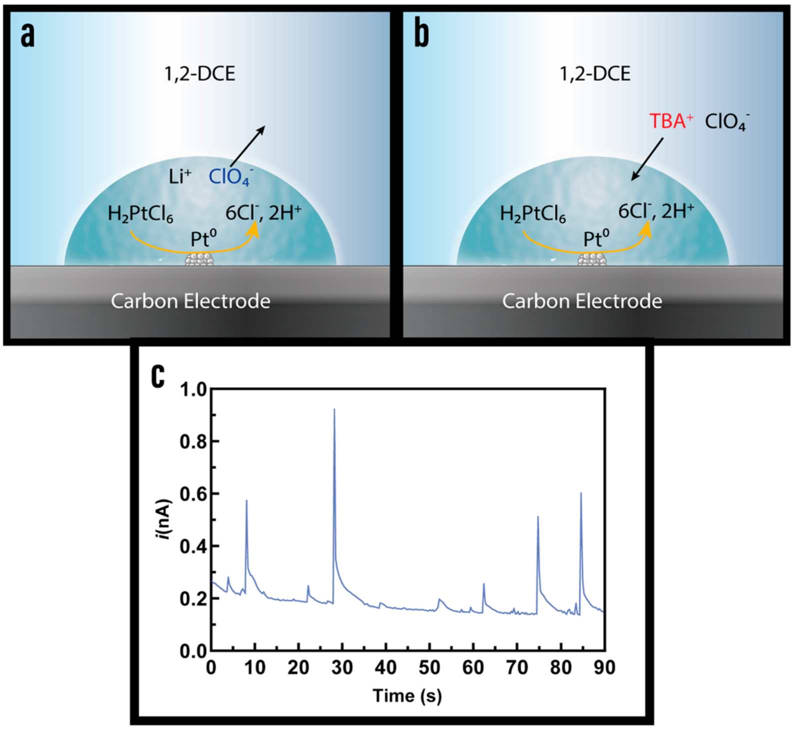

Figure 5. Mechanism for the electrodeposition of Pt nanoparticles using nanodroplet-mediated electrodeposition in the presence of (a) $LiClO_4$ in the water phase or (b) tetrabutylammonium perchlorate (TBAP) in the 1,2-dichloroethane phase. (c) Representative chronoamperogram of single collision events at an ultramicroelectrode. Each spike corresponds to the formation of a Pt nanoparticle in a single water nanodroplet. Data from ref 44.

diffraction. Figure 4d shows one of the most remarkable powers of the method: the ability to tune the composition of metals within the alloy. While this can be probed semi-quantitatively with EDX, we used inductively coupled plasma mass spectrometry (ICP-MS) to confirm that by simply controlling the initial stoichiometry of metal salts, one could control the stoichiometry of atoms in the nanoparticle.

Our report on high entropy alloy nanoparticles was among the first reports at room temperature. This method has been extended to other high entropy alloy systems. One interesting advantage of the nanodroplet system is the ability of the user to design a multifunctional nanoparticle by mixing metals that are quite good at an anodic reaction and also good at a cathodic reaction for multifunctionality. Such multifunctional electrocatalysts could have synergistic effects. At this time, the importance of the high entropy state on electrocatalysis is an open question. Perhaps some other mixture of metal atoms would be a better electrocatalyst for the oxygen reduction reaction. There is also the possibility of making oxyhydroxide nanoparticles. Using a similar droplet method, Ahn and coworkers were able to cathodically create cobalt oxyhydroxide nanoparticles.[43] At sufficiently negative potentials, one may also drive the reduction of water, liberating hydroxide ions that can precipitate metal salts. The electroprecipitation and direct electro-reduction of metals and the implication for the resultant nanoparticle microstructure is still an open avenue of inquiry.

