

**PRF #57708-DNI10: Tailored Bimetallic Catalysts with Highly Stepped Facets for Selective and Energy-Efficient Epoxidation and Hydrogenation Reactions**

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**Overview**

The aims of the funded work are (1) to develop design parameters for the solution-phase synthesis of shaped palladium and platinum nanoparticles with dilute surface coverages of a secondary metal and (2) to systematically evaluate the reactivity of these bimetallic catalysts as a function of their surface composition and structure in important chemical transformations. Overall, the goal is to enable the tailored fabrication of new catalytic materials and to define structure-activity relationships for dilute bimetallic nanomaterials with controlled facets. Research efforts during year two of the award continued to focus on designing syntheses for shaped noble metal nanoparticles composed primarily of one metal with a dilute coverage of a second metal. Toward the end of year 1, our work on the synthesis of these dilute bimetallic nanoparticles yielded terraced palladium-copper nanostructures through control of the relative rates of reduction of two different metal ion precursors in a single-pot synthesis. This differential control of metal ion reduction rate was provided by the deliberate incorporation of low micromolar concentrations of iodide ions. In year two, we further developed this halide-assisted metal ion reduction technique with an emphasis on understanding the mechanism and materials scope of this process. The goal of this work was to elucidate generalizable design parameters for tailorable dilute bimetallic catalysts moving forward.

**Control of Metal Ion Reduction in Complex Bimetallic Systems**

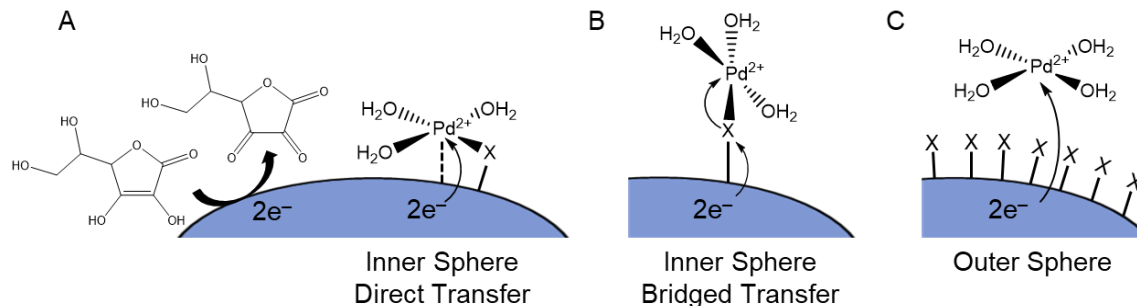
To understand the emergent effects of micromolar concentrations of halide ions in metal nanoparticle synthesis without convoluting halide contributions present in typical aqueous based particle growth solutions (most often from halide counterions present in cetyltrimethylammonium surfactants), we employed a halide-free analogue to these common synthetic protocols. Palladium nanoparticles were grown in the presence of a halide-free surfactant, cetyltrimethylammonium hydrogen sulfate (CTA- $\text{HSO}_4^-$ ), starting from the halide-free metal salt precursor palladium nitrate. Monitoring of nanoparticle growth over time via inductively coupled plasma mass spectrometry (ICP-MS) showed that not only iodide, but also chloride and bromide, may be used to accelerate metal ion reduction when added to the nanoparticle growth solution in micromolar concentrations. The magnitude of this rate enhancing effect correlates with the binding affinity of each halide for palladium ( $\text{Cl}^- < \text{Br}^- < \text{I}^-$ ), and with increased binding affinity less halide is required to achieve a comparable enhancement of metal ion reduction rate (Figure 1). We propose that these low concentrations of halides facilitate inner sphere electron transfer by assisting binding of the palladium precursor to the nanoparticle surface, where it is reduced by electrons from the reducing agent, ascorbic acid (Figure 2).

