Preface

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This is a special issue on “Superatomic Clusters and Nanoparticles.” The prospect of using superatomic clusters as building blocks in the construction of novel materials with tailorable, and often tunable, physical, chemical, or biological properties is the driving force behind the rapid development of the idea of “superatomic clusters.” The potential applications are virtually limitless in all aspects of nanoscience and nanotechnology. Examples are: superatomic catalysts, superatomic alloys, superatomic semiconductors for nanoelectronics and nanophotonics and superatomic magnetic materials for spintronics, to name just a few.

The concept of superatomic clusters has its roots in Jellium model (JM) of clusters. Indeed, JM forms the theoretical basis for describing the electronic structures of superatomic clusters. Jellium model was developed in the 1980s for simple gas-phase alkali-metal clusters. Confinement of the delocalized electrons to spherical or ellipsoidal regions leads to shell structure similar to the electronic structures of atoms:

$$1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6 1g^{18} 2d^{10} 3s^2 1h^{22} 2f^{14} 3p^6 1i^{26} 2g^{18} 1j^{30} 3d^{10} 4s^2 \dots$$

As expected, close-shell superatomic clusters, like close-shell atoms, are more stable than open-shell superatoms which tend to be more reactive (*vide infra*).

In the 80s and 90s, JM was applied to high-nuclearity coinage-metal clusters. As an example, polyicosahedral Au–Ag clusters were characterized as “clusters of clusters” whereby the constituent icosahedron behaves like superatoms. This “cluster-of-clusters” growth mechanism parallels the atom-by-atom growth pathway, giving rise to “clusters of superatoms.” A specific set of rules was discovered that governs the stereochemical and electronic requirements in the aggregation of these superatoms.

In recent years, aluminum-based icosahedral clusters have also been shown to behave like superatoms. In the gas phase, aluminum clusters adopt the jelliumatic growth pathway. Remarkably, the centered icosahedral Al₁₃ cluster, with an electronic configuration of $1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^5$, behaves like a pseudo halogen, forming ionic compounds such as K⁺Al₁₃[−] and will not get oxidized by oxygen (while most other anionic Al compounds do). This is a nice demonstration that the open-shell superatom Al₁₃ is highly reactive whereas the close-shell superatom Al₁₃[−] is extraordinarily stable.

For a brief historical perspective of Jellium Model, see Ref. [1] and references cited therein.

About This Issue

This is a mixed issue, with five invited papers and seven contributed papers.

In “Identification of an Eight-Electron Superatomic Cluster and Its Alloy in One Co-crystal Structure,” J.-Y. Saillard, C. W. Liu, and coworkers report the crystal structure of [Au_{0.5}Ag_{0.5}@Ag₂₀{S₂P(O-*i*Pr)₂}₁₂](PF₆) and [Cl@Ag₈{S₂P(O-*i*Pr)₂}₆](PF₆), whose compositions were supported by positive-mode electrospray ionization mass spectrometry. The structural elucidation indicates that the encapsulated atom of an Ag₁₃ the entered icosahedron can be replaced by a gold atom.

In “Hydride Induced Formation and Optical Properties of Tetrahedral [Cu₄(μ₄-H)(μ₂-X)₂(PPh₂Py)₄]⁺ Clusters (X = Cl, Br; Py = pyridyl),” S.-Y. Yang, B. K. Teo, and coworkers reported three tetrahedral copper hydride clusters, [Cu₄(μ₄-H)(μ₂-X)₂(PPh₂Py)₄]⁺ (X = Cl, Br; Py = pyridyl), containing the standalone tetrahedral [Cu₄(μ₄-H)] unit. The six Cu–Cu distances of the [Cu₄(μ₄-H)] unit can be divided into three groups (2.65, 2.85, and 2.95 Å), lowering the idealized point group of the Cu₄ core to D₂ symmetry, thereby resulting in intrinsically chiral metal clusters (which exist as racemic pairs of enantiomers in the centrosymmetric crystal structures). Strong

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photoluminescence (attributable to the existence of the two short Cu–Cu distances of 2.65 Å) was observed in solution and in the solid state upon near-UV irradiation. According to the Jellium model, the title clusters can be considered as two-shell Jelliumatic systems with superatomic electron counts of $2e@0e$ corresponding to the two shells of $H^-@[Cu_4X_2(PPh_2Py)_4]^{2+}$.

In “Structural evolution and superatoms in molybdenum atom stabilized boron clusters: MoB_n ($n = 10–24$),” J. Zhao and coworkers report the effect of molybdenum doping on the structural evolution of medium-sized boron clusters. The lowest-energy structures of MoB_n ($n = 10, 12, 14, 16, 18, 20, 22, 24$) clusters are globally searched using genetic algorithm combined with density functional theory calculations. They found that Mo doping has significantly affected the grow behaviors of B_n clusters, leading to a structural evolution from bowl-like to tubular and finally endohedral cage. Interestingly, the endohedral MoB_{22} cage was identified as an 18-electron closed-shell superatom.

In “Superalkali Cations with Trivalent Anion MF_6^{3-} ($M = Al, Ga, Sc$) as Central Core,” D. Wu and coworkers reported theoretical investigation of a new series of polynuclear cations $[MF_6Li_4]^+$ ($M = Al, Ga, Sc$) based on density functional theory (DFT) calculations. It was found that the Li ligands prefer to occupy the bridge- or hollow-site of the MF_6 core. The regular octahedral MF_6 groups,

though maintaining their integrity, distorted to some degree upon the introduction of Li ligands. It was concluded that large HOMO–LUMO gaps, binding energies per atom, and positive fragmentation energies ensure the stability of these cations.

In “Influence of Ring Structures on Optical Properties of Trivalent Bismuth in Bi-Doped Silica Optical Fiber,” P. Lu, et al. reported optical properties of silica fibers doped with trivalent bismuth (Bi^{3+}) ions via first-principle calculations. It was found that the luminescence of Bi^{3+} -doped optical fiber is the result of a combination of Bi^{3+} ions and silica matrix with different ring structures, which explained why Bi^{3+} -doped silica fiber cover a broad spectral range from the UV to visible light.

The six contributed papers, listed in the Table of Contents, are self explanatory. We thank the authors for their nice contributions.

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Co-Editor, *J. Cluster Sci.*

Reference

1. B. K. Teo (2013). *J. Cluster. Sci.* **25**, 5–28. (and references cited therein).