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Gregory V Hartland

University of Notre Dame

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Assembling Atoms to Clusters and Clusters to Crystals

Understanding how atoms connect to form clusters and the properties of the clusters is a longstanding and important area of research in physical chemistry. Initial work in this field includes observation of magic numbers in metal clusters^{1,2} and the discovery of C₆₀ in mass spectrometry experiments.^{3,4} The field has undergone tremendous development over the past several years, so that clusters with precisely defined atomic compositions can now be produced in large numbers and in solution.^{5,6} Crystallization of these “cluster molecules” allows X-ray analysis,^{7,8} which gives precise information about their structure. The three Perspectives in the current issue of *The Journal of Physical Chemistry Letters* highlight different aspects of current research in this field.

The article by Noguez et al.⁹ describes research on the optical properties of monolayer-protected metal clusters. When chiral ligands are used in the synthesis of these materials, intense optical activity is observed that is much larger than that of the ligands alone.¹⁰ The origin of the circular dichroism is analyzed by Noguez et al. through high-level time-dependent density functional theory. These calculations are enabled by the precise structural information available for these materials.^{11,12} The results show that there is a complex interplay between the structure of the ligands and the gold core and the electronic states of the cluster.

The Perspective by Castleman describes studies of the electronic states and chemical reactivities of small charged clusters in the gas phase.¹³ The results show that isoelectronic clusters have similar electronic states, which implies that clusters can be thought of as “superatoms” with predictable properties. A number of superatom clusters have been identified, both by the Castleman group and others,¹³ and their reactions and the way that they can be used to make complex new materials are described. The control that can be achieved in making these materials is also extremely helpful for understanding the reaction mechanism for nanocatalysts.¹⁴

The above two Perspectives deal with the assembly of atoms to make clusters and the properties of the clusters. The Perspective by Goubet and Pileni describes how the clusters can be used as building blocks to form supracrystals.¹⁵ These structures are assembled from tetrahedral subunits and have face-centered cubic crystal structures. The supracrystals grow into a variety of shapes — cubooctahedrons, decahedrons, isocahedrons — that are analogous to the shapes of metal nanoparticles.¹⁶ The physical properties of the supracrystals have been studied, such as their magnetic anisotropy (for supracrystals constructed from Co nanoparticles) and their vibrational response, both in Raman and ultrafast spectroscopy experiments.¹⁷ The results show that the high degree of ordering in the supracrystals impacts their properties. The study of these unique materials also provides insight into how crystals grow, in particular, the role of twinning in determining the overall crystal shape.

These three Perspectives provide snapshots of different aspects of a very diverse and dynamic area of study. Even though this field is over 2 decades old, new developments and new discoveries are still being made. This ensures that cluster science/nanoparticle

research will remain one of the core areas of research in physical chemistry for many years to come, with many opportunities for investigating the properties of these fascinating materials.^{18,19}

Gregory V. Hartland

Senior Editor

Department of Chemistry and Biochemistry, University of Notre Dame

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