■ UNDERSTANDING ION TRANSFER

We have previously established that electroneutrality must be maintained to drive nanoparticle electrodeposition in water nanodroplets.[44] As mentioned above, we initially elected to put tetra-*n*-butylammonium perchlorate into the 1,2-dichloroethane phase. To drive an electrodeposition reaction (for instance, to reduce chloroplatinate to zerovalent platinum), electroneutrality must be maintained (Figure 5b). One can maintain electroneutrality by bringing in a cation from the oil phase or expelling an anion from the aqueous nanodroplet phase. In our experiments, we usually use about 10 mL of an oil phase and only a few tens of microliters of the aqueous dispersed phase. Therefore, it is advantageous to only use electrolyte in the water phase. We were hesitant to do this in the beginning because we were concerned with uncompensated resistance in the oil phase; however, when we only use electrolyte in the water phase, we still realize nanoparticles. This is largely because of the low amount of current that is needed to form nanoparticles (Figure 5c). We have recently shown that we can drive down the cost of each experiment by several orders of magnitude by simply putting a perchlorate salt into the water phase (Figure 5a).[44] This is also better for the resultant metal nanoparticle because, instead of introducing tetra-*n*-butylammonium, we are simplifying the system by expelling perchlorate.

Tetra-*n*-butylammonium is a phase-transfer agent. Phase-transfer agents will allow ions to cross a phase boundary because of ion pairing (keep in mind, however, electroneutrality must be maintained). For salts that consist of very soft metals like chloroaurate, phase transfer happens almost automatically. When chloroaurate diffuses to the water|1,2-dichloroethane interface and interacts with tetra-*n*-butylammonium, the complex ion $[NBu_4][AuCl_4]$ is readily soluble in 1,2-dichloroethane.[27] The ion can transfer into the oil phase if perchlorate transfers into the aqueous phase to maintain electroneutrality.[45] Interestingly, we have recently shown that this effect can spontaneously produce emulsion droplets at the liquid|liquid interface. Thus, the electrodeposition of gold nanoparticles from water nanodroplets necessitates the use of a salt in the aqueous phase.[4] We recently showed that $LiClO_4$ dissolved in the

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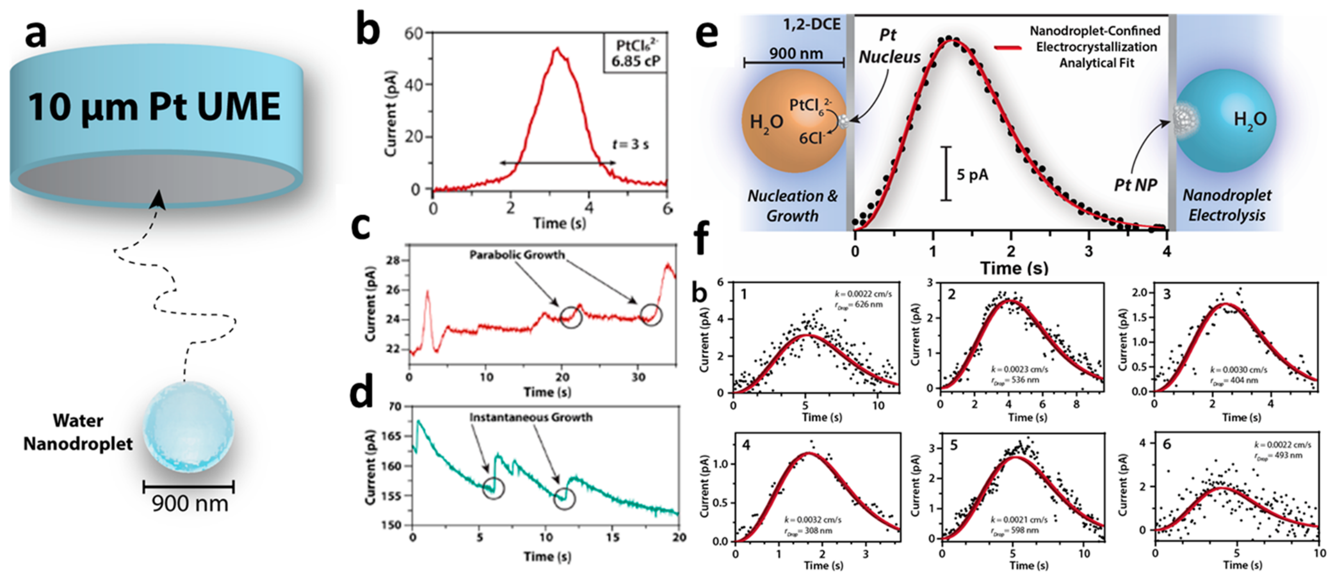

