

The Multi-Faceted Nature of Crystal Growth

Kristen Fichthorn

Departments of Chemical Engineering and Physics, The Pennsylvania State University, 37
Greenberg Complex, University Park, PA, 16802, USA

Email: fichthorn@psu.edu

Achieving the controlled synthesis of colloidal nanomaterials with selected shapes and sizes is an important goal for a variety of applications that can exploit their unique properties (e.g., optical, catalytic, magnetic, etc.). In the past decade, a number of promising solution-phase synthesis techniques have been developed to fabricate various nanostructures. A deep, fundamental understanding of the phenomena that promote selective growth and assembly in these syntheses would enable tight control of nanostructure morphologies in next-generation techniques. I will present several aspects of our efforts to understand how shape-selective growth occurs in these syntheses.

First, I will discuss how PVP, a structure-directing polymer, facilitates the formation of {100}-faceted Ag nanocubes. In these studies, we use first-principles density-functional theory (DFT) to characterize the binding of PVP repeat units to Ag(100) and Ag(111) surfaces. These studies indicate a binding preference of PVP to Ag(100) that is consistent with experimental observations. To understand the solution-phase binding of PVP to these Ag surfaces, we develop a new metal-organic many-body (MOMB) force field with high fidelity to DFT. We implement this force field in molecular-dynamics (MD) simulations to characterize the potential of mean force and the mean first-passage times for solution-phase Ag atoms to reach PVP covered Ag facets. Using these mean first-passage times, we predict kinetic Wulff shapes of large Ag nanocrystals (around 100 nm) and show that these should be {100}-faceted cubes. We also use MD simulations to characterize the interfacial free energies of PVP-covered Ag facets in solution. The thermodynamic Wulff shapes that we predict in these calculations exhibit {111} facets. These findings are consistent with experimental observations that sufficiently small Ag nanocrystals with sizes ≤ 20 nm are not {100}-faceted and larger nanocrystals become {100}-faceted in the presence of PVP.

In experimental studies, Cl⁻ is often added in the synthesis of Ag nanocubes to achieve “pointy” corners. We use *ab initio* thermodynamics to characterize the surface energies of various Cl covered surfaces as a function of the solution-phase Cl⁻ chemical potential. Our studies indicate that Cl adsorption can enhance the thermodynamic tendency for {100}-faceted Ag nanocubes, in agreement with our experimental collaborators.