

Harnessing Chemical Transformation Reactions to Tailor the Atoms in Nanoparticles

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Our research group works to gain a fundamental understanding of how to program and process nanoscale building blocks into functional structures, and the structure-property relationships of the resulting nanostructured materials. In this talk I will discuss our recent results overcoming critical challenges to the goal of creating functional nanostructured materials, including our methods for scaling the synthesis and our work chemically transforming nanoparticles.

I'll discuss our work on a rational method for the synthesis of monodisperse metal sulfide nanocrystals in organic solutions by using $(\text{NH}_4)_2\text{S}$ as a sulfide precursor. The method enables low temperature syntheses, open-air reactions, high conversion yields, and large-scale production of monodisperse nanocrystals. I will also discuss our scalable results using ultra-high concentrations in a heat-up synthesis. Ultra-high concentrations alter the kinetics of the reaction and diverge from the classical LaMer model on solution-phase synthesis. Specifically, we synthesize high-quality metal sulfide nanoparticles ($< 7\%$ relative standard deviation), and demonstrate a 1000-fold increase in production (>200 g). Surprisingly, the nanoparticles in the matrix are resistant to Ostwald ripening over hours under high heat. To understand the mechanism we probed the interplay between chemical, thermal, and rheological properties on growth and dissolution. Our work reveals that ultra-high concentrations have an order of magnitude increase in viscosity, reducing mass diffusion, and a $\sim 67\%$ increase in heat capacity, stabilizing the reaction to perturbations. We find that nanoparticle growth at ultra-high concentration more closely align with a step coalescence growth model, while conventional synthesis conditions fall within a living coalescence model.

Finally, I'll discuss our work using chemical transformations to post-synthetically tailor the atoms in nanoparticles, altering their composition, morphology, and/or phase. These reactions can create atomic arrangements that are impossible to reach in bulk materials due to kinetic limitations. Through a cation exchange reaction on copper sulfide nanoparticles we have created dual interface Cu_2S -ZnS heterostructures. The copper sulfide phase region can be tuned to form two-dimensional (2D), single atomic layers (<1 nm). As the nanoparticles transform we observe a solid-solid phase transformation of the copper sulfide phase from the initial low-copper phase $\text{Cu}_{1.8}\text{S}$ into a higher copper phase djurleite ($\text{Cu}_{1.94}\text{S}$), but as the epitaxial strain increases a second phase transformation back to roxbyite $\text{Cu}_{1.8}\text{S}$ occurs to minimize strain energy. This work demonstrates novel routes to metastable phases through strain stabilization. The copper sulfide can be etched with phosphines in oxidizing conditions. Importantly, this etching reaction is capable of removing Cu_{2-x}S from Cu_{2-x}S -ZnS epitaxial heterostructures with perfect selectivity, that is, the phosphines completely remove the Cu_{2-x}S without disturbing the ZnS. Through correlation of FTIR, EPR, XRD, and titration experiments we characterize the fundamental mechanisms of this reaction and find that, upon exposure to oxygen, Cu_{2-x}S in the presence of phosphines is dissolved into a mixture of phosphine sulfides and solvated Cu^{2+} ions. The etching reaction is preceded by abstraction of sulfur from the particles, destabilizing the $\text{Cu}_{1.81}\text{S}$ roxbyite phase.