Figure 6. Schematic of single nanoparticle growth kinetics. (a) Nanodroplet colliding with the electrode surface, b) representative traces of the growth of a single Pt nanoparticle inside the droplet, and (c, d) different traces of nanoparticle growth under kinetic vs mass transfer conditions. (e) Schematic of the reduction of chloroplatinic acid inside the water droplet to generate a Pt nanoparticle. (f) Chronoamperograms with the analytical fit to quantify growth kinetics of a single Pt nanoparticle as a function of the droplet size. Data from ref 19.

aqueous phase disallows phase transfer and sets the stage for gold nanoparticle electrodeposition by the nanodroplet-mediated electrodeposition method.[4] These results highlight the importance of a detailed understanding of ion transfer mechanisms to enhance the library of metals that can be electrodeposited using nanodroplets. Because ion transfer plays a critical role in the electrodeposition process, one must also consider the energetics and kinetics of the transferring ion.[34] Furthermore, given the complex nature of the oil|water|electrode interface,[13,46−49] special considerations must be given to study the reactivity in these water-in-oil systems.[46,50]

■ SINGLE NANODROPLET AND NANOPARTICLE METHODS

In this section, we set out to justify single nanodroplet methods as a means of studying the chemistry of single nanoparticles. As mentioned in the introduction, single nanodroplet and nanoparticle techniques allow one to study chemistry at the single nanodroplet level. We have also shown that electrochemistry can elucidate new properties of nanomaterials.[51−53] To highlight why this may be important, consider a simple question: Why are our cells the size they are? This simple question has important implications: is enzymology as studied in a beaker representative of enzymology that occurs in our cells?[54−56] Our group recently showed that enzymatic reactions can be accelerated by orders of magnitude in sub-femtoliter volumes.[57] Chemistry changes in tiny volumes. Only in 2014 did Bard and Kim develop a method of electrochemically interrogating attoliter droplets.[58−63] In their experiment, toluene droplets stabilized by an ionic liquid were loaded with ferrocene. When a single droplet is incident on the electrode surface biased sufficiently positive to oxidize ferrocene, blip-type responses were observed when measuring current as a function of time. The blip occurs because of a rapid rise in current when the droplet irreversibly adsorbs to the electrode followed by an exponential decay back to baseline due to the electrolysis of droplet contents. Studying single entities, one at a time, opens the door to studying physicochemical properties of single nanoparticles.[51−53,64−66] Such stochastic electrochemical experiments have elucidated physicochemical properties of single atoms,[67] molecules,[68] and nanoparticles.[69]

Nucleation and Growth

Another question that follows is: What can be learned with single droplet experiments that cannot be learned with measurements on very many droplets, especially from a nanoparticle synthesis standpoint? In short, it enables the study of single nanoparticle synthesis problems, which during nanoparticle synthesis is problematic due to the formation of several nucleation sites. One exciting aspect about using nanodroplets is that when a sub-femtoliter droplet sits on an electrode surface, the contact radius that arises is effectively a nanoelectrode. While bulk electrolysis models have been used to quantify this contact radius,[62,70] no independent validation of contact radii for sub-femtoliter droplets has been reported to date. This must be considered moving forward since some contact radii extracted from bulk electrolysis theory are on the order of sub-nanometer. Furthermore, there are currently few techniques that can be used to rigorously quantify the contact angle of single droplets that are smaller than the diffraction limit.[71]

