CMET/CNS Seminar

UNIVERSITY OF DELAWARE

Zachary Farrell

Ph.D. Student, Chemical Engineering

University of Virginia

DATE:
August 12, 2015
TIME:
11:00
LOCATION:
366 CLB

"Metallic Nanoparticles with Phase-Separated Ligand Monolayers: Theory, Synthesis, and Characterization"

Noble metal nanoparticles with phase separated ligand monolayers are materials of great interest for medical, research, and industrial applications as they possess unique optoelectronic properties and are easily functionalized. The structure formed by the adsorbed ligands is the self-assembled monolayer (SAM), which dictates interactions between the nanoparticle and its surroundings. SAMs may be composed of more than one ligand (mixed SAM), where ligand interactions can lead to degrees of ligand phase separation. Complex SAM patterns have been observed, including striped, patchy, and hemispherically (Janus) phase-separated. For nanoparticles with phase-separated ligand monolayers, ligand patterning influences final properties as much as actual ligand composition. It is therefore imperative that ligand pattern determination be possible for a given material in order to make connections between nanoparticle structure and bulk material properties. It is the goal of this research to provide new techniques for mixed SAM nanoparticle synthesis and characterization.

As there were no mechanistic one-phase literature methods for production of alkanethiol-functionalized silver nanoparticles, we utilized Derjaguin-Landau-Verwey-Overbeek theory with a classical nucleation model to examine nanoparticle formation mechanisms. Our approach was based on the aggregative growth model of Dr. Charles Zukoski, which provided an insight that separation of timescales between nucleation and growth should permit functionalization of nanoparticles at early reaction times, arresting their growth. This permitted us to develop of a mechanistic, one-phase synthesis for dodecanethiol silver nanoparticles. Additionally, we demonstrated that this synthesis is viable for a range of mixed and homogenous SAM alkanethiol-functionalized silver and gold nanoparticles.

To quantify ligand phase-separation, we utilized matrix-assisted laser desorption ionization mass spectrometry (MALDI). Silver nanoparticles with mixed-ligand monolayers, when analyzed with MALDI, form characteristic nanoparticle fragments which retain a memory of their nearest neighbor distribution from the nanoparticle surface. Comparing statistics of ligand fragment frequency from MALDI with expected random distributions permitted determination of degree of ligand phase-separation for a given nanoparticle system. We found good agreement between MALDI experiments and the predicted spectra from self-consistent mean-field simulation, indicating that MALDI is useful for quantification of ligand phase-separation.

The lack of ligand phase-separation visualization techniques available led us to pioneer the use of energy-filtered transmission electron microscopy (EFTEM) for mapping of oxygen-containing ligand locations on a nanoparticle. Silver nanoparticles functionalized with a mixture of dodecanethiol and 2-mercaptoethanol were synthesized and analyzed with EFTEM. The images produced show Janus particle morphologies with oxygen on one nanoparticle hemisphere, as we would expect for a Janus morphology. These results were corroborated with MALDI analysis which also indicated a Janus phase-separated ligand monolayer.

Overall, our studies have contributed significantly to both the synthetic and characterization techniques available in this area. As nanoparticles with mixed-ligand monolayers gain wider use in both research and industrial settings, we anticipate these results finding utility with anyone interested in their production and application.