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 discuss our efforts to understand how colloidal nanostructures assume selected shapes during their synthesis. To highlight one of our research directions, I will discuss our efforts to understand the workings of PVP, a structure-directing molecule that facilitates the formation of selective Ag nanoparticle shapes. In these studies, we use first-principles density-functional theory to understand how PVP binds to Ag surfaces. Based on these calculations, we fit an empirical, many-body force field to describe how PVP binds to Ag crystal facets in solution. Using this force field, in combination with theory, we probe several aspects of how PVP promotes shape-selective, \{100\}-faceted Ag nanoparticles in the 10-100 nm size range.