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The Light Years: Combined optical and environmental electron microscopy to visualize photonic processes with atomic-scale resolution

Jennifer A. Dionne[1], Fariah Hayee[2], Michal Vadai[1], Daniel Angell[1], Amr Saleh[2], and Katherine Sytwu[3]

[1.] Department of Materials Science and Engineering, Stanford University, Stanford, CA USA
[2.] Department of Electrical Engineering, Stanford University, Stanford, CA USA
[3.] Department of Applied Physics, Stanford University, Stanford, CA USA

Pearl Jam's hit, "The Light Years," declares "We were but stones, light made us stars." Bringing light to the transmission electron microscope (TEM) promises to transform our understanding of materials, enabling both direct observation of light-mediated processes and detection of optical emission with atomic scale resolution. To help achieve this goal, my lab is developing capabilities for concurrent optical and electron microscopy within an environmental TEM. This presentation will describe our efforts to visualize a variety of photochemical processes *in situ* with nanometer-to-atomic scale resolution. We focus in particular on i) observing photocatalytic phase transitions in nanoparticles; ii) detecting quantum light emission from two-dimensional materials; and iii) developing TEM-Raman with nanometer-scale resolution.

First, we present methods to visualize plasmon-induced chemical transformations with sub-2nm spatial resolution. Our goal is to help unravel the means by which plasmons mediate and control the local chemistry, and ultimately, use that knowledge to optimize catalyst performance. As a model reaction, we study the gas-phase photocatalytic dehydrogenation of Au-Pd systems, in which the Au acts as a plasmonic light absorber and Pd serves as the catalyst. Under controlled hydrogen pressures, temperatures, and illumination conditions, we study the study the kinetics of the desorption reaction triggered by the optical excitation of plasmons. We find that plasmons control photochemistry in three ways. First, plasmons modify the rate of distinct reaction steps differently, increasing the overall rate more than ten-fold. Secondly, plasmons open a new reaction pathway that is not observed without illumination. Finally, reaction nucleation occurs more often at electromagnetic hot-spots. Our results help elucidate the role of plasmons in light-driven phase transformations, en-route to design of site-selective and product-specific photocatalysts [1-3].

Secondly, we use scanning transmission electron microscopy and cathodoluminescence spectroscopy to investigate color centers in two-dimensional hexagonal boron nitride, a wide bandgap material capable of room-temperature, high-brightness visible quantum emission. Through high resolution transmission electron imaging, we find that multiple emitters are located within a diffraction-limited spot, each contributing to the observed quantum emission. The emitters are located in regions with multiple fork-like dislocations. Additionally, local strain maps indicate that strain is not responsible for the observed broad spectral range, though it can enable spectral tuning of particular emitters. These results highlight the sensitivity of defect-driven quantum emission to the surrounding crystallography, providing a foundation for atomic-scale optical characterization.[2]

Finally, we describe a new technique for high-resolution spectroscopy in the TEM: electron-and-light-induced stimulated Raman scattering (ELISR). Unlike conventional stimulated Raman measurements, our technique uses a laser source as the pump and the electron beam as the broadband Stokes excitation. Particularly, we leverage the electron beam as a highly-localized Angstrom-scale source to locally excite the plasmonic resonances of individual nanoparticles. The resonant wavelength of the nanoparticles is tuned such that it is red-shifted from the pump laser to resemble the Stokes excitation when excited with

the electron beam. Accordingly, the Raman scattering is locally enhanced by the electron beam and the spatial resolution is determined by the electron beam spot size and the nanoparticle size.[5]

Combined, our studies show how light in the TEM can illuminate dynamic nanoscale processes spanning energy, quantum information, and biology.

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