Understanding and Synthetically Controlling the Properties and Catalytic Activity of Ligand-Protected Metal Nanoclusters

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Nanostructures hold much promise as “designer materials,” but full realization of this promise requires an understanding of the structural and electronic effects driving their behavior. Some smaller nanoparticles, often called nanoclusters, can be synthesized monodispersely and crystallized to determine their geometric structures. However, crystallization of nanoclusters is the exception, not the rule, and no general and similarly powerful technique exists for the determination of their electronic structures. The lack of a generalizable approach to separation and isolation of nanoclusters makes it challenging to determine structure-property relationships and optimize them for applications.

We have adapted mass-spectrometry-based spectroscopic and thermochemical techniques to these nanoclusters as a general approach to study them without the need for arduous purification. This approach allows us to understand underlying design principles for their synthetic manipulation and optimization, as well as track their catalytic reaction mechanisms. I will discuss recent results that guide the use of electron donating and withdrawing effects in ligands to control the cluster HOMO-LUMO gap localized on the cluster core, the nature of metal-bound hydrogen atoms and their potential role in catalytic mechanisms, and quantum doping effects of silver atoms in gold clusters. Taken together, these studies provide detailed experimental windows guiding the use of classic coordination-chemistry-type methods to tune the electronic properties of these clusters for chemical and technological applications.