Nanoelectrodes have previously been used to study the nucleation and growth of single nanoparticles. The main argument behind whether or not a single nanoparticle is being interrogated is based on the small size of the nanoelectrode, which lowers the probability of multiple nuclei forming. Previously, Fleischmann[72] used microelectrodes and Kucernak[73] used carbon nanoelectrodes to study the nucleation and growth of single nanoparticles. Mirkin has also studied nucleation and growth at the single nanoparticle level.[74] While nanoelectrodes are powerful in quantifying single nanoparticle nucleation and growth parameters, they are difficult to make. As mentioned above, when a nanodroplet collides with a microelectrode, a nanoelectrode effectively forms at the microelectrode|nanodroplet interface.[2,75]

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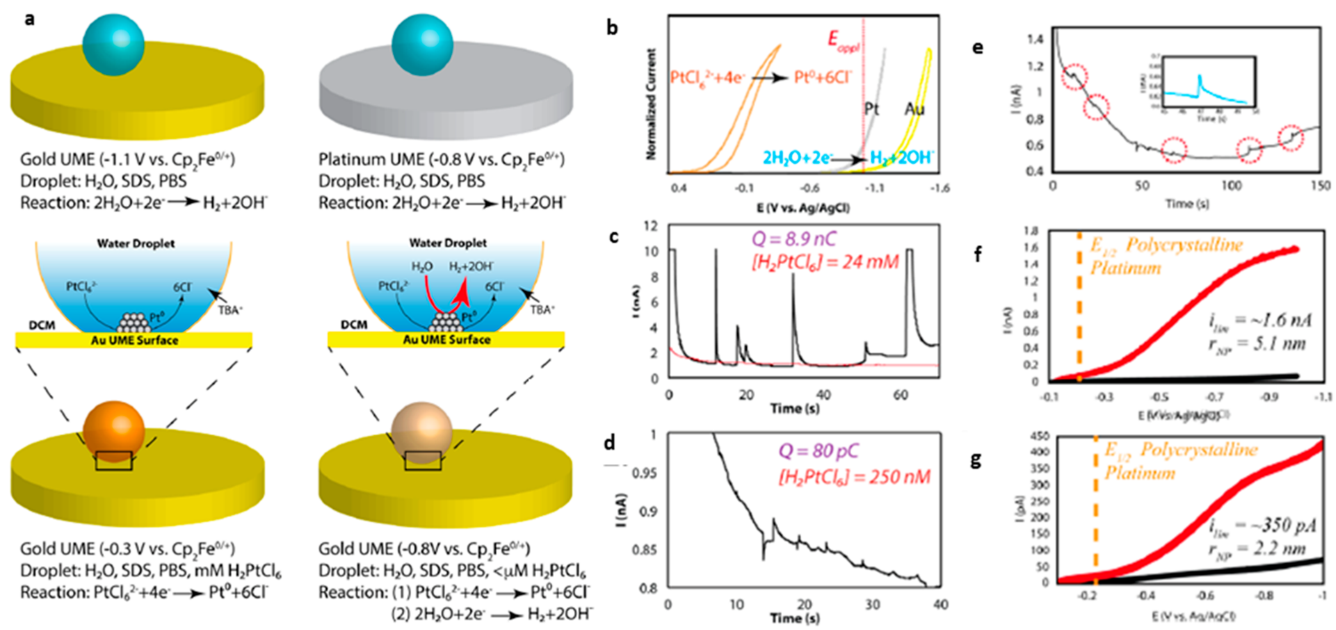

Figure 7. Schematic representation of the nucleation and growth of platinum. If a potential higher than the formal potential of chloroplatinic reduction is applied, water reduction can happen on the newly formed Pt nanoparticle. Additionally, representative transients of the reduction of chloroplatinic acid in different concentrations and cyclic voltammograms with an electrode containing platinum nanoparticles are shown. Data from ref 83.

