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Editorial

Whole-Process Precision Chemistry for Clusters

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Clusters occupy a unique position in the material world, bridging the gap between individual atoms and bulk materials. This distinct state is not limited to metallic elements but extends across the periodic table, encompassing a variety of materials, such as ligand-protected metal nanoclusters,[1] "naked" supported clusters,[2] magic-sized semiconductor clusters,[3] polyoxometalates,[4] as well as nonmetal clusters like borates,[5] fullerenes,[6] and their nanocomposites.[7] The atomically precise structures and tunable quantum properties of these clusters make them highly attractive for a wide range of applications, including catalysis,[8] biomedicine,[9] optoelectronic devices,[10] and energy conversion.[11] Importantly, the number of atoms in a cluster is typically limited to several hundreds, making each atom crucial to its properties. In many cases involving colloidal ligand-protected metal nanoclusters, even subtle changes in composition, such as metal doping,[12] ligand exchange,[13] or molecular-like isomerization,[14] can lead to drastic changes in their properties. Thus, from controlled synthesis and characterization to understanding properties and designing applications, a whole-process precision chemistry approach is essential for realizing the full potential of diverse clusters.

Whole-process precision chemistry plays a critical role in cluster chemsitry. The development of cluster synthesis usually began in the gas phase,[15] and significant advances have since been made in stabilized colloidal clusters. Ligand-protected metal nanoclusters, now among the most extensively studied systems, leverage precision chemistry to modify both their metallic cores and surface ligands, enabling precise control over their optical, electronic, and catalytic properties. For supported clusters without ligand protection, precise deposition and stabilization on substrates are crucial for maintaining activity and stability, especially in catalysis.[2] Recent advances include integrating smart synthesis and artificial intelligence into the precision chemistry of cluster synthesis.[16,17] Precise characterization is equally essential for understanding clusters at the atomic level.[18] Techniques such as mass spectrometry are used to determine atomic composition and monitor the real-time evolution of synthesis, thereby guiding optimization efforts.[19] Recent advances in transmission electron microscopy,[20,21] X-ray absorption spectroscopy,[22] small-angle X-ray scattering,[23] and neturon diffraction[24] are providing critical insights into cluster structure, composition, bonding environments, and surface dynamics. Establishing precise structure−property relationships is key to harnessing the properties of clusters for specific applications. For instance, the interplay between metallic cores and ligands jointly affects charge transfer, thereby influencing photoluminescence and catalytic activity.[12] A traceless removal of two kernel gold atoms in Au_{48} cluster could induce a 10-fold photoluminescence enhancement.[25] Furthermore, ligand engineering has been employed to tailor the electron−phonon interaction in $Au_{25}(SR)_{18}$ (SR = thiolate) clusters.[26] Precise structure-to-property relationships are even more compelling in the context of cluster catalysis. For example, the design of anchoring points in clusters fine-tunes the electrocatalytic microenvironment for CO_2 reduction reactions.[27] Novel nanocomposites, such as Ag clusters loaded in polyoxometalates, exhibit superior catalytic activity and enhanced stability due to their exposed surfaces.[28] Consequently, clusters offer great potential for precision-designed applications in catalysis, biomedicine, sensing, and energy storage due to their unique attributes of atomic precision and tunability.

This **Collection** in ***Precision Chemistry***, titled "Whole-Process Precision Chemistry for Clusters", features the latest research articles, reviews, and perspectives from leading scientists in this rapidly developing field. It highlights the whole-process practices of precision chemistry in material design and synthesis, characterization, establishing precise structure-to-property relationships, and practical applications, emphasizing how a holistic approach to precision chemistry can unlock the full potential of clusters. With advancements in this area, clusters are poised to play transformative roles in catalysis, energy storage, biomedicine, and beyond.

Recent advances in ligand-protected, atomically precise Au nanoclusters have sparked interest in catalysis. Unlike traditional nanoparticles, they offer insights into atomic-level size effects, enabling a deeper understanding of structure−property relationships. *Rongchao Jin* and co-workers explored catalytic size effects in thiolate-protected Au nanoclusters, covering electrochemical, photocatalytic, and thermal catalysis, and discussing how surface area, electronic properties, and active sites influence their performance.[29]

Ligands in such clusters often inhibit catalytic activity by deactivating surfaces. *Zhikun Wu*, *Manbo Li*, and co-workers used nanoclusters for single-electron transfer without compromising stability, balancing activity and stability.[30] Demonstrated in alkyne hydroborylation, this approach featured low catalyst loading, high turnover frequency, mild conditions, and easy recycling, as well as enabling efficient tandem reactions

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like hydroborylation-deuteration. This catalytic mode highlights the potential of ligand-protected nanoclusters in new reaction pathways.

Removal of ligands and loading atomically precise clusters onto supports stands as superior strategies to design heterogeneous catalysts, allowing for rational design and deeper understanding of structure−property relationships. *Dingsheng Wang, Shufang Ji,* and co-workers summarized atomic-level tuning strategies, focusing on controlling active sites (single, dual, and complex atoms).[31] Examples illustrate how such regulation impacts catalytic performance, and perspectives on advancing this approach are discussed, highlighting opportunities for designing efficient, well-defined catalysts.