A	Cl <sup>-</sup> : Pd <sup>2+</sup>	Average Rate of Pd <sup>2+</sup> Reduction <sup>a</sup> (ppm/min)	Change in Rate <sup>b</sup> (relative to Pd-only control)
	Pd Only	1.4	–
	1:10	5.6	4.0 x
	1:1	17.0	12.1 x
	2:1	11.7	8.4 x
	3:1	8.2	5.9 x
	4:1	0.65	0.5 x
	16:1	0.54	0.4 x

B	Br <sup>-</sup> : Pd <sup>2+</sup>	Average Rate of Pd <sup>2+</sup> Reduction <sup>a</sup> (ppm/min)	Change in Rate <sup>b</sup> (relative to Pd-only control)
	Pd Only	1.4	–
	1:100	3.7	1.9 x
	1:20	5.8	4.1 x
	1:10	9.0	6.4 x
	1:1	7.0	5 x
	2:1	4.3	3.1 x
	3:1	1.4	–

C	I <sup>-</sup> : Pd <sup>2+</sup>	Average Rate of Pd <sup>2+</sup> Reduction <sup>a</sup> (ppm/min)	Change in Rate <sup>b</sup> (relative to Pd-only control)
	Pd Only	1.4	–
	1:1000	3.0	2.1 x
	1:250	5.2	3.7 x
	1:100	5.4	3.9 x
	1:25	0.2	0.14 x
	1:10	0.1	0.07 x

**Figure 1.** Tables showing the effect of added halide ions on the rate of palladium ion reduction: (A) chloride ions; (B) bromide ions; and (C) iodide ions. Conditions that lead to a four-fold enhancement of palladium ion reduction rate are highlighted for each halide to show that lower concentrations of stronger binding halides are required to achieve the same degree of rate enhancement. At higher halide concentrations, surface passivation leads to the classically observed slowing of palladium ion reduction. <sup>a</sup> Initial rate of Pd<sup>2+</sup> reduction is calculated as the increase in the amount of palladium incorporated into nanoparticles from zero to two minutes of growth (slope of the data in Figure 1), as measured by ICP-MS. <sup>b</sup> Ratio of the observed initial rate for a given condition to rate observed for the Pd-only control.



**Figure 2.** Schematic representation of possible electron transfer pathways for the reduction of palladium ions onto a growing metal nanoparticle. (A) Direct inner sphere electron transfer from the surface where the adsorption of the palladium complex is facilitated by coordination with a surface-bound halide. (B) Inner sphere electron transfer via a halide bridging ligand. (C) Outer sphere electron transfer, which is followed by halide displacement for metal atom adsorption. Control experiments and the decrease in reduction rate at millimolar halide concentrations (ie. at high surface coverages of halide) support mechanism (A) as the origin of halide-assisted metal ion reduction. In addition, calculations of solution speciation of palladium suggest minimal to no formation of metal-halide complexes at the conditions where rate enhancement is observed, suggestion that the origin of the halide-induced rate enhancement is localized at the particle surface rather than in solution.

Importantly, this halide-assisted metal ion reduction effect is fundamentally different from what is widely observed in the literature when even slightly higher (micromolar) concentrations of halide ions are used in metal nanoparticle synthesis, where the addition of halide ions slows metal ion reduction due to surface passivation or modification of the metal precursor's reduction potential. Moreover, this halide-assisted metal ion reduction approach can be used to selectively tune reduction kinetics in growth solutions containing not only palladium but also other metal combinations such as gold and palladium, palladium and copper, and gold and silver. These findings suggest that halide ions can be employed more broadly in one-pot syntheses containing multiple metals to yield particles with desired compositions and morphologies for selective catalysis.

## Impact

Over the past year, funding from the ACS PRF has supported the scientific training of many students in the PI's lab, both directly through stipend support and indirectly through supply funds. At the graduate level, the grant directly supported one Ph.D. student, who has successfully defended her thesis and will graduate in October. In addition, during this past year, two undergraduates worked on the project supported by supply funding from the grant. These students worked for course credit during the school year, and were supported by university fellowships during the summer. One of the two undergraduates completed a senior honors thesis in the PI's lab, and the other intends to do so this year. This year, funding from the award also supported a stipend for a high school summer intern from Middletown High School, who carried out research full time from mid-June to late August. The high school student was mentored by senior lab members and participated in the same summer science programing that Wesleyan offers for its undergraduate students. Last fall, the PI and a previously-supported undergraduate received honorable mention for the ACS Division of Inorganic Chemistry Award for Undergraduate Research (R1 division) for their work as a student-preceptor team on the PRF-funded research. The same undergraduate was recently the lead author on a perspective article in *Chemistry of Materials* co-written with the PI. Another previously supported undergraduate wrote a mini review for *Current Opinion in Colloid and Interface Science* as co-first author with the supported graduate student. The PRF award has enabled the PI to present her research at the American Chemical Society National Meeting this past spring, as well as in multiple invited departmental seminars. Data from this project provided preliminary results for a NSF CAREER proposal submitted this past summer.