A nanodroplet approaching a microelectrode is schematically depicted in Figure 6a. When the rate (current) is measured as a function of time (amperometry), the electrochemical response from single sub-femtoliter water droplets can be observed. Figure 6b shows the response of a single sub-femtoliter droplet colliding with a platinum microelectrode. The droplet contains hexachloroplatinic acid, and the microelectrode is biased more negative of the formal potential for chloroplatinate reduction to platinum metal. Figure 6c shows an amperometric trace when the difference in potential between the applied potential and formal potential for chloroplatinate reduction is low, and Figure 6d shows the response when the potential difference is high. The responses in Figure 6c,d report on the electrokinetically controlled growth of a single platinum nanoparticle in a single, sub-femtoliter water droplet. Figure 6d shows the diffusion-controlled growth of the nanoparticle. The current increases due to the nanoparticle growth and decreases back to baseline because the growth kinetics begin to compete with the rate of electrolysis (consumption of droplet contents). We have also developed a closed-form solution describing the growth of a single nanoparticle in a sub-femtoliter reactor.[19] Figure 6e shows a schematic with data and the simulated results, indicating quite good agreement. Such experiments allow one to study the growth kinetics of single nanoparticles in very small volumes. Figure 6f shows several transients fitted to the analytical solution, where the only adjustable parameter is the heterogeneous rate constant.

Using single nanodroplets enables the study of single nanoparticle formation. Therefore, quantifying the growth kinetics of single nanoparticles is possible. These studies can enable us to find parameters that can tune growth kinetics that will lead to fine control over nanoparticle structure. The study of single nanoparticles, one at a time, has yielded new knowledge that is washed out in ensemble measurements.[76]

Electrocatalysis of Platinum Clusters

Another interesting application of using small droplets is that they can be used to entrap very few molecules of a species of interest that, upon electrochemical activation, can heterogeneously catalyze a reaction. The average radii of droplets after ultrasonication are on the order of 100s of nanometers, which translates to 100s of attoliters. This is why we have chosen to term the nanodroplet volume sub-femtoliter.

Previously, Bard and co-workers demonstrated the ability to take advantage of differences in inner-sphere heterogeneous kinetics to observe the electrocatalysis on single nanoparticles[77] and even single atoms[67,78,79] and molecular catalysts.[80] A hallmark of these experiments is that the concentration of the metal salt precursor is low enough such that a single molecule of metal salt would interact with the nanoelectrode every few seconds (this concentration is on the order of femtomolar). In those experiments, the authors assumed that atoms would electrodeposit on nanoelectrodes and find another, allowing a cluster of atoms to grow on an atom-by-atom basis. It is worth mentioning that the meaning of clusters in the article meant that ten to thousands of Pt atoms are agglomerated; therefore, they make a single nanoparticle.

Motivated to remove this assumption and with the understanding that contact radii of droplets can be on the order of nanometers, we were interested in the electrocatalysis of isolated platinum clusters in water nanodroplets. We should also note that measuring the contact radius of sub-diffraction limited droplets is difficult. Generally, bulk electrolysis theory is used to fit the transient decay and extract a contact radius (the rate of decay is exponentially proportional to the size of the electrode). Using this method, contact radii of 10s of picometers have been reported.[70] This type of analysis, while common in the literature, neglects droplet wetting kinetics.

Figure 7a shows a schematic representation of an experiment, where a certain concentration of hexachloroplatinic acid is dissolved in the aqueous phase that is dispersed into

