1. PRF # 57029-DNI10
2. Project title: Nanoscale monitoring of noble metal catalyst sulfidation using plasmonic nanostructures
3. PI: Vivian E. Ferry, University of Minnesota

Project Background. The objectives of this project are to synthesize nanocrystal heterostructures consisting of a plasmonic nanocrystal (Au) and a catalytic nanocrystal (Pd), and to characterize the optical properties of these heterostructures. Pd nanocubes are widely used in catalytic applications, but can exhibit size and shape dependent properties. During hydrogenation reactions, Pd reacts to form palladium hydride, which is accompanied by a change in refractive index of the nanoparticle. This project aims to detect chemical changes in the Pd nanostructures based on the spectral changes in a nearby plasmonic nanocrystal. The plasmonic nanocrystal must be isolated from the chemical reaction, but also be sufficiently close to detect chemical changes. The goals are to prepare these combinations of Pd nanocrystals and plasmonic nanocrystals using self-assembly, to understand the optical properties of the assemblies using electromagnetic simulation, and to characterize the assemblies using single particle dark field spectroscopy.

Summary of Results.

1. Electromagnetic simulations on Au-Ag alloy nanoparticles

Part of the goal of this project is to design plasmonic nanocrystals that show large spectral changes in response to refractive index variations, using nanoshells tuned to the near-IR. We performed several electromagnetic simulations on gold nanoshells to study the influence of shell thickness, shape (cubes with rounded corners), and alloy composition. Rather than consisting of pure Au, these nanoshells are experimentally synthesized from Ag nanocubes with a galvanic replacement reaction that produces a Ag-Au alloy.

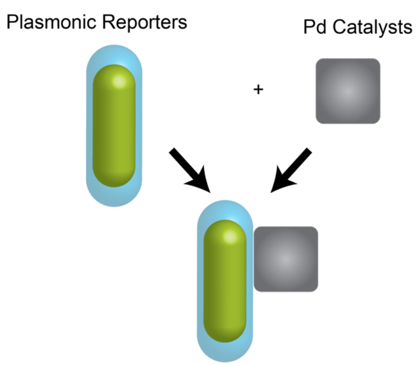

Figure 1. Schematic overview of one heterostructure, combining a silica-coated Au nanorod and a Pd nanocube. Chemical changes in the Pd nanocube are detected through shifts of the localized surface plasmon resonance of the Au nanorod.

The simulations revealed several important characteristics of this system. First, we studied the resonance of shells as the alloy composition changed from pure Ag to pure Au. For a single size of nanocrystal, increasing the fraction of Ag in the alloy leads to a blue shifted and broadened resonance compared to pure Au. As expected, decreasing the thickness of the shell leads to a substantial red shift (Fig. 2(a)). We also found that the degree of curvature on the corners of the cube had a significant effect on the resonance; Fig. 2(b) shows calculations performed for the same diameter nanoparticle, for the transformation from a sphere to a cube with varying degrees of rounding at the edges. The cube exhibits a red-shifted resonance compared to the sphere. We also show results below for the ratio of the scattering cross section to the extinction cross section (scattering + absorption) for these nanocrystals. To detect these structures using dark field spectroscopy, we will need structures that show significant scattering cross sections for the incident power on the sample. The structures that have the thinnest shells will be challenging to measure in this way, as the fraction of the total extinction that goes into scattering is higher for larger particles with thicker shells.

2. Self-assembly of Au nanorods and Pd nanocubes

Much of our work this year has been devoted to preparing self-assembled heterostructures. We synthesize Au nanorods with tunable localized surface plasmon resonance wavelengths, targeting structures that are resonant in the near infrared. We then coat the Au nanorods in a thin layer of silica to serve as the passivation layer. Pd nanocubes are synthesized separately, and the ligand compositions of each nanostructure tuned to facilitate electrostatic assembly. However, successful assembly requires careful manipulation of the self-assembly conditions. Most recently we have worked to understand the conditions under which electrostatic self-assembly will occur, as monitored with UV-Vis spectroscopy, by varying concentrations of each type of nanocrystal as well as the surrounding ligands.

