SPP10 Template
The light stuff: enabling sustainable chemical manufacturing with atomically-optimized photocatalysts

Jennifer Dionne[1], **Briley Bourgeois, Lin Yuan, Claire Carlin, Alan Dai**

1. Stanford University, Department of Materials Science and Engineering

E-mail: jdionne@stanford.edu

Chemical manufacturing is critical for industries spanning construction, plastics, pharmaceuticals, food, and fertilizers, yet remains among the most energy-demanding practices. Optical excitation of plasmons offers a route to more sustainable chemical synthesis. Plasmons create nanoscopic regions of high electromagnetic field intensity that can modify electronic and molecular energy levels, enable access to excited-state dynamics, and open new reaction pathways that are impossible to achieve under typical conditions. Further, plasmons can be efficiently excited with sunlight or solar-driven LEDs, for sustainable chemical transformations.

Here, we present our research advancing plasmon photocatalysis from the atomic to the reactor scale (see Figure 1). First, we describe advances in in-situ atomic-scale catalyst characterization, using environmental optically-coupled transmission electron microscopy. With both light and reactive gases introduced into the column of an electron microscope, we can monitor chemical transformations under various illumination conditions, gaseous environments, and at controlled temperatures, correlating three-dimensional atomic-scale catalyst structure with photo-chemical reactivity. Then, we describe how these atomic-scale insights enable optimized reactor-scale performance. As model systems, we consider three reactions: 1) acetylene hydrogenation with Ag-Pd catalysts; 2) CO2 reduction with Au-Pd catalysts; and 3) nitrogen fixation with AuRu catalysts. Here, Au/Ag acts as a strong plasmonic light absorber while Pd/Ru serves as the catalyst. We find that plasmons modify the rate of distinct reaction steps differently and that reaction nucleation occurs at electromagnetic hot-spots – even when those hot-spots do not occur in the preferred nucleation site. Plasmons also open new reaction pathways that are not observed without illumination, enabling both high-efficiency and selective catalysis with tuned bimetallic catalyst composition. Our results provide a roadmap for how atomically-architected photocatalysts can precisely control molecular interactions for high-efficiency and product-selective chemistry.

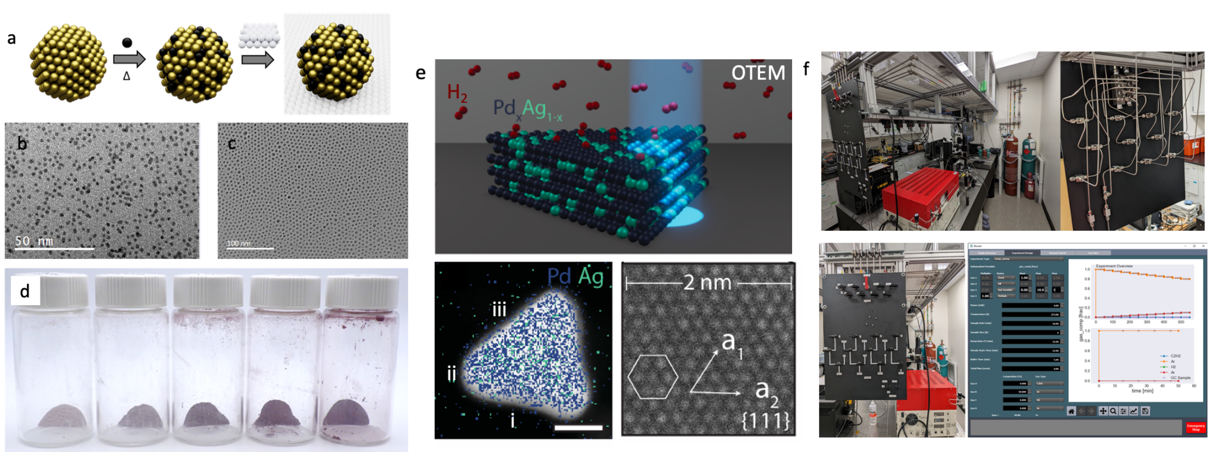

Fig. 1 a) Synthesis of monodisperse, bimetallic alloys for plasmon catalysis. b,c) Example electron micrographs of AuPd nanoparticles with controlled composition. d) Alloyed AuPd nanoparticles on a Al_2O_3 substrate, with varying weight concentration. e) In-situ transmission electron microscopy to probe plasmonic processes like H_2 and D_2 intercalation, and oxidation at the atomic scale. f) Photos of our lab's home-built bench-scale ensemble, and screen-shot of our open-source reactor software.