Bridging Colloidal and Electrochemical Nanoparticle Growth with *In Situ* Electrochemical Measurements

*Gabriel C. Halford and Michelle L. Personick**

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459, United States

CONSPECTUS Prospective applications involving electrification of industrial chemical processes and electrical energy to chemical fuels interconversion as part of the energy transition to renewable energy sources have led to an increasing need for highly-tailored nanostructures immobilized on electrode surfaces. Control of surface facet structure across materials compositions is of particular importance for ensuring performance in such applications. Colloidal methods for producing shaped nanoparticles in solution are abundant, particularly for noble metals. However, significant technical challenges still remain with respect to rationally designing syntheses for the novel compositions and morphologies required to sustainably enable the above technological advances as well as in developing methods for uniformly and reproducibly dispersing colloidally-synthesized nanostructures on electrode surfaces. The direct synthesis of nanoparticles on electrodes using chemical reduction approaches remains challenging, though recent advances have been made for certain materials and structures. Electrochemical nanoparticle synthesis—where an applied current or potential instead of a chemical reducing agent drives the redox chemistry of nanoparticle growth—is poised to play an important role in advancing in the fabrication of nanostructured electrodes. Specifically, this Account focuses on colloidal-inspired design of electrochemical syntheses and the interplay between colloidal and electrochemical approaches in

terms of understanding the fundamental chemical reaction mechanisms of nanoparticle growth. An initial discussion of the development of electrochemical particle syntheses that incorporate colloidal synthetic tools highlights the promising emergent capabilities that result from blending these two approaches. Further, it demonstrates how existing colloidal syntheses can be directly translated to electrochemical growth on a conductive surface using real-time electrochemical measurements of the chemistry of the growth solution. Measuring the open circuit potential of a colloidal synthesis over time and then replicating that measured potential during electrochemical deposition leads to the formation of the same nanoparticle shape. These *in situ* open circuit and chronopotentiometric measurements also give fundamental insight about the changing chemical environment during particle growth. We highlight how these time-resolved electrochemical measurements, as well as correlated spectroelectrochemical monitoring of particle formation kinetics, enable extraction of information regarding mechanisms of particle formation that is difficult to obtain using other approaches. This information can be translated back into colloidal synthesis design via a directed, intentional approach to synthetic development. We additionally explore the added flexibility of synthetic design for methods involving electrochemically-driven reduction as compared to the use of chemical reducing agents. The Account concludes with a brief perspective on potential future directions in both fundamental studies and synthetic development enabled by this emerging integrated electrochemical approach.

KEY REFERENCES

- McDarby, S. P.; Wang, C. J.; King, M. E.; Personick, M. L. "An Integrated Electrochemistry Approach to the Design and Synthesis of Polyhedral Noble Metal Nanoparticles." *J. Am. Chem. Soc.* **2020**, *142*, 21322-21335.[1] *This work showed that in situ electrochemical measurements can be used to design electrochemical and chemical syntheses of shaped*

palladium nanoparticles. In addition, it demonstrated that electrochemical growth of nanoparticles can provide insight into fundamental colloidal reaction mechanisms.

- King, M. E.; Personick, M. L. "Defects by Design: Synthesis of Palladium Nanoparticles with Extended Twin Defects and Corrugated Surfaces." *Nanoscale* **2017**, *9*, 17914-17921.[2] *This work showed that a complex interaction between the surface passivating and etching effects of bromide and chloride leads the formation of twinned, corrugated palladium nanostructures. It also provides the basis for further fundamental study in the above reference.*

1. Introduction

An increasing focus on electrical-to-chemical energy interconversion and electrification of chemical synthesis processes has generated demand for precisely tailored nanoparticles immobilized on electrode surfaces.[3–7] Meeting these needs requires confronting numerous technical barriers. Control of nanostructure morphology is important for these applications, as exemplified by the importance of faceted structure in dictating product selectivity during electrochemical catalysis.[3] For instance, in carbon dioxide reduction, the ratio of {100} faces to {110} edges on copper (Cu) nanocubes is responsible for tuning selectivity toward ethylene, a desired product.[8] Cu octahedra with {111} faces are selective catalysts for methane production under otherwise identical conditions.[8–10] Many existing syntheses for shape-controlled nanoparticles are colloidal.[3,11–19] While particles synthesized in solution can be processed and cast onto electrodes, this adds an additional fabrication step—increasing time and cost—and faces challenges in controlling the uniformity and density of particle dispersion on the surface.[20–22] Meanwhile, direct chemical reduction-based synthesis of well-defined nanoparticles on electrodes has proven to be difficult, though progress has been made.[7,23–26] Additionally, colloidal

nanoparticle growth pathways can be difficult to fully define due to the interdependent nature of the many chemical and physical interactions. This complexity limits directed design of synthesis conditions for nanoparticles with desired compositions and architectures that require novel reaction environments, as opposed to conditions that iterate on existing approaches. Direct electrochemical deposition of morphology-controlled nanoparticles on surfaces in combination with real-time, *in situ* electrochemical measurements of the chemistry of nanoparticle growth presents opportunities for addressing these numerous uncertainties and meeting these critical needs.[1]

Electrochemical synthetic approaches have been integral to the history of shaped metal nanoparticles, particularly for nanorods. Templated electrodeposition syntheses were developed in the 1990's to generate gold (Au) nanorods—among other compositions—in anodized aluminum oxide membranes, which could then be dissolved to release the templated nanorods.[27–30] Meanwhile, a non-templated electrochemical synthesis of a suspension of Au nanorods with controlled aspect ratios was published in 1997.[31,32] These particles were formed through controlled-current electrolysis of an Au electrode in the presence of the surfactant cetyltrimethylammonium bromide (CTAB). Importantly, this latter synthesis represented one of the first examples of non-templated shaped nanoparticles produced by any approach—colloidal or electrochemical—and provided inspiration for the development of subsequent colloidal syntheses for Au nanorods and numerous other shapes. However, as the field of shaped metal nanoparticles has continued to grow and encompass a wider variety of metals and particle morphologies, colloidal syntheses employing a chemical reducing agent have become far more common than electrochemical approaches.

The establishment of comprehensive, predictive mechanistic principles for colloidal synthesis of shaped nanoparticles is still an ongoing effort; this is doubly true for electrochemical nanoparticle syntheses, where such information is especially limited.[33] Much of the electrochemical particle synthesis literature, such as square wave applied potential syntheses, access synthetic spaces that are not possible to achieve via colloidal chemical processes.[34–38] While such approaches are a powerful method for the synthesis of high-index nanoparticles, particularly for palladium (Pd) and platinum (Pt), making direct comparisons between these and colloidal approaches is difficult. Even among electrochemical nanoparticle syntheses that are more analogous to colloidal synthetic processes, mechanistic understanding has often been less of a focus than performance-based metrics, such as catalytic activity testing, and many fundamental questions remain. Some of the most common tunable parameters in electrochemical and colloidal synthesis are outlined in Table 1 along with a brief description of their relevance to controlling the nanoparticle growth environment. These parameters will be discussed throughout this Account, with a particular focus on how mechanistic insight into their role in particle growth can be gained from interfacing electrochemistry with nanoparticle synthesis.

Table 1. Comparison of the Most Common Tunable Parameters in Electrochemical and Colloidal Nanoparticle Syntheses and Summary of their Implementation.

Parameter	Electrochemical Synthesis		Colloidal Synthesis	
	Handle	**Implementation**	**Handle**	**Implementation**
reducing strength	applied potential (magnitude)	sets reaction potential while allowing a variable flow of electrons (current) to achieve that potential	chemical reducing agent	molecular structure directly controls redox potential ratio of reducing agent to metal precursor can also tune reduction environment
	applied current (magnitude)	sets the electron flow to the reaction while allowing a variable reaction potential to achieve that current	pH	changing the protonation state of many common reducing agents can tune their activity
reaction rate dynamics	variable applied potential	application of a varying applied potential will induce changes in the current and thus rate	depletion of reducing agent	as the reducing agent is depleted, the reaction rate will decrease
	variable applied current	rate can be directly controlled via the current (the rate of electron supply to the reaction)	continuous addition of reducing agent and/or metal precursor	controlled reactant addition, such as with a syringe pump, can be used to tune reduction rate over time
surface passivation	stabilizers and capping agents	can passivate particle surface; may have charge attraction to working electrode stabilizer not required	stabilizers and capping agents	can passivate particle surface stabilizer required
	halide ions	can act as selective or nonspecific surface passivators	halide ions	can act as selective or nonspecific surface passivators
etching	chemical additives	acid, base, and/or halides can facilitate oxidative etching	chemical additives	acid, base, and/or halides can facilitate oxidative etching

In this Account, we illustrate how the combination of electrochemical synthesis techniques with *in situ* electrochemical measurements of reaction chemistry has promising prospects to fill important knowledge gaps in nanoparticle growth and to expand the boundaries of synthetic design for both electrochemical and colloidal syntheses. We first describe the advantages of merging synthetic tools from colloidal growth with the programmable redox environment of electrochemical deposition to synthesize morphology-controlled materials on electrode surfaces. Then, by highlighting recent work from our research group, we demonstrate how electrochemical

measurements can be central to a multi-pronged approach for understanding shaped particle growth. We present an integrated strategy that enables the translation of mechanistic insights and synthetic approaches back and forth between colloidal and electrochemical synthesis environments, thereby providing robust tools for (1) developing a more complete understanding of the fundamental mechanisms of nanoparticle growth and (2) directing targeted design of new syntheses. Finally, we identify complementary approaches for gathering *in situ* information about electrodeposition—such as spectroelectrochemistry—and provide an outlook on emerging future directions enabled by these advances.