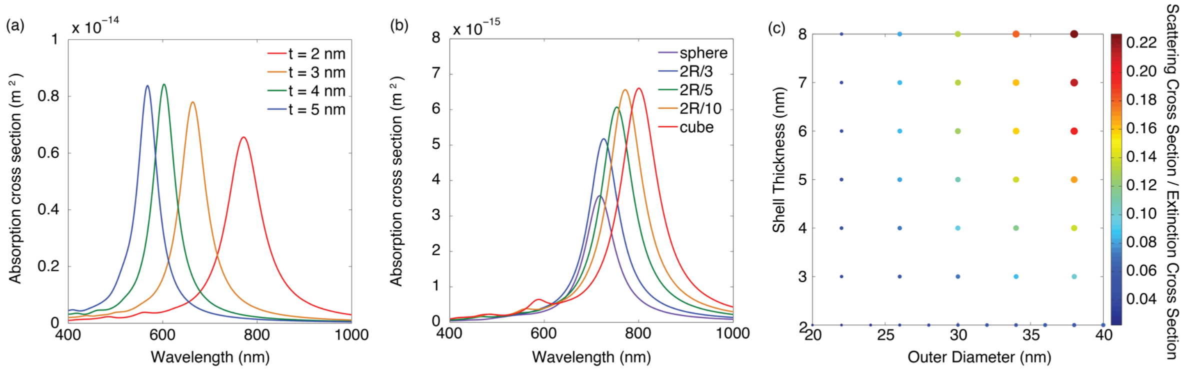

Figure 2. Electromagnetic simulations on hollow Au-Ag alloy nanoshell structures with 30 nm diameter. (a) As the thickness of the walls decreases, the resonance red shifts. (b) Calculated absorption cross sections for a constant shell thickness of 2 nm, with varying sharpness of the cube edge. (c) Calculated ratio of the scattering cross section to the total extinction cross section for various outer diameters and shell thicknesses. Larger particles and thicker shells exhibit more significant scattering, but all the hollow Au nanostructures studied have more absorption than scattering.

3. Characterization methods

To characterize the optical properties of these self-assembled heterostructures, we use both ensemble and single particle spectroscopy. Ensemble measurements are performed on a UV-Vis spectrometer, and can assess both the properties in solution and structures deposited on a substrate. We have also performed single particle dark field spectroscopy on the structures to study variations between particles without averaging by the ensemble. While we can take standard single particle dark field spectra using a white light source and dispersing the collected signal through a monochromator and onto a camera, we have particularly focused on constructing a hyperspectral dark field measurement setup where the incident wavelengths are changed and an image of the sample is recorded, thereby recording the spectra from many particles simultaneously. This year we have modified the hyperspectral dark field setup to allow for a broader range of incident wavelengths.

Impact on Career

The ACS DNI has been very important for helping to establish the PI's laboratory. Funds from the award have primarily been used to support graduate and undergraduate researchers, and have enabled the laboratory to develop synthetic and characterization capabilities that are critical for additional funding. These capabilities have enabled us to receive MRSEC SEED funding on the ultrafast response of Au nanostructures, among others.

Impact on Students/Education

Throughout 2018, two students have worked on this project. The first year graduate student supported by this project acquired fundamental training in optical characterization, which is critical for the rest of his PhD. The senior undergraduate who was supported by this project throughout Summer 2018 led the synthetic efforts on nanocrystals and the self-assembly experiments. This student plans to apply to graduate school in Chemical Engineering or Materials Science this year. This project has allowed him to give presentations at several undergraduate meetings, including the AICHE national meeting in 2017, the Winchell Undergraduate Research Symposium, the Undergraduate Research Symposium at the University of Minnesota, and he will be submitting an abstract to present additional work at the AICHE national meeting in 2018.