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nanodroplets with ultrasonication. On a gold microelectrode, water reduction occurs less favorably than on platinum. Thus, if the potential of the gold electrode is biased more negative than the formal potential of chloroplatinate reduction, platinum clusters can form. If the potential is also negative enough to drive water reduction on the resultant platinum phase, an increase in current can be observed. Figure 7b shows the voltammetry of chloroplatinate reduction on gold (orange trace) and water reduction on platinum (gray trace) and on gold (gold trace). One can apply a potential and watch single nanodroplets collide with a microelectrode one at a time in the current−time response, as shown in Figure 7c. The transients observed in Figure 7c are most likely the direct reduction of chloroplatinic acid because it is in a high enough concentration to dominate the signal. However, as Figure 7d,e show, lowering the concentration to 250 nM (Figure 7d) and then 20 nM (Figure 7e), one can still observe transients. These transients are most likely due to the electrocatalysis of single platinum nanoparticles and clusters in the water nanodroplets. For calibration, a 100 nM concentration in a 1 fL droplet is only 60 molecules of hexachloroplatinic acid. To further validate these systems, it is possible to "fish out" a platinum cluster on the gold electrode, submerge it in a solution of acid, and perform a voltammetric analysis. Figure 7f,g shows voltammograms of single platinum nanoparticles formed with this method. These experiments enable us to observe the reactivity of single nanoparticles, which can serve as a way to characterize the single nanoparticles that have been synthesized through an electrocatalytic reaction.[36,42,81,82]

CONCLUDING REMARKS

Methods to create new nanoparticles are incredibly important given the growing use of nanoparticles in a variety of industries, such as sensing[12] and energy storage and conversion.[23] Even though Faraday was making nanoparticles in the 19th century, new techniques are becoming available to synthesize nanoparticles. Electrodeposition is a robust and rigorous technique with key limitations in electrodepositing nanoparticles.[84] Because of diffusion layer overlap, nanoparticle size and morphology is difficult to control. Trapping metal salts within nanodroplets has key advantages. Nanoparticle size can be easily controlled by controlling the droplet size. Surprisingly, new and interesting morphologies (porosity, for instance) can be realized and tuned. High entropy alloy nanoparticles can also be electrodeposited with a variety of microstructures (amorphous versus solid solution). Common methods require the addition of stabilizing agents, high temperatures, a long time to synthesize materials, expensive experimental costs, etc.[85,86] With the nanodroplet-mediated electrodeposition method, all these problems are addressed by just using a water-in-oil system. This enables the generation of nanoparticles with different morphology and sizes that go from a few to hundreds of thousands of nanometers in diameter. Moreover, the polydispersity of the system can be controlled by adding different agents to stabilize the water droplets in the organic phase. Still, some limitations include complete control over the crystal structure and a small polydispersity index, which is still under investigation.

There are still quite interesting unknowns in this avenue of inquiry: Which is faster, droplet wetting kinetics or consumption of droplet contents? What is the geometry of the nanodroplet on the electrode, and how does it change during electrodeposition? We find these questions tantalizing. With the recent claims and validation that chemical reactions proceed differently in confined spaces, we expect this technique to offer not only a variety of solutions to problems surrounding electrodeposition but also a variety of exciting, unsolved puzzles that require new measurement tools.

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Notes

The authors declare no competing financial interest.

Biographies

Joshua Reyes-Morales obtained his certified ACS B.S. in Chemistry from Universidad Ana G. Mendez at Gurabo, Puerto Rico, in 2019. Joshua started his graduate studies in 2019 at the University of North Carolina at Chapel Hill under the mentorship of Dr. Jeffrey E. Dick, where he obtained a M.A. in chemistry in 2022. Joshua moved with the Jeffrey Dick Laboratory to Purdue University in 2022. Joshua's research interest focuses on the electrodeposition of metallic nanoparticles using a water-in-oil system and the fundamental studies of electrodeposition from water droplets. His goal overall is to use these materials for energy applications to obtain a better performance and to study the stability of these systems.

Jeffrey E. Dick received a B.S. in Chemistry from Ball State University in 2013 and completed a Ph.D. with Prof. Allen J. Bard at the University of Texas at Austin in 2017. Jeffrey began his independent career at the University of North Carolina at Chapel Hill in 2018 before moving to Purdue University as the Richard B. Wetherill Associate Professor in 2022. Jeffrey's research interests are in developing new measurement tools to understand chemistry in small volumes and how Nature takes advantage of nanoconfinement for the genesis and propagation of life.

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