2. Using Colloidal Synthesis Techniques to Advance Electrochemical Materials Synthesis

Just as an electrochemical synthesis of Au nanorods inspired the development of some of the first colloidal syntheses for shaped nanoparticles, the now well-established field of colloidal synthesis is ideally positioned to inspire advances in electrochemical nanoparticle growth. Many research groups, including our own, have contributed to the development of a broad range of techniques for controlling colloidal nanoparticle shape using reaction kinetics, molecular and ionic additives, secondary metals, seed structure, and other means.[2,11,15,16,39–52] For example, surfactants and their corresponding counterions are common components of colloidal growth solutions because of their ability to modify crystal growth pathways through preferential adsorption onto particular facets in addition to their primary role of stabilizing particles against aggregation.[45,53–58] However, while additives are often present in electrochemical plating solutions, they are not used deliberately to define particle morphology. Using strategies from colloidal approaches in combination with the ability to facilely tune applied current or potential in electrodeposition opens exciting pathways for moving well beyond the existing limitations of both synthetic methods.

2.1 Electrochemical Nanoparticle Growth Inspired by Colloidal Synthesis

In their work on the electrodeposition of micrometer-size cuprous oxide (Cu_2O) particles via reduction of $Cu(NO_3)_2$ and subsequent precipitation of crystalline oxides, Seigfried and Choi employed surfactants as components of their deposition solution with the aim of addressing the challenges associated with shape modification of electrode-bound semiconducting particles.[59] Specifically, electrodeposition of Cu_2O particles onto Au electrodes in a surfactantless solution was found to exclusively form {100}-faceted cubes. However, the addition of the surfactant sodium dodecyl sulfate (SDS) enabled successful passivation, or blocking, of {111}-faceted surfaces as a result of selective adsorption of SDS on this facet. In addition, SDS has a pH-dependent adsorption strength on Cu oxide surfaces, which allowed the authors to use pH to further tune particle shape. Increasing the pH, which increases SDS adsorption to the particle surface, led to shape evolution from cubes, through intermediate shapes such as cuboctahedra, to octahedra (Figure 1).

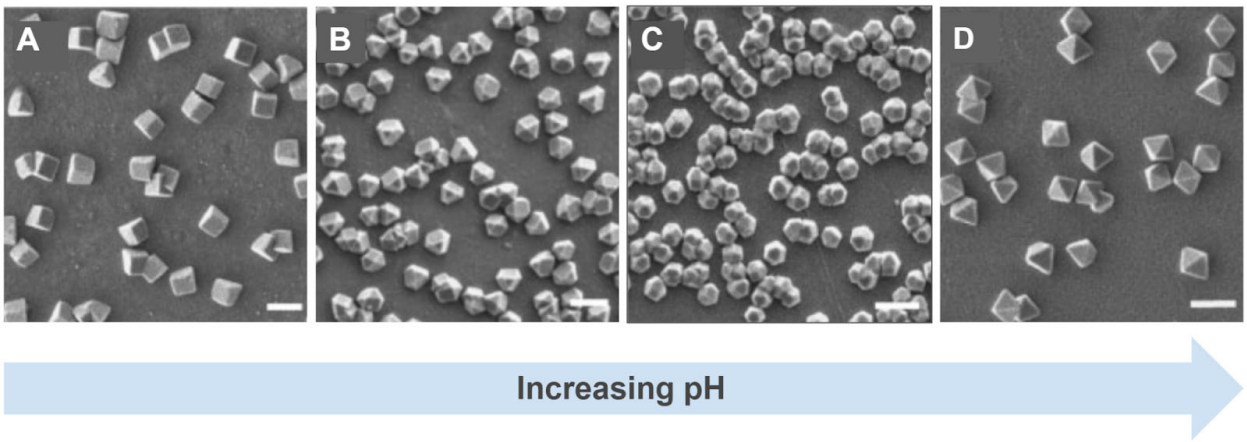

Figure 1. SEM images of Cu_2O shape evolution from {100}-faceted cubes to {111}-faceted octahedra as a function of pH: (A) cubes, pH = 3.4; (B) cuboctahedra, pH = 3.7; (C) truncated octahedra, pH = 3.9; (D) octahedra, pH = 4.1. Scale bars: 1 μm. All particles were synthesized in the presence of SDS. Adapted with permission from reference 59. Copyright 2004 Wiley-VCH.

While tuning of deposition potential is a more traditional approach to electrochemical materials deposition, in the context of shaped particle growth both the Choi group and our research group have found that there are advantages to using galvanostatic methods to control reaction rate. Most metal and metal oxide particle shapes are kinetic products and therefore maintaining fine control over the precursor reduction rate is important. For example, the above work used galvanostatic electrodeposition of shaped microparticles in combination with manipulation of temperature to tune particle deposition density without sacrificing shape control.[59] As the temperature is decreased, the reaction requires a stronger driving force—in this case a more negative potential—to maintain the same current density, or reaction rate, due to the changing kinetic parameters. The purpose of this approach was to maintain constant current density—since a particular current density was found to be critical for achieving the desired shapes—while using decreasing temperatures to increase the strength of the deposition potential and thus achieve higher surface coverages of particles.

2.2 Directly Translating from Colloidal to Electrochemical Growth

Alongside other developments of electrodeposition approaches that take inspiration from colloidal growth, our group has shown that it is also possible to directly replicate colloidal syntheses by replacing the chemical driving force for precursor reduction with an electrochemical one. This is exemplified by our electrochemical replication of our previously-developed colloidal synthesis for twinned, corrugated Pd particles.[1,2] Beyond demonstrating the use of applied current as a viable approach for the electrochemical replication of chemical reduction-based colloidal syntheses, the translation of this colloidal synthesis to growth on a surface also enabled us to gain increased mechanistic understanding of the formation of the corrugated particles in colloidal solution.[1]

The original colloidal synthesis followed a seed-mediated approach, where Pd seed particles (<10 nm) were generated via rapid reduction of Na_2PdCl_4 by $NaBH_4$ in a low-concentration solution of the surfactant cetyltrimethylammonium bromide (CTAB).[2] The seed particles were then diluted and injected into a surfactant-based solution containing a 100:1 mixture of cetyltrimethylammonium chloride (CTAC) and CTAB, a Pd precursor (Na_2PdCl_4), L-ascorbic acid as a reducing agent, and nitric acid (HNO_3) to control pH. In the colloidal synthesis, tuning of pH was used to control the protonation—and thus reducing strength—of the chemical reducing agent, here ascorbic acid.

The analogous electrochemical approach replaced the chemical reducing agent, ascorbic acid, with applied current; this change also eliminated the need for HNO_3 in the growth solution, as there is no need for control of a reducing agent's protonation state and the electrochemical measurements appear robust to changes in pH.[1] Seeds were synthesized as previously described, and then dropcast onto a glassy carbon (GC) electrode and dried rather than being injected directly into the growth solution. No ligand removal process was required. The GC working electrode with seeds, a Ag/AgCl reference electrode, and a Pt counter electrode were placed in a solution containing the same 100:1 ratio of CTAC:CTAB surfactant and a Pd precursor (H_2PdCl_4) as in the colloidal synthesis. However, rather than injecting a chemical reducing agent, the reaction was initiated through application of a current of −2.55 μA/cm^2 for 30 seconds followed by −25.5 μA/cm^2 for 30 minutes (Figure 2A). The particles produced on the GC electrode were comparable in shape, surface structure, and size distribution to those generated by the colloidal synthesis, indicating successful replication (Figure 2B,E). Chronopotentiometry measurements during electrochemical growth were also used to determine the potential at the electrode surface in real time. This measurement exhibited similar features to an open circuit measurement of the potential

of the reaction solution during the colloidal growth reaction. In addition, accelerating the rate of reaction by increasing the applied current density led to particles that were analogous to the products of increasing the rate of the colloidal reaction using elevated pH (Figure 2B-G).

