

## ***In situ* Visualization of Plasmon-Mediated Chemical Transformations at the Single and Sub-particle Level**

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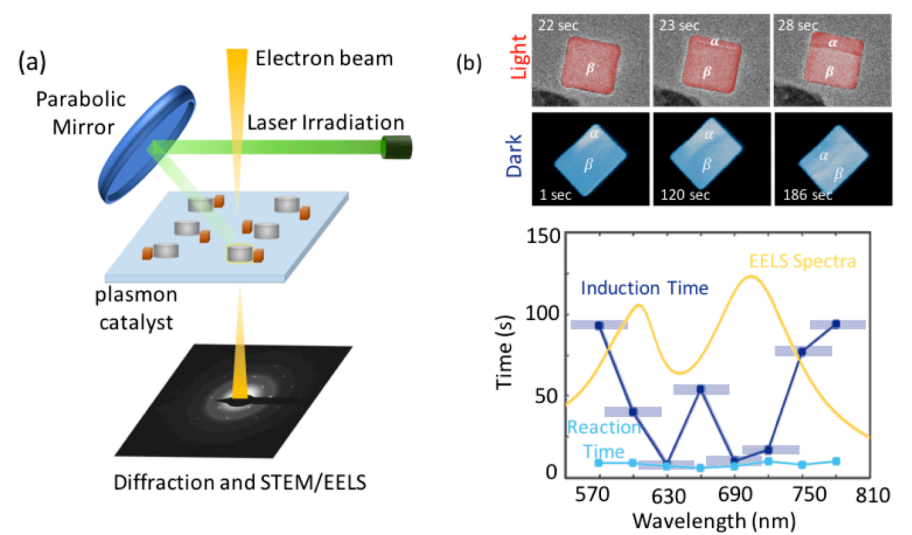
Photocatalysts are integral to many processes underpinning environmental and energy sustainability, including artificial photosynthesis, organic pollutant degradation, and water purification. These processes rely on nanostructured materials in which photoexcited carriers power the relevant chemical transformations. Traditional semiconducting photocatalysts as well as metal complexes and clusters have proven invaluable in industry, but generally suffer from low efficiency due to their limited optical absorption and their short electron-hole pair recombination times. Plasmonic particles have recently emerged as promising complements to traditional photocatalysts, either on their own or as co-catalysts.[1-5] These plasmonic particles possess a number of useful features for photocatalysis, including optical near-field enhancement, local heat generation, and efficient hot carrier generation, which can be exploited to control and enhance photocatalytic reactions. However, the understanding of plasmon catalysts is often limited to ensemble measurements, in which nanoparticle heterogeneity conceals many important and interesting structure-dependent catalytic properties. Further, many studies lack the nanometer-scale spatial resolution to help elucidate the role of plasmons in photocatalytic reactions.

Here, we present methods to visualize plasmon-induced chemical transformations at the single and sub-particle level *in situ*. As a model reaction, we study the gas-phase photocatalytic dehydrogenation of Au-Pd antenna-reactor systems, in which the Au particle acts as a plasmonic light absorber and Pd serves as the catalyst. Under controlled hydrogen pressures, temperatures, and optical illumination conditions in an environmental transmission electron microscope, we study the kinetics of the desorption reaction triggered by the optical excitation of plasmons. Upon illumination, the system is pushed out of equilibrium, resulting in a Pd phase change from the hydrogen-rich  $\beta$  phase to the hydrogen-dilute  $\alpha$  phase. We monitor these changes using a combination of single particle electron diffraction, electron energy loss spectroscopy, and direct imaging. Our *in situ* approach allows us to investigate the wavelength, power, and polarization dependence with  $\sim 2$  nm spatial resolution and millisecond time resolution.

We observe two main reaction steps in the dehydrogenation transformation and show that plasmons enhance the reaction rate of these steps in distinct ways, with a more than ten-fold increase in total rate compared to the dark reaction. Additionally, we find that plasmons enable a new phase transformation mechanism, namely edge nucleation, that is never observed without illumination; in the dark, the new phase always nucleates from the lowest-coordination-number sites. We also show that phase nucleation occurs more often at electromagnetic hot-spots, demonstrating the contribution of plasmons to site-selectivity. Our results help elucidate the role of plasmons in light-driven phase transformations, en route to design of site-selective and product-specific photocatalysts.

## References:

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**Figure 1.** Visualizing plasmon photocatalysis with optical illumination in a TEM. (a) Experimental schematic. (b) Real-time STEM snapshots (top) and wavelength dependence (bottom) of the dehydrogenation reaction upon illumination and in the dark, suggesting distinct kinetics and reaction mechanisms.