

# CBE Fall 2022 Seminar Series

## Surface Science of Shape-Selective Metal Nanocrystal Synthesis from First-Principles

**Monday,  
November 28, 2022  
10:30 AM  
EB1 1011**



**Dr. Kristen Fichthorn**

**Penn State University**

***Host: Professors Hall,  
Santiso and Westmoreland***

Refreshments will be served  
from 11:40-12:00 in  
EB1 2014 (Student Lounge)

A significant challenge in the development of functional nanomaterials is understanding the growth and transformations of colloidal metal nanocrystals. Despite the tremendous strides made in nanocrystal synthesis science, it is still difficult to achieve high, selective yields in most synthesis protocols. Many aspects of these complex syntheses remain poorly understood and fundamental studies can be beneficial. Since the shapes of metal nanocrystals are largely governed by phenomena occurring at their surfaces, studies based on principles in surface science are useful.

I will discuss our efforts to understand the growth of Cu and Ag nanocrystals through a multi-scale approach. Using first-principles density-functional theory (DFT), we confirm experimental hypotheses that several commonly used capping molecules, such as PVP and various alkylamines, could facilitate nanoshape formation through their selective binding to particular crystal facets. To scale our calculations to the solution phase, we develop a metal-organic many-body force field with high fidelity to DFT. Using the example of the PVP-mediated growth of Ag nanocubes, we employ molecular-dynamics simulations to predict both thermodynamic and kinetic Wulff shapes of Ag crystals. These studies indicate that the relatively large (100 nm) cubic nanoshapes grown in experiments are kinetic in origin and can originate from differences in the Ag flux to different crystal facets. Fivefold-twinned Ag nanowires can also be grown in solution with PVP. Our calculations with absorbing Markov chains indicate that Ag nanowires with high aspect ratios, comparable to experiment, arise from surface diffusion. On the other hand, a synergistic interaction between adsorbed chloride and capping molecules leads to a higher flux of solution-phase cuprous ions to the ends of Cu nanowires and promotes their growth. We also find that surface diffusion can play a significant role in producing chlorine-covered Cu nanowires with high aspect ratios.

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