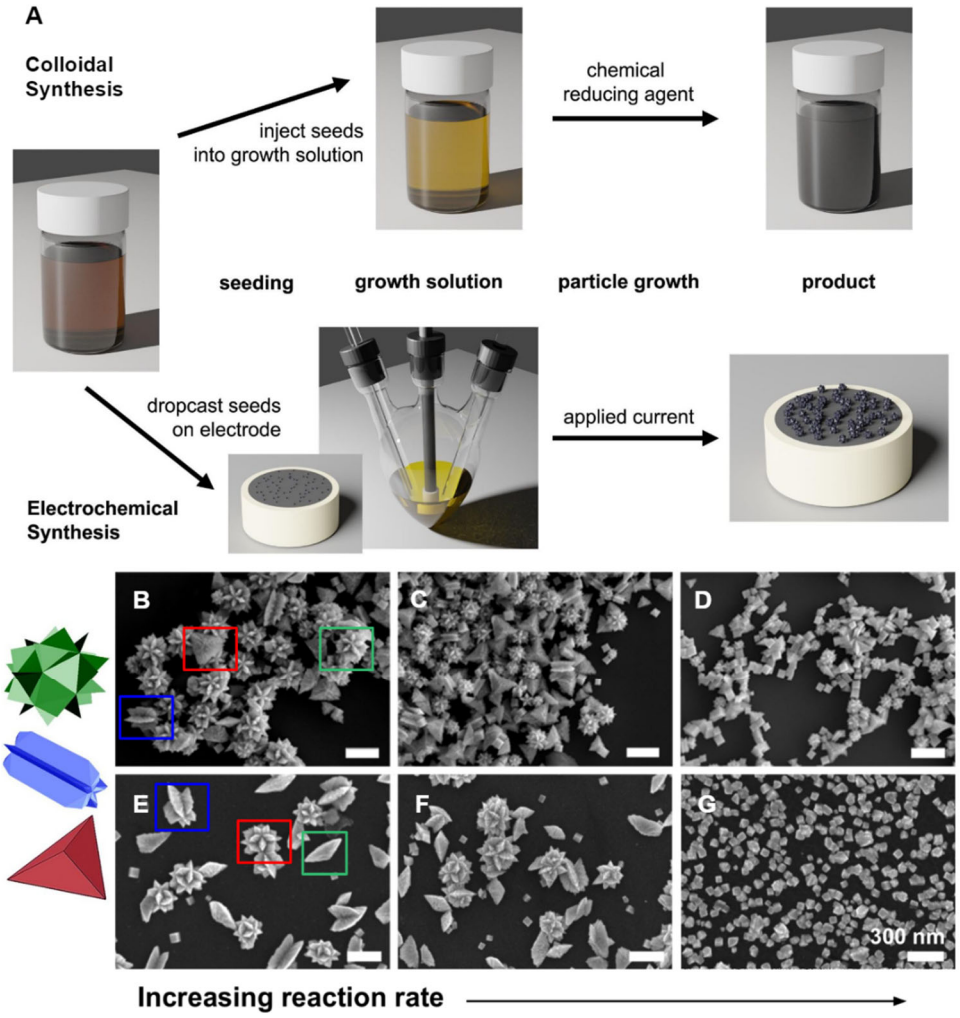

Figure 2. (A) Scheme comparing the colloidal and electrochemical seed-mediated synthesis routes. (B-G) SEM images of the effects of increasing reaction rate on corrugated Pd nanoparticle morphology, as tuned by increasing pH for the colloidal reactions (B-D) and increasing current density for the electrochemical reactions (E-G). Representative particle morphologies, including concave icosahedra (green), pentatwinned rods (blue), and bipyramids (red), are highlighted. As the reaction rate increases, both sets of products shift from corrugated particles to single-crystalline

cubes. Scale bars: 300 nm. Adapted with permission from reference 1. Copyright 2020 American Chemical Society.

While the applied current in the electrochemical synthesis of the corrugated particles was selected empirically, the chronopotentiometry and open circuit potential measurements taken following completion of synthetic development suggested that electrochemical measurements could be used as a tool for directed synthetic design. Electrochemical measurements of reactions for shaped metal nanoparticle growth have the advantage of being an *in situ*, nondestructive technique for providing quantitative data about the real-time *chemistry* of the reaction solution. In contrast, most existing techniques for understanding nanoparticle growth kinetics provide temporal snapshots of the metal content of the nanoparticles or growth solution (inductively coupled plasma atomic emission spectroscopy (ICP-AES), UV-visible spectroscopy) or physical insight into nanoparticle structure and size (electron microscopy or X-ray absorption spectroscopy).[44,47,60–62] Electrochemical measurement approaches such as chronopotentiometry and chronoamperometry therefore represent a powerful set of tools for increasing mechanistic understanding of shaped nanoparticle formation under both chemical and electrochemical growth conditions.

Based on this idea, we hypothesized that it was possible to directly design electrochemical synthesis parameters by taking open circuit potential measurements of existing colloidal reactions and then using a potentiostat to apply a matching electrochemical potential, thereby reproducing the shape formation observed in the colloidal solution. We provided proof of concept for this approach by mimicking colloidal syntheses for Pd cubes and octahedra adapted from the literature.[1,63] Measurement of the open circuit potential of the growth solutions for these colloidal syntheses as particle growth proceeded provided information regarding how the reaction potential

of the solution changed over time (Figure 3A-B).[1] Subsequently, we developed electrochemical reactions using a growth solution analogous to the colloidal synthesis—but without the chemical reducing agent—and a programmed current profile. Chronopotentiometry measurements of these reactions were then compared to the open circuit potential measured from the colloidal reactions to iteratively design a current profile that produced a similar dynamic reaction potential (Figure 3A-B). The synthesis reactions for both shapes display a fairly linear upward slope in potential throughout the reaction, which is attributable to the close matching of the stoichiometry of the metal salt and reducing agent in the original reaction and their depletion throughout the reaction. This depletion is mimicked by decreasing the supply of electrons (i.e., decreasing the magnitude of the applied current) throughout the reaction in the electrochemical synthesis. The particle morphologies resulting from both matched electrochemical syntheses exhibited a close shape correspondence to their colloidal counterparts (Figure 3C-F). These results suggest that qualitative and quantitative comparisons between colloidal and electrochemical syntheses are possible and relevant to understanding mechanisms, despite the differences in the two systems.

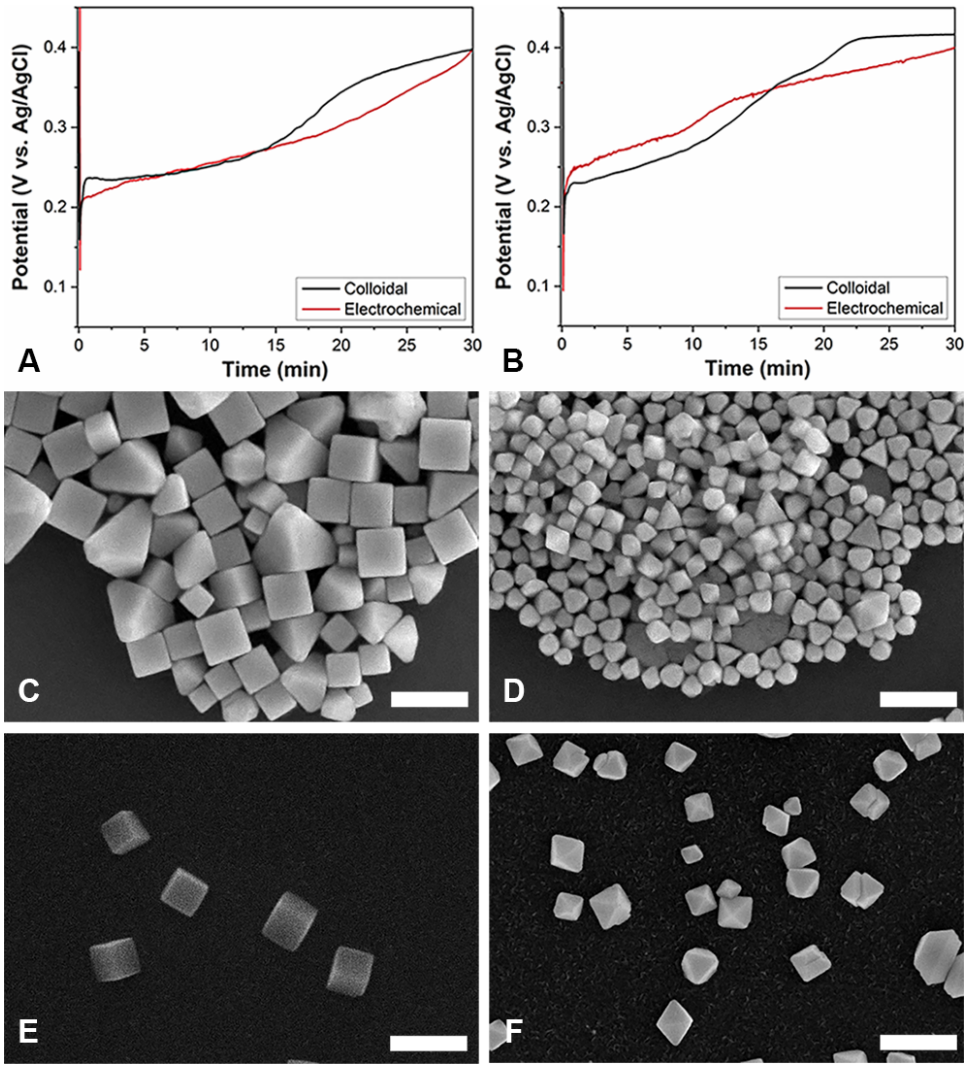

Figure 3. (A-B) Electrochemical (chronopotentiometry) and colloidal (open circuit potential) profiles for Pd cubes (A) and octahedra (B) over 30 minutes of reaction time. (C-F) SEM images of the corresponding colloidally-synthesized Pd cubes (C) and octahedra (D), and electrochemically-synthesized Pd cubes (E) (galvanodynamic current scan from −25.5 to 0 $\mu A/cm^2$) and octahedra (F) (galvanodynamic current scan −20.4 to −2.55 $\mu A/cm^2$). Scale bars: 200 nm. Adapted with permission from reference 1. Copyright 2020 American Chemical Society.

