Chemical Engineering

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Understanding and Controlling Key Driving Forces in Nanomaterials Growth and Assembly

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3:00pm, 66-110
or via Livestream (link to be sent day of seminar)

ABSTRACT: Metal and semiconductor nanomaterials hold great promise for cutting-edge applications such as high-performance electronics, photovoltaics, bio-sensing and imaging, and their functions can be finely controlled by tailoring the sizes, shapes, and patterns of assembly. Central to morphology control are surface-binding molecules or ligands, which serve as structure-directing agents (SDAs). These molecules can be found in various forms, such as ions, polymers, and biomolecules, and often exhibit a facet-dependent or solution-dependent binding behavior. To date, much of the success in optimization for precise control of nanomaterial properties has been empirical and driven by Edisonian approaches. Significant advances in the field could be realized by discovering the fundamental nanoscale interactions that govern how the ligands guide shape evolution or join particles. Computer simulations can be useful to achieve this, given their ideal spatiotemporal resolution and capability to reveal complex phenomena. However, the ubiquitous presence of rare events often prevents the direct application of black-box simulation methods. This talk presents recent advances in both the simulation methodologies as well as their use in complex real-world problems in nanomaterials science.

First, I will discuss new ways to deconvolute the role of SDAs in the polyvinylpyrrolidone (PVP)-mediated growth of Ag nanocrystals. Despite their drastically different morphology, both Ag nanocubes and nanowires can be synthesized with the aid of PVP. By combining statistical mechanics theory and all-atom molecular dynamics (MD) simulations, we find that it requires a strong preference to a specific facet to induce a new equilibrium shape, and the moderate selectivity from PVP assist the formation of nanocubes by regulating the deposition fluxes through a two-step "capture-trap" mechanism. The highly anisotropic growth of Ag nanowires, however, is beyond the regulation capability of PVP. Ag nanowires are five-fold twinned structures that bear significant internal strain. We show such internal strain introduces notches on the twin edges along the growth axis and induces patched aggregation on the end facets. Interestingly, these notches serve as "super-highways" to quickly channel surface atoms towards the two ends, and the patched aggregation stabilizes these atoms once they are adsorbed by the ends to grow the length.

I will then discuss an interesting pH-dependent reversible self-assembly system driven by binding of biomolecules to inorganic nanoparticles. We reveal that the origins of the reversibility emerge from a delicate interplay between long-range and short-range interactions. To understand reversible self-assembly of green fluorescent protein (GFP)-silica nanoparticles, we construct a multi-scale computational framework by coupling the long-range forces calculated from colloidal theory and short-range molecular interactions obtained from all-atom simulations and enhanced sampling into a single coarse-grained (CG) model. The different levels of theory in the framework allow us to identify the molecular driving force while predicting the aggregation behavior. Our model successfully predicts assembly under various solution conditions and is informative to guide rational design because the interactions used in the CG model are directly related to tunable properties in the system and can be inferred from MD.