Supported catalysts like atomically dispersed metals and metal clusters are crucial for industrial catalysis but often face stability issues, particularly sintering under reducing conditions. Embedding metals in supports such as polymers or zeolites enhances stability but limits active site accessibility. *Bruce C. Gates* and co-workers reviewed this promising approach involves anchoring metals in molecular-scale nests, such as zeolite pore mouths or oxophilic metal islands, which maintains stability while ensuring active site availability.[32]

Supported metal clusters also combine the benefits of single-atom catalysts and nanoparticles, offering potential for efficient electrocatalytic CO_2 reduction. *Xinbo Zhang, Haixia Zhong,* and co-workers proposed a simple method to synthesize Cu and Ni clusters on porous carbon and achieved enhanced catalytic performance, demonstrating stable electrolysis for 30 h with 95.1% CO Faradaic efficiency.[33] *In situ* analysis suggested Ni−Cu synergy promotes water dissociation, accelerating CO_2 hydrogenation and improving reaction rates.

For propane dehydrogenation, Pt-based catalysts often deactivate due to sintering and coking. Atomically precise design of adding Sn as a promoter improves stability and selectivity, but its effectiveness depends on the synthesis method. By varying the deposition sequence of Pt and Sn, *Junling Lu, Lina Cao,* and co-workers found catalysts with Sn deposited before Pt showed superior stability and selectivity.[34] The presence of Sn at the Pt-SiO_2 interface enhances charge transfer and stabilizes the clusters, emphasizing the importance of precise compositional tuning in catalyst design.

The atomic precision of clusters enables buildup of structure−property relationships beyond catalysis, such as photoluminescence and responses to the environment. *Manzhou Zhu, Xi Kang, Xuejuan Zou,* and co-workers synthesized $Au_{26.3}Ag_{17.7}$(4-*tert*-butylbenzenethiolate)$_{26}$, which showed enhanced photoluminescence due to lower symmetry and stronger $\pi-\pi$ interactions.[35] This work highlights how ligand effects and asymmetrical dopant arrangements influence properties. Such studies extend the understanding of atomic-level structure−property relationships in metal clusters.

Achieving atomic-level manipulation of the molecular interactions with the external environments in nanochemistry is challenging but possible with metal nanoclusters. These nanoclusters allow systematic modifications from the core to the ligand shell, enabling control over self-assembly and tuning of photoluminescence and catalytic performance. *Jianping Xie, Qiaofeng Yao,* and co-workers discussed strategies to enhance nanocluster properties at the atomic level, providing insights into customizing their structures for improved functionality.[36]

Notably, novel atomically precise nanostrcutures including new elements and composites are emerging. Metal−nitrogen double bonds are common in complexes, but coexistence of both transition metal−nitrogen and lanthanide-nitrogen double bonds in a single compound is rarely reported. By encapsulating a ternary transition metal-lanthanide dimetallic nitride in a C_{84} fullerene, *Shangfeng Yang, Ziqi Hu,* and co-workers stabilized Ti═N and Ce═N double bonds in TiCeN@C_1(12)-C_{84}.[37] Single-crystal X-ray diffraction revealed bond lengths consistent with double bonds, and DFT calculations showed three-center two-electron bonds, ensuring their coexistence. The fullerene cage plays a crucial role in stabilizing these bonds, highlighting its potential for developing novel bonding configurations.

Guo-Yu Yang and co-worker reported three pentaborates synthesized under hydrothermal conditions and demonstrated how precise structural regulation influences symmetry and dimensional evolution.[38] Removing CO_3^{2-} groups transformed 2D centric layers into chiral layers, with further adjustments creating chiral porous layers. The structural modifications influenced their nonlinear optical properties, with implications for future applications in photonics and electronics.

H_2 is a promising energy storage medium due to its high energy density and clean nature. However, its low volumetric density limits applications. Chemical storage through reversible H_2 incorporation into bonds, such as metal hydrides, offers a solution. Electrochemical metal hydride/H_2 interconversion addresses challenges of traditional methods, such as thermodynamic inefficiency and slow kinetics. In a Perspective, *Matthew Nava* and co-workers proposed to use molecular mediators to improve hydride solubility and morphology, making hydrogen storage more efficient at room temperature.[39]

Water-soluble, atomically precise Au nanoclusters have gained attention as theranostic tools due to their small size, excellent photoluminescence, biocompatibility, and nontoxicity. Their well-defined structures offer a platform to understand biodistribution and pharmacokinetics, expanding their applications in bioimaging, biosensing, and biotherapy. *Yan Zhu, Nianhua Xue, Dan Yang,* and co-workers reviewed the effects of ligands and cluster size on biomedical properties, providing insights into their future applications in biomedicine.[40]

The papers featured in this **Collection** present a fascinating array of recent advancements in the field of clusters, spanning a wide range of topics from catalysis and electrochemical processes to photoluminescence, hydrogen storage, and biomecial applications. The research showcased here not only deepens our understanding of structure−property relationships at the atomic level but also points to new directions for the rational design of efficient and well-defined catalysts, materials, and therapeutic agents, underscoring the importance of whole-process precision chemistry in unlocking the full potential of clusters for applications in catalysis, energy storage, biomedicine, and beyond. As we continue to explore the boundaries of what is possible with these remarkable nanostructures through whole-process precision chemical control, the future of nanochemistry and its applications appears increasingly bright.

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Notes

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