The electrochemical replication of the colloidal Pd cube and octahedra syntheses demonstrates the utility of *in situ* electrochemical measurements for informing electrochemical synthetic design.

Additionally, it highlights the importance of the dynamic nature of the reducing environment during colloidal growth, both in designing electrochemical syntheses and—moving one step further—in building relationships between colloidal and electrochemical particle syntheses to understand colloidal growth mechanisms. The changing nature of a colloidal growth solution throughout a reaction points to constant applied current or potential as being a poor electrochemical analogues for colloidal reactions that do not have great excesses of reducing agent. Conversely, only considering colloidal syntheses with large excesses of reducing agent leaves out vast swaths of synthetic space that are inaccessible without slower reaction kinetics. To electrochemically synthesize a full range of possible particle morphologies, a galvanodynamic or potentiodynamic approach must be considered as an alternative to constant current or constant potential application, particularly in replication of colloidal work.

3. Using Electrochemistry to Inform Synthetic Development in Colloidal Synthesis

The electrochemical adaption of the corrugated particle synthesis discussed in Section 2.2 provides interesting opportunities for empirically probing colloidal growth mechanism in ways that are not possible in the colloidal reactions themselves. For example, the lack of any pH-based effects on a chemical reducing agent allows for greater pH tuning of the growth solution without affecting reduction kinetics; and immobilization of the particles on the electrode surface results in a decreased likelihood of aggregation, thus enabling the surfactant concentration to be decreased below the limit that is required for colloidal synthesis or completely removed.[1] These practical differences allow for better isolation of the competing influences of the various chemical components in colloidal reactions, for example, reduction rate tuning vs. etching for acids; or surface passivation vs. reduction rate tuning vs. etching for the halide counterions in surfactants. Thus, carefully designed electrochemical growth studies can provide critical insight into colloidal

growth mechanisms. Perhaps more important than this broadening of the parameter space for empirical study is the ability to track the details of the changing chemical environment of the growth solution over the course of the nanoparticle growth reaction—something that is not generally considered in the study of colloidal growth mechanisms and the design of colloidal reaction conditions. This information can also be used to translate in the reverse direction—from electrochemical to colloidal growth.

3.1 *In Situ* Electrochemical Measurements to Enable Real-Time Insight into Nanoparticle Growth Chemistry

Further analysis of the open circuit measurements used to translate the colloidal Pd octahedra and cube syntheses to electrochemical growth provides an initial demonstration of how these measurements give important added insight into nanoparticle growth.[1] The open circuit potential measurements of these two reactions suggest that, in this particular set of syntheses, the octahedra growth reaction is complete after 23 minutes vs. 30 minutes for growth of the cubes (Figure 3A-B). In our reaction a small amount of bromide (7 μM) was added to the CTAC-based growth solution to produce cubes, while 0.7 μM iodide was instead added to the growth solution for the octahedra. Higher (millimolar) concentrations of halides such as bromide and iodide are well-known to slow the rate of metal ion reduction due to complexation with the ionic metal precursor and passivation of the particle surface, with iodide slowing the rate more than bromide.[45,64] However, the above measurements are consistent with our previous work showing that micromolar amounts of halide accelerate the rate of metal ion reduction for Pd and other metals, with iodide having a stronger rate-enhancing effect at lower concentrations than bromide does.[43,44,47] Thus, these results suggest that a similar rate-enhancing mechanisms of halide ions may be operative in this case.

Another example of this form of real-time chemical analysis can be seen in our group's use of open circuit potential measurements to study the time-dependent redox behavior of common reducing agents (Figure 4A).[1] The measured solutions contained an aqueous solution of surfactant (cetyltrimethylammonium bisulfate, $CTAHSO_4$) and a Pd precursor (H_2PdCl_4) into which a two-fold stoichiometric excess (relative to the metal precursor) of the reducing agents sodium borohydride ($NaBH_4$), ascorbic acid, hydroquinone (HQ), or trisodium citrate was rapidly injected. Immediately upon addition, $NaBH_4$, the strongest reducing agent studied, displayed a steep potential drop followed by a swift increase in potential, demonstrating the rapid consumption of this strong reducing agent and fast metal ion reduction kinetics that are consistent with the phenomenologically observed reactivity of this reducing agent during the rapid (< 2 min) formation of Pd seed particles.[2,43,44,47] The addition of ascorbic acid and hydroquinone, reducing agents of intermediate strength, also leads to an initial drop in potential. However, the dip is smaller in magnitude than that of $NaBH_4$ as a consequence of the higher reduction potentials of these reducing agents. Ascorbic acid is then depleted in the solution more quickly than hydroquinone—the open circuit potential of the reaction containing ascorbic acid rises more swiftly—and there is an interesting inflection point in the potential of the ascorbic acid-containing growth solution after twelve minutes that is distinct from the behavior of hydroquinone or $NaBH_4$. Of note, an analogous inflection point is observed in the open circuit measurements of the Pd cube and octahedra syntheses, described earlier, which use ascorbic acid as the reducing agent. This suggests that this measured behavior is indicative of the fundamental kinetics of reaction with this reducing agent, at least for reaction with Pd ions. Further work to understand the chemical mechanisms that lead to this observed profile is ongoing. The growth solution containing citrate displays no change in open circuit potential, demonstrating that citrate is not able to react with the Pd precursor under

these conditions.[1] Understanding the behavior of common reducing agents enables the informed selection of a reducing agent with both a reduction potential and reaction kinetics that match the desired reaction trajectory, allowing for streamlining and acceleration of synthesis development from current combinatorial approaches. The full extent of chemical information that can be extracted from these real-time electrochemical measurements remains to be determined, and we are currently working to answer this question. This additional inquiry will specifically address the role of diffusion in the electrochemical growth environment as compared to the colloidal environment, the influence of pH in the absence of a chemical reducing agent, and the effect of electrolyte concentration on both measurement and particle growth.

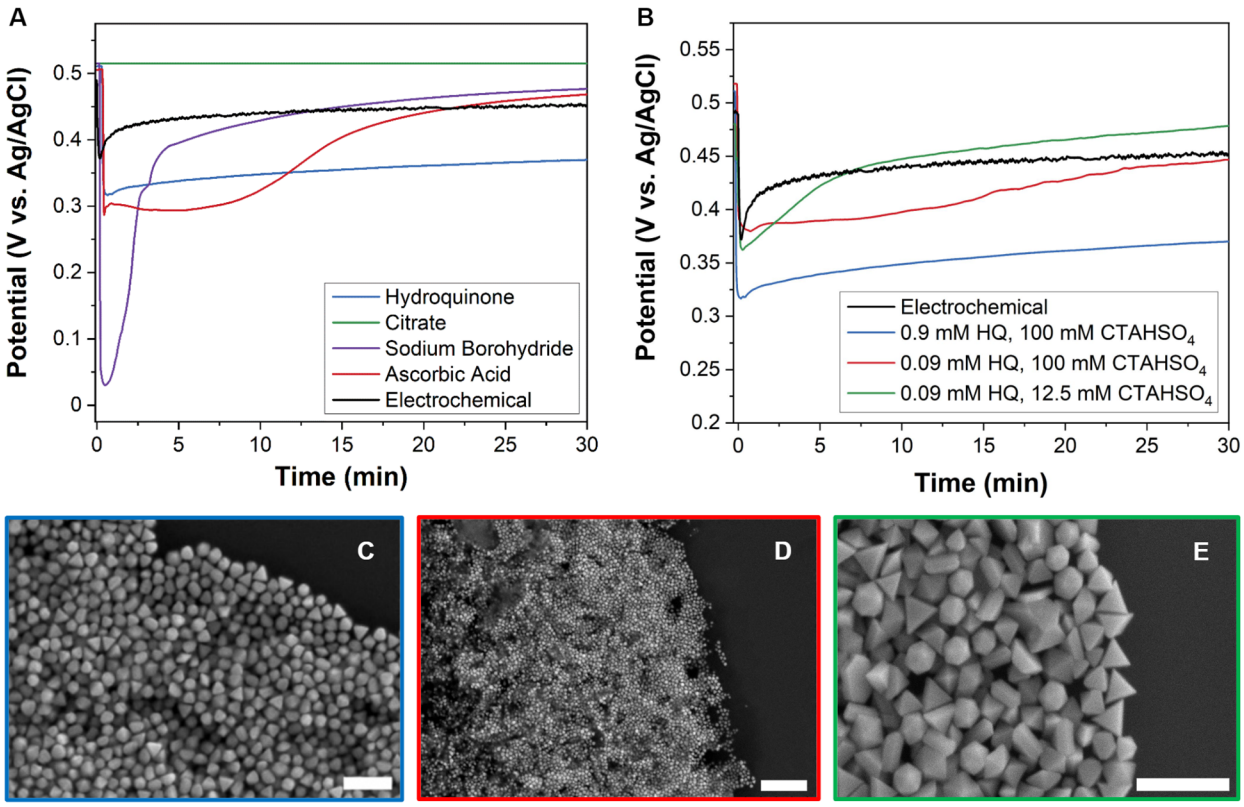

Figure 4. (A) Comparison of the open circuit potential measurements of colloidal reactions with several common reducing agents along with a chronopotentiometric measurement of an electrochemical synthesis for Pd icosahedra. All six growth solutions contained 100 mM

$CTAHSO_4$ and 5 mM H_2PdCl_4. (B) Comparison of open circuit potential measurements of different colloidal reaction conditions for Pd nanoparticles with the chronopotentiometry measurement for electrochemical synthesis for Pd icosahedra. HQ = hydroquinone, $[Pd^{2+}] = 5$ mM. (C-E) SEM images of the particles that result from the colloidal reaction conditions measured in (B), in order from top to bottom. Scale bars: 300 nm. Adapted with permission from reference 1. Copyright 2020 American Chemical Society.

3.2 *In Situ* Electrochemical Measurements for Directed Synthetic Design

To provide proof of concept for the feasibility of a directed design process, we first developed a fully electrochemical synthesis of twenty-fold twinned Pd icosahedra and then used the above open circuit measurements of the small reducing agent library to translate the synthesis to a colloidal growth environment.[1] The electrochemical synthesis involved a simple growth solution containing $CTAHSO_4$, along with H_2PdCl_4 as a Pd precursor, and the particle morphology was modulated primarily through tuning of the applied current. Pd seeds were dropcast onto a GC electrode, which was introduced to the growth solution in a three-electrode configuration. The solution was subjected to an applied current of -2.55 $\mu A/cm^2$ for 30 minutes, which was sufficiently weak to prevent nucleation and formation of additional small particles early in the reaction, but was strong enough for subsequent growth of large (> 50 nm) faceted particles on the dropcast seeds. Our research group first introduced the use of $CTAHSO_4$ as a surfactant for noble metal nanoparticle growth in our studies of halide-assisted metal ion reduction.[47] In these previous colloidal experiments, the lack of halide counterions from the $CTAHSO_4$ surfactant generally led to the formation of small, polydisperse particles due a fast metal ion reduction rate and significant homogeneous nucleation.[47] This had, to this point, prevented the colloidal synthesis of larger faceted particles using this halide-free surfactant. The flexibility of reduction rate control with an

applied current in the electrochemical synthesis provides a facile means of identifying an appropriate reaction rate for the growth of targeted larger nanostructures. We were thus able to use the measured potential from the successful electrochemical reduction conditions in combination with the open circuit measurements of the common reducing agents from Figure 4A to deliberately design conditions for the colloidal growth of analogous large polyhedral nanostructures in $CTAHSO_4$.

Based on chronopotentiometry measurements of the electrochemical growth reaction over time, hydroquinone was identified as the closest match in terms of reduction potential and depletion rate and was selected for further study.[1] However, at the conditions of two-fold stoichiometric excess of reducing agent, the measured open circuit potential of the colloidal growth solution was significantly stronger than that of the electrochemical process (Figure 4B). Consequently, the particles that formed colloidally under this condition were much smaller than those formed electrochemically and a mixture of different shapes was observed (Figure 4C). To weaken the reducing environment of the growth solution, the concentration of hydroquinone was decreased ten-fold. As expected, this increased the measured open circuit potential of the solution. However, this change in reducing agent concentration also led to a very slow rise in the solution potential, indicating a slow depletion of the chemical reducing agent, and the particles that formed were very small (Figure 4D). Together, these results suggest a diffusion-limited reaction as a result of the sub-stoichiometric amount of reducing agent relative to Pd precursor. Therefore, to increase diffusion rates, the concentration of the $CTAHSO_4$ surfactant was decreased from 100 mM to 12.5 mM. As predicted, this increased the rate of diffusion of reactants in the growth solution, yielding a faster increase in the open circuit potential. The net product was larger nanoparticles with a significant population of icosahedra that better matched the size and shape of the electrochemically

synthesized particle (Figure 4E). We note that the colloidally synthesized particles were not an exact match for the icosahedra synthesized electrochemically, indicating that hydroquinone may not be the perfect reducing agent for this synthesis. However, the successful improvement of the synthesis using this method suggests that a library of open circuit potential measurements of the reaction of various redox-active molecules with different metals could be used to identify novel reducing agents with desired reduction potentials and reaction kinetics.

3.3 Spectroelectrochemical Techniques

Integrated spectroelectrochemical techniques represent a complementary approach for using electrochemical measurements to enhance mechanistic insight and design new syntheses. Oh *et al.* recorded combined *in situ* chonoamperometry and dark-field spectroscopy measurements during the electrodeposition of Cu onto silver (Ag) nanocubes.[65] Using these single-particle measurements, they were able to correlate Cu deposition kinetics with morphological changes, building a clear mechanistic picture of the generation of three distinct nanostructure types: atop tetrapods, dendritic spheres, and multiple cube complexes (Figure 5). The atop tetrapods were generated during linear sweep voltammetry (LSV) at a rate of 10 mV s^{-1}, with deposition taking place at a potential of -0.34 V—the potential required for bulk reduction of Cu onto Ag. However, in the range of -0.23 to -0.33 V during low sweep rates (0.5 mV s^{-1} or 1 mV s^{-1})—in the underpotential deposition (UPD) range—plasmon peak shifts indicated some additional mechanisms of Cu deposition that occur only at the nanoscale.

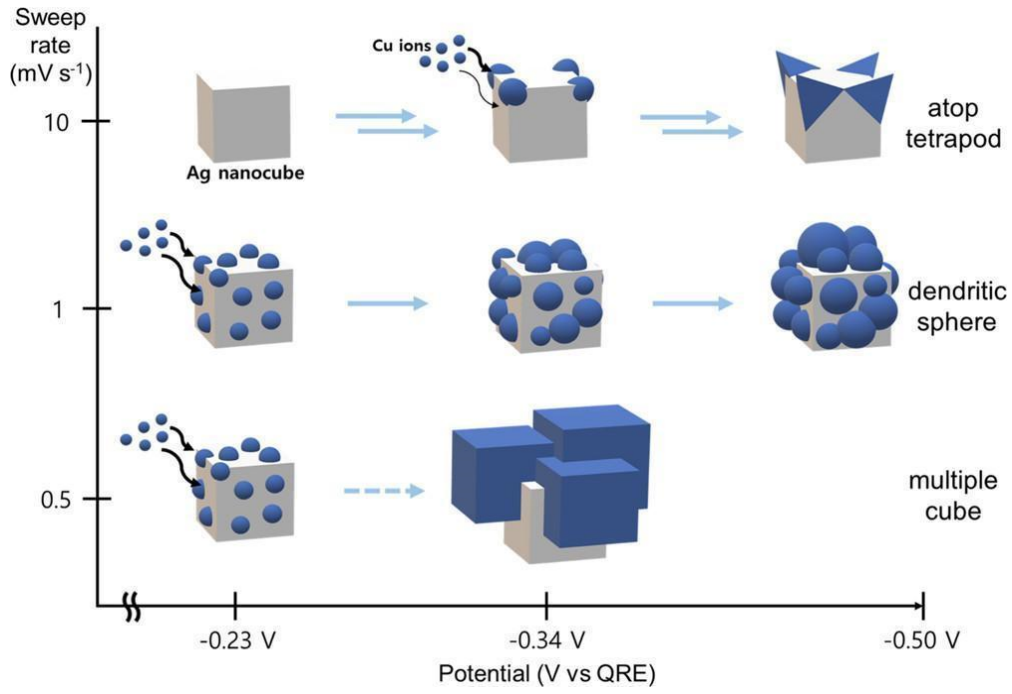

Figure 5. Schematic of the use of a 1inear potential sweep rate to control reaction rate and overpotential vs. underpotential deposition in the electrodeposition of Cu on Ag nanoparticles, enabling the formation of multiple Cu deposition morphologies. Adapted with permission from reference 65. Copyright 2020 American Chemical Society.

Determination of the formation mechanisms for these dendritic sphere and multiple cube products was undertaken through exploration of the reaction kinetics using correlated electrochemical, spectroscopic, and microscopic techniques.[65] At applied constant potentials of -0.23 to -0.25 V, the presence of bright spots on the Ag surface in SEM images and a plasmon peak shift without any corresponding faradaic current in the chronoamperometry measurements indicated local nucleation events of Cu on defects or edges of the Ag cubes without any bulk deposition. At -0.34 V a faradaic current response was observed; this response became stronger with increasing magnitude of applied potential. The mechanistic interpretation of these results was that dendritic sphere and multiple cube depositions, which occur at different sweep rates (1 mV s^{-1} and 0.5 mV s^{-1}, respectively), were both associated with the UPD plasmonic shift feature.

Distinguished only by sweep rate, the two kinetic products were both driven by local random nucleation of Cu due to UPD on the Ag surface. The reaction kinetics then determined whether these random Cu domains grew in a more squared-off or rounded fashion. The atop tetrapods, meanwhile, followed a different bulk-reduction mechanism at -0.34 V where Cu was only deposited onto the corners of the nanocubes, which were proposed to have a lower coverage of the capping agent, polyvinylpyrrolidone. The sweep rate of 10 mV s^{-1} was too fast for random nucleation of Cu onto cube faces via UPD, as minimal time was spent in this potential range.[65] This use of chronoamperometry in elucidating deposition mechanisms points to opportunities for the further integration of *in situ* electrochemical monitoring with single-particle imaging techniques, as well as the utility of electrochemical measurement in understanding deposition in bimetallic systems.

4. Summary and Outlook

Coupling the flexibility of electrochemical particle deposition with inspiration from colloidal synthesis allows sets of parameters that are traditionally only found in either colloidal or electrochemical approaches to be simultaneously tuned in the same reaction, increasing the scope of the synthetic parameter space. In addition, given the kinetically-driven nature of shaped nanoparticle growth, innovative tools for obtaining insight into growth dynamics in changing chemical environments, such as the examples showcased in this Account, are precisely what is needed to drive the design of syntheses for the increasingly complex materials required to enable emerging applications. *In situ* electrochemical measurements provide a promising alternative and/or complementary approach to other techniques for studying reaction kinetics. Further, electrochemical measurement can be a powerful guide for identifying new reducing agents, which

is key to unlocking new synthetic strategies for presently unachievable nanoparticle compositions and structures.

Many fundamental questions remain regarding how to best interpret the real-time electrochemical data acquired using these approaches to gain more detailed, quantitative chemical information. Computational modeling will likely contribute to this effort. Opportunities also exist for developing programs to automate the process of converting a measured open circuit potential for a colloidal reaction to an applied current or potential on an electrode to take full advantage of the breadth of published colloidal syntheses in the fabrication of nanostructured electrodes.

Integration of insights from these approaches with those from other emerging *in situ* techniques—such as the spectroelectrochemical approach described above—as well as model electrochemical surface science studies will also be important to gaining comprehensive mechanistic understanding. Work by Wiley and co-workers using electrochemical measurements to understand the adsorption of ionic surfactants and halides onto single-crystal metal surfaces, for instance, has important implications for moving from phenomenological to quantitative understanding of the many factors affecting particle growth.[66–68] Overall, conversation between the colloidal and electrochemical approaches to particle growth shows significant promise for generating novel materials syntheses and for answering fundamental questions in both solution and surface-based nanoparticle growth.

AUTHOR INFORMATION

Corresponding Author

Michelle L. Personick — *Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459, United States*; orcid.org/0000-0003-4747-9429; Email: mpersonick@wesleyan.edu; Phone: (860) 685-2592

Authors

Gabriel C. Halford — *Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459, United States*

Notes

The authors declare no competing financial interest.

Biographies

Gabriel C. Halford received his undergraduate degrees in chemistry and art history from Wellesley College in 2021, where he conducted research under Professor Rebecca A. Belisle. Since Fall 2021, he has been a Ph.D. student in Michelle L. Personick's lab at Wesleyan University. His research focuses on both colloidal and electrochemical synthesis and measurement of shaped palladium nanostructures.

Michelle L. Personick is an Associate Professor in the Chemistry Department at Wesleyan University in Connecticut. She received a B.A. degree from Middlebury College in 2009, where she was an undergraduate researcher with Prof. Sunhee Choi. In 2013, Michelle obtained a Ph.D. from Northwestern University under the supervision of Prof. Chad A. Mirkin. From 2013 to 2015, she was a postdoctoral researcher at Harvard University working with Prof. Cynthia M. Friend and

co-advised by Prof. Robert J. Madix. She joined the faculty at Wesleyan in 2015, where her research group focuses on the precision synthesis of metal nanomaterials and the use of these materials to enable fundamental research toward improved catalysts for resource-efficient chemical synthesis and the clean production of energy.

ACKNOWLEDGMENT

This material is based upon work supported by the National Science Foundation under Grant No. 2203465.

REFERENCES

(1) McDarby, S. P.; Wang, C. J.; King, M. E.; Personick, M. L. An Integrated Electrochemistry Approach to the Design and Synthesis of Polyhedral Noble Metal Nanoparticles. *J. Am. Chem. Soc.* **2020**, *142*, 21322–21335. https://doi.org/10.1021/jacs.0c07987.

(2) King, M. E.; Personick, M. L. Defects by Design: Synthesis of Palladium Nanoparticles with Extended Twin Defects and Corrugated Surfaces. *Nanoscale* **2017**, *9*, 17914–17921. https://doi.org/10.1039/C7NR06969C.

(3) Shi, Y.; Lyu, Z.; Zhao, M.; Chen, R.; Nguyen, Q. N.; Xia, Y. Noble-Metal Nanocrystals with Controlled Shapes for Catalytic and Electrocatalytic Applications. *Chem. Rev.* **2021**, *121*, 649–735. https://doi.org/10.1021/acs.chemrev.0c00454.

(4) Schiffer, Z. J.; Manthiram, K. Electrification and Decarbonization of the Chemical Industry. *Joule* **2017**, *1*, 10–14. https://doi.org/10.1016/j.joule.2017.07.008.

(5) *Basic Research Needs for Catalysis Science*; 1545774; 2017; p 1545774. https://doi.org/10.2172/1545774.

(6) Chen, A.; Holt-Hindle, P. Platinum-Based Nanostructured Materials: Synthesis, Properties, and Applications. *Chem. Rev.* **2010**, *110*, 3767–3804. https://doi.org/10.1021/cr9003902.

(7) Neal, R. D.; Hughes, R. A.; Preston, A. S.; Golze, S. D.; Demille, T. B.; Neretina, S. Substrate-Immobilized Noble Metal Nanoplates: A Review of Their Synthesis, Assembly, and Application. *J. Mater. Chem. C* **2021**, *9*, 12974–13012. https://doi.org/10.1039/D1TC01494C.

(8) Zaza, L.; Rossi, K.; Buonsanti, R. Well-Defined Copper-Based Nanocatalysts for Selective Electrochemical Reduction of CO_2 to C_2 Products. *ACS Energy Lett.* **2022**, *7*, 1284–1291. https://doi.org/10.1021/acsenergylett.2c00035.

(9) Iyengar, P.; Huang, J.; Gregorio, G. L. D.; Gadiyar, C.; Buonsanti, R. Size Dependent Selectivity of Cu Nano-Octahedra Catalysts for the Electrochemical Reduction of CO2 to CH4. *Chem. Commun.* **2019**, *55*, 8796–8799. https://doi.org/10.1039/C9CC02522G.

(10) Mangione, G.; Huang, J.; Buonsanti, R.; Corminboeuf, C. Dual-Facet Mechanism in Copper Nanocubes for Electrochemical CO_2 Reduction into Ethylene. *J. Phys. Chem. Lett.* **2019**, *10*, 4259–4265. https://doi.org/10.1021/acs.jpclett.9b01471.

(11) Xia, Y.; Xia, X.; Peng, H.-C. Shape-Controlled Synthesis of Colloidal Metal Nanocrystals: Thermodynamic versus Kinetic Products. *J. Am. Chem. Soc.* **2015**, *137*, 7947–7966. https://doi.org/10.1021/jacs.5b04641.

(12) Langille, M. R.; Personick, M. L.; Zhang, J.; Mirkin, C. A. Defining Rules for the Shape Evolution of Gold Nanoparticles. *J. Am. Chem. Soc.* **2012**, *134*, 14542–14554. https://doi.org/10.1021/ja305245g.

(13) Personick, M. L. Plasmon-Mediated Syntheses of Polyhedral Noble Metal Nanoparticles. In *Plasmonic Nanoparticles: Synthesis and (Bio)functionalization*; Plasmonic Nanomaterials:

Principles, Design and Bio-Applications; World Scientific, 2022; Vol. Volume 2, pp 47–88. https://doi.org/10.1142/9789811235221_0002.

(14) Jung, H.; King, M. E.; Personick, M. L. Strategic Synergy: Advances in the Shape Control of Bimetallic Nanoparticles with Dilute Alloyed Surfaces. *Curr. Opin. Colloid Interface Sci.* **2019**, *40*, 104–117. https://doi.org/10.1016/j.cocis.2019.02.004.

(15) Skrabalak, S. E. Symmetry in Seeded Metal Nanocrystal Growth. *Acc. Mater. Res.* **2021**, *2*, 621–629. https://doi.org/10.1021/accountsmr.1c00077.

(16) Lohse, S. E.; Murphy, C. J. The Quest for Shape Control: A History of Gold Nanorod Synthesis. *Chem. Mater.* **2013**, *25*, 1250–1261. https://doi.org/10.1021/cm303708p.

(17) Talukdar, B.; Mendiratta, S.; Huang, M. H.; Kuo, C.-H. Recent Advances in Bimetallic Cu-Based Nanocrystals for Electrocatalytic CO2 Conversion. *Chem. Asian J.* **2021**, *16*, 2168–2184. https://doi.org/10.1002/asia.202100583.

(18) Xiao, C.; Lu, B.-A.; Xue, P.; Tian, N.; Zhou, Z.-Y.; Lin, X.; Lin, W.-F.; Sun, S.-G. High-Index-Facet- and High-Surface-Energy Nanocrystals of Metals and Metal Oxides as Highly Efficient Catalysts. *Joule* **2020**, *4*, 2562–2598. https://doi.org/10.1016/j.joule.2020.10.002.

(19) Baek, W.; Chang, H.; Bootharaju, M. S.; Kim, J. H.; Park, S.; Hyeon, T. Recent Advances and Prospects in Colloidal Nanomaterials. *JACS Au* **2021**, *1*, 1849–1859. https://doi.org/10.1021/jacsau.1c00339.

(20) Hughes, R. A.; Menumerov, E.; Neretina, S. When Lithography Meets Self-Assembly: A Review of Recent Advances in the Directed Assembly of Complex Metal Nanostructures on Planar and Textured Surfaces. *Nanotechnology* **2017**, *28*, 282002. https://doi.org/10.1088/1361-6528/aa77ce.

(21) Zhang, H.; Kinnear, C.; Mulvaney, P. Fabrication of Single-Nanocrystal Arrays. *Adv. Mater.* **2020**, *32*, 1904551. https://doi.org/10.1002/adma.201904551.

(22) Neretina, S.; Hughes, R. A.; Gilroy, K. D.; Hajfathalian, M. Noble Metal Nanostructure Synthesis at the Liquid–Substrate Interface: New Structures, New Insights, and New Possibilities. *Acc. Chem. Res.* **2016**, *49*, 2243–2250. https://doi.org/10.1021/acs.accounts.6b00393.

(23) Beeram, S. R.; Zamborini, F. P. Purification of Gold Nanoplates Grown Directly on Surfaces for Enhanced Localized Surface Plasmon Resonance Biosensing. *ACS Nano* **2010**, *4*, 3633–3646. https://doi.org/10.1021/nn1007397.

(24) Ali Umar, A.; Oyama, M. Formation of Gold Nanoplates on Indium Tin Oxide Surface: Two-Dimensional Crystal Growth from Gold Nanoseed Particles in the Presence of Poly(Vinylpyrrolidone). *Cryst. Growth Des.* **2006**, *6*, 818–821. https://doi.org/10.1021/cg050548n.

(25) Umar, A. A.; Oyama, M.; Salleh, M. M.; Majlis, B. Y. Formation of High-Yield Gold Nanoplates on the Surface: Effective Two-Dimensional Crystal Growth of Nanoseed in the Presence of Poly(Vinylpyrrolidone) and Cetyltrimethylammonium Bromide. *Cryst. Growth Des.* **2009**, *9*, 2835–2840. https://doi.org/10.1021/cg900109x.

(26) Paul, A.; Kenens, B.; Hofkens, J.; Uji-i, H. Excitation Polarization Sensitivity of Plasmon-Mediated Silver Nanotriangle Growth on a Surface. *Langmuir* **2012**, *28*, 8920–8925. https://doi.org/10.1021/la300533h.

(27) Foss, C. A. Jr.; Tierney, M. J.; Martin, C. R. Template Synthesis of Infrared-Transparent Metal Microcylinders: Comparison of Optical Properties with the Predictions of Effective Medium Theory. *J. Phys. Chem.* **1992**, *96* , 9001–9007. https://doi.org/10.1021/j100201a057.

(28) Martin, C. R. Membrane-Based Synthesis of Nanomaterials. *Chem. Mater.* **1996**, *8*, 1739–1746. https://doi.org/10.1021/cm960166s.

(29) van der Zande, B. M. I.; Böhmer, M. R.; Fokkink, L. G. J.; Schönenberger, C. Aqueous Gold Sols of Rod-Shaped Particles. *J. Phys. Chem. B* **1997**, *101*, 852–854. https://doi.org/10.1021/jp963348i.

(30) Lee, W.; Park, S.-J. Porous Anodic Aluminum Oxide: Anodization and Templated Synthesis of Functional Nanostructures. *Chem. Rev.* **2014**, *114*, 7487–7556. https://doi.org/10.1021/cr500002z.

(31) Yu; Chang, S.-S.; Lee, C.-L.; Wang, C. R. C. Gold Nanorods: Electrochemical Synthesis and Optical Properties. *J. Phys. Chem. B* **1997**, *101*, 6661–6664. https://doi.org/10.1021/jp971656q.

(32) Chang, S.-S.; Shih, C.-W.; Chen, C.-D.; Lai, W.-C.; Wang, C. R. C. The Shape Transition of Gold Nanorods. *Langmuir* **1999**, *15*, 701–709. https://doi.org/10.1021/la980929l.

(33) McDarby, S. P.; Personick, M. L. Potential-Controlled (R)Evolution: Electrochemical Synthesis of Nanoparticles with Well-Defined Shapes. *ChemNanoMat* **2022**, *8*, e202100472. https://doi.org/10.1002/cnma.202100472.

(34) Xiao, J.; Liu, S.; Tian, N.; Zhou, Z.-Y.; Liu, H.-X.; Xu, B.-B.; Sun, S.-G. Synthesis of Convex Hexoctahedral Pt Micro/Nanocrystals with High-Index Facets and Electrochemistry-Mediated Shape Evolution. *J. Am. Chem. Soc.* **2013**, *135*, 18754–18757. https://doi.org/10.1021/ja410583b.

(35) Li, Y.-Y.; Liao, H.-G.; Rao, L.; Jiang, Y.-X.; Huang, R.; Zhang, B.-W.; He, C.-L.; Tian, N.; Sun, S.-G. Shape Evolution of Platinum Nanocrystals by Electrochemistry. *Electrochim. Acta* **2014**, *140*, 345–351. https://doi.org/10.1016/j.electacta.2014.04.147.

(36) Tian, N.; Zhou, Z.-Y.; Sun, S.-G.; Ding, Y.; Wang, Z. L. Synthesis of Tetrahexahedral Platinum Nanocrystals with High-Index Facets and High Electro-Oxidation Activity. *Science* **2007**, *316*, 732–735. https://doi.org/10.1126/science.1140484.

(37) Wei, L.; Lu, B.; Sun, M.; Tian, N.; Zhou, Z.; Xu, B.; Zhao, X.; Sun, S. Overpotential-Dependent Shape Evolution of Gold Nanocrystals Grown in a Deep Eutectic Solvent. *Nano Res.* **2016**, *9*, 3547–3557. https://doi.org/10.1007/s12274-016-1236-1.

(38) Mao, Y.-J.; Liu, F.; Chen, Y.-H.; Jiang, X.; Zhao, X.-S.; Sheng, T.; Ye, J.-Y.; Liao, H.-G.; Wei, L.; Sun, S.-G. Enhancing Electrocatalytic Nitrogen Reduction to Ammonia with Rare Earths (La, Y, and Sc) on High-Index Faceted Platinum Alloy Concave Nanocubes. *J. Mater. Chem. A* **2021**, *9*, 26277–26285. https://doi.org/10.1039/D1TA05515A.

(39) Zhang, J.; Langille, M. R.; Personick, M. L.; Zhang, K.; Li, S.; Mirkin, C. A. Concave Cubic Gold Nanocrystals with High-Index Facets. *J. Am. Chem. Soc.* **2010**, *132*, 14012–14014. https://doi.org/10.1021/ja106394k.

(40) Sneed, B. T.; Kuo, C.-H.; Brodsky, C. N.; Tsung, C.-K. Iodide-Mediated Control of Rhodium Epitaxial Growth on Well-Defined Noble Metal Nanocrystals: Synthesis, Characterization, and Structure-Dependent Catalytic Properties. *J. Am. Chem. Soc.* **2012**, *134*, 18417–18426. https://doi.org/10.1021/ja308030h.

(41) O'Brien, M. N.; Jones, M. R.; Brown, K. A.; Mirkin, C. A. Universal Noble Metal Nanoparticle Seeds Realized Through Iterative Reductive Growth and Oxidative Dissolution Reactions. *J. Am. Chem. Soc.* **2014**, *136*, 7603–7606. https://doi.org/10.1021/ja503509k.

(42) Weiner, R. G.; Kunz, M. R.; Skrabalak, S. E. Seeding a New Kind of Garden: Synthesis of Architecturally Defined Multimetallic Nanostructures by Seed-Mediated Co-Reduction. *Acc. Chem. Res.* **2015**, *48*, 2688–2695. https://doi.org/10.1021/acs.accounts.5b00300.

(43) King, M. E.; Personick, M. L. Bimetallic Nanoparticles with Exotic Facet Structures via Iodide-Assisted Reduction of Palladium. *Part. Part. Syst. Charact.* **2017**, *34*, 1600422. https://doi.org/10.1002/ppsc.201600422.

(44) King, M. E.; Personick, M. L. Iodide-Induced Differential Control of Metal Ion Reduction Rates: Synthesis of Terraced Palladium–Copper Nanoparticles with Dilute Bimetallic Surfaces. *J. Mater. Chem. A* **2018**, *6*, 22179–22188. https://doi.org/10.1039/C8TA06256K.

(45) Ghosh, S.; Manna, L. The Many "Facets" of Halide Ions in the Chemistry of Colloidal Inorganic Nanocrystals. *Chem. Rev.* **2018**, *118*, 7804–7864. https://doi.org/10.1021/acs.chemrev.8b00158.

(46) Lee, H.-E.; Ahn, H.-Y.; Mun, J.; Lee, Y. Y.; Kim, M.; Cho, N. H.; Chang, K.; Kim, W. S.; Rho, J.; Nam, K. T. Amino-Acid- and Peptide-Directed Synthesis of Chiral Plasmonic Gold Nanoparticles. *Nature* **2018**, *556*, 360–365. https://doi.org/10.1038/s41586-018-0034-1.

(47) King, M. E.; Kent, I. A.; Personick, M. L. Halide-Assisted Metal Ion Reduction: Emergent Effects of Dilute Chloride, Bromide, and Iodide in Nanoparticle Synthesis. *Nanoscale* **2019**, *11*, 15612–15621. https://doi.org/10.1039/C9NR04647J.

(48) Madasu, M.; Hsieh, P.-L.; Chen, Y.-J.; Huang, M. H. Formation of Silver Rhombic Dodecahedra, Octahedra, and Cubes through Pseudomorphic Conversion of Ag_2O Crystals with Nitroarene Reduction Activity. *ACS Appl. Mater. Interfaces* **2019**, *11*, 38039–38045. https://doi.org/10.1021/acsami.9b12344.

(49) Habib, A.; King, M. E.; Etemad, L. L.; Distler, M. E.; Morrissey, K. H.; Personick, M. L. Plasmon-Mediated Synthesis of Hybrid Silver–Platinum Nanostructures. *J. Phys. Chem. C* **2020**, *124*, 6853–6860. https://doi.org/10.1021/acs.jpcc.0c00918.

(50) Crane, C. C.; Manso, R. H.; Li, J.; Benamara, M.; Tao, J.; Zhu, Y.; Wang, F.; Chen, J. A Metal-on-Metal Growth Approach to Metal–Metal Oxide Core–Shell Nanostructures with Plasmonic Properties. *J. Phys. Chem. C* **2020**, *124*, 17191–17203. https://doi.org/10.1021/acs.jpcc.0c03226.

(51) Yang, T.-H.; Ahn, J.; Shi, S.; Wang, P.; Gao, R.; Qin, D. Noble-Metal Nanoframes and Their Catalytic Applications. *Chem. Rev.* **2021**, *121*, 796–833. https://doi.org/10.1021/acs.chemrev.0c00940.

(52) Argento, G. M.; Judd, D. R.; Etemad, L. L.; Bechard, M. M.; Personick, M. L. Plasmon-Mediated Reconfiguration of Twin Defect Structures in Silver Nanoparticles. *J. Phys. Chem. C* **2023**, *127*, 3890–3897. https://doi.org/10.1021/acs.jpcc.2c09062.

(53) Ahn, H.-Y.; Lee, H.-E.; Jin, K.; Nam, K. T. Extended Gold Nano-Morphology Diagram: Synthesis of Rhombic Dodecahedra Using CTAB and Ascorbic Acid. *J. Mater. Chem. C* **2013**, *1*, 6861–6868. https://doi.org/10.1039/C3TC31135J.

(54) Heuer-Jungemann, A.; Feliu, N.; Bakaimi, I.; Hamaly, M.; Alkilany, A.; Chakraborty, I.; Masood, A.; Casula, M. F.; Kostopoulou, A.; Oh, E.; Susumu, K.; Stewart, M. H.; Medintz, I. L.; Stratakis, E.; Parak, W. J.; Kanaras, A. G. The Role of Ligands in the Chemical Synthesis and Applications of Inorganic Nanoparticles. *Chem. Rev.* **2019**, *119*, 4819–4880. https://doi.org/10.1021/acs.chemrev.8b00733.

(55) González-Rubio, G.; Scarabelli, L.; Guerrero-Martínez, A.; Liz-Marzán, L. M. Surfactant-Assisted Symmetry Breaking in Colloidal Gold Nanocrystal Growth. *ChemNanoMat* **2020**, *6*, 698–707. https://doi.org/10.1002/cnma.201900754.

(56) Yang, T.-H.; Shi, Y.; Janssen, A.; Xia, Y. Surface Capping Agents and Their Roles in Shape-Controlled Synthesis of Colloidal Metal Nanocrystals. *Angew. Chem. Int. Ed.* **2020**, *59*, 15378–15401. https://doi.org/10.1002/anie.201911135.

(57) Song, T.; Gao, F.; Guo, S.; Zhang, Y.; Li, S.; You, H.; Du, Y. A Review of the Role and Mechanism of Surfactants in the Morphology Control of Metal Nanoparticles. *Nanoscale* **2021**, *13*, 3895–3910. https://doi.org/10.1039/D0NR07339C.

(58) Jharimune, S.; Pfukwa, R.; Chen, Z.; Anderson, J.; Klumperman, B.; Rioux, R. M. Chemical Identity of Poly(N-Vinylpyrrolidone) End Groups Impact Shape Evolution During the Synthesis of Ag Nanostructures. *J. Am. Chem. Soc.* **2021**, *143*, 184–195. https://doi.org/10.1021/jacs.0c08528.

(59) Siegfried, M. J.; Choi, K.-S. Electrochemical Crystallization of Cuprous Oxide with Systematic Shape Evolution. *Adv. Mater.* **2004**, *16*, 1743–1746. https://doi.org/10.1002/adma.200400177.

(60) Yang, T.-H.; Peng, H.-C.; Zhou, S.; Lee, C.-T.; Bao, S.; Lee, Y.-H.; Wu, J.-M.; Xia, Y. Toward a Quantitative Understanding of the Reduction Pathways of a Salt Precursor in the Synthesis of Metal Nanocrystals. *Nano Lett.* **2017**, *17*, 334–340. https://doi.org/10.1021/acs.nanolett.6b04151.

(61) Hauwiller, M. R.; Frechette, L. B.; Jones, M. R.; Ondry, J. C.; Rotskoff, G. M.; Geissler, P.; Alivisatos, A. P. Unraveling Kinetically-Driven Mechanisms of Gold Nanocrystal Shape Transformations Using Graphene Liquid Cell Electron Microscopy. *Nano Lett.* **2018**, *18*, 5731–5737. https://doi.org/10.1021/acs.nanolett.8b02337.

(62) Li, W.; Taylor, M. G.; Bayerl, D.; Mozaffari, S.; Dixit, M.; Ivanov, S.; Seifert, S.; Lee, B.; Shanaiah, N.; Lu, Y.; Kovarik, L.; Mpourmpakis, G.; Karim, A. M. Solvent Manipulation of

the Pre-Reduction Metal–Ligand Complex and Particle-Ligand Binding for Controlled Synthesis of Pd Nanoparticles. *Nanoscale* **2021**, *13*, 206–217. https://doi.org/10.1039/D0NR06078J.

(63) Liu, S.-Y.; Shen, Y.-T.; Chiu, C.-Y.; Rej, S.; Lin, P.-H.; Tsao, Y.-C.; Huang, M. H. Direct Synthesis of Palladium Nanocrystals in Aqueous Solution with Systematic Shape Evolution. *Langmuir* **2015**, *31*, 6538–6545. https://doi.org/10.1021/acs.langmuir.5b01337.

(64) Wang, C. J.; Shapiro, E. F.; Personick, M. L. Halide Ions on Metal Nanoparticles for Shape- and Composition-Controlled Synthesis. In *Surface Functionalization of Nanomaterials*; The Encyclopedia of Nanomaterials; Elsevier, 2022.

(65) Oh, H.; Park, Y.; Song, H. Tracking Underpotential Deposition of Copper on Individual Silver Nanocubes by Real-Time Single-Particle Plasmon Scattering Imaging. *J. Phys. Chem. C* **2020**, *124*, 20398–20409. https://doi.org/10.1021/acs.jpcc.0c05258.

(66) Brown, M.; Wiley, B. J. Bromide Causes Facet-Selective Atomic Addition in Gold Nanorod Syntheses. *Chem. Mater.* **2020**, *32*, 6410–6415. https://doi.org/10.1021/acs.chemmater.0c01494.

(67) Kim, M. J.; Cruz, M. A.; Chen, Z.; Xu, H.; Brown, M.; Fichthorn, K. A.; Wiley, B. J. Isotropic Iodide Adsorption Causes Anisotropic Growth of Copper Microplates. *Chem. Mater.* **2021**, *33*, 881–891. https://doi.org/10.1021/acs.chemmater.0c03596.

(68) Xu, H.; Wiley, B. J. The Roles of Citrate and Defects in the Anisotropic Growth of Ag Nanostructures. *Chem. Mater.* **2021**, *33*, 8301–8311. https://doi.org/10.1021/acs.chemmater.1c02474.

Conspectus Graphic