

Atomically Precise Nanochemistry

Edited by
Rongchao Jin
De-en Jiang

By seeing the structures,
a new journey begins...

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This edition first published 2023
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Library of Congress Cataloging-in-Publication Data

Names: Jin, Rongchao, editor. | Jiang, De-en, 1975– editor.

Title: Atomically precise nanochemistry / edited by Rongchao Jin and De-en Jiang.

Description: Hoboken, NJ : Wiley, 2023. | Includes bibliographical references and index.

Identifiers: LCCN 2022051975 (print) | LCCN 2022051976 (ebook) | ISBN 9781119788645 (cloth) | ISBN 9781119788683 (adobe pdf) | ISBN 9781119788652 (epub)

Subjects: LCSH: Nanochemistry.

Classification: LCC QC176.8.N35 A88 2023 (print) | LCC QC176.8.N35 (ebook) | DDC 620/.5–dc23/eng20230119

LC record available at <https://lcn.loc.gov/2022051975>

LC ebook record available at <https://lcn.loc.gov/2022051976>

Cover Design: Wiley

Cover Image: Courtesy of Dr. Yingwei Li.

Set in 9.5/12.5pt STIXTwoText by Straive, Pondicherry, India

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Preface

Chemists have long been motivated to create atomically precise nanoclusters, not only for addressing some fundamental issues that were not possible to tackle with imprecise nanoparticles but also to provide new opportunities for applications such as catalysis, optics, and biomedicine. Given the breadth of the book, De-en and I decided to invite a number of experts who are working on various types of atomically precise nanoclusters. We thank all the experts for their warm support of the book and timely completion of the chapters. Due to space limitations, we must apologize to some colleagues for missing their excellent work that could not be included in this book.

This book comprises 16 chapters. Chapter 1 provides an introduction to atomically precise nanotechnology. Chapters 2 to 10 cover atomically precise metal nanoclusters, such as Au, Ag, Cu, Ni, Rh, and the doped/alloyed nanoclusters, as well as the electrocatalytic application in CO₂ reduction and water splitting. Endohedral metallofullerenes, graphene nanoribbons, Zintl clusters, and Ti-oxo nanoclusters are discussed in Chapters 11 to 14, respectively. Finally, Chapters 15 and 16 are devoted to the assembly of nanoclusters (such as Au, Ag, and Cu), including the crystalline assembly and the use of nanoclusters as nodes for constructing special types of metal-organic frameworks, as well as the sensing and other applications. The atomic-level control in the synthesis, the new types of structures, and the physical/chemical properties of nanoclusters are illustrated in various chapters. This book contains not only experimental contributions but also theoretical insights into the atomic and electronic structures, as well as the catalytic mechanisms. We expect this book to be suitable for graduate and undergraduate students, researchers, and industry practitioners.

Overall, the concept of atomic precision is expected to have a major impact on future nanoscience research and other areas. We hope that atomically precise nanotechnology will serve as a hub for the unification of various research areas in which precision materials are being created and studied. In future research, exquisite nanotechnology will surely bring exciting opportunities in both fundamental research and practical applications. Progress in various types of atomically precise nanoclusters and the hybridization of two or more types of nanoclusters, as well as the assembly of nanoclusters into meso- and macroscopic functional materials, will lead to more exciting frontiers.

Rongchao Jin and De-en Jiang
October 2022

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Introduction to Atomically Precise Nanochemistry

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1.1 Why Atomically Precise Nanochemistry?

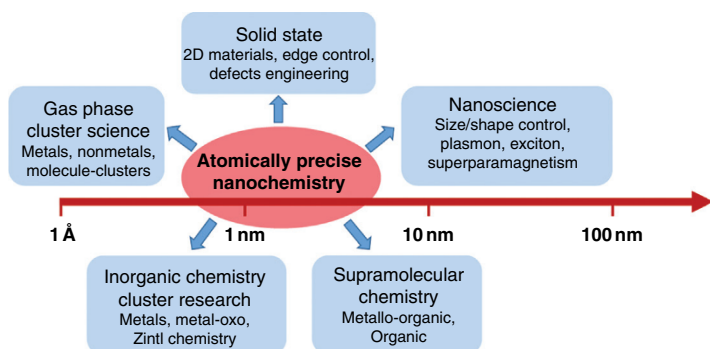
Since the beginning of the twenty-first century, nanoscience has made significant progress [1–8], especially in the creation of a variety of nanostructures with size and shape control and the discovery of new phenomena at the nanoscale. The rapid progress of nanoscience heavily relies on the synthetic breakthroughs [1–7, 9]. In terms of chemical synthesis, Mother Nature is indeed the master, evidenced by, for example, the creation of giant molecules such as DNA and proteins from atomic building blocks, and even the buildup of complex photosynthesis machinery, all being at the level of atomic precision. While there is still a long way to go for chemists to be on par with Mother Nature, we expect that nanochemistry will make giant leaps in the near future toward controlling nanostructures with atomic precision [10].

Beside the nanoscience field, the pursuit of atomic precision is also of critical importance in other areas (Scheme 1.1), including inorganic cluster chemistry, gas phase cluster science and solid-state materials science, as well as supramolecular chemistry. In moving toward larger sizes and building up complex architectures (Figure 1.1), precise control over size and structure will certainly become more challenging, yet highly exciting and rewarding [11].

1.1.1 Motivations from Nanoscience Research

Over the past two decades, significant advances have been made in controlling the size, shape, crystallinity, and composition of many types of nanoparticles, including metal nanoparticles (e.g. Au, Ag, Pt, Pd, Rh), semiconductor nanocrystals (e.g. CdSe, InP), and magnetic nanoparticles (e.g. Fe, Co, Ni), all with high monodispersity (e.g. size distributions of 5–10%). In addition, several shape-controlled nanostructures have been successfully developed, [1–9] such as the nanorods/nanowires (1D) and nanoprisms (2D). Research on the anisotropic nanostructures (both 1D and 2D) has significantly expanded the fundamental understanding of the new physicochemical properties of nanostructures enabled by shape control. Based on the new properties observed, a wide range of applications, such as sensing, catalysis, optics, and electronics, have been designed. New frontiers keep emerging, which has greatly pushed the frontier of nanoscience research.

Despite the impressive progress in nanoscience, some issues still exist. Below we briefly discuss a few issues that hamper nanoscience research from going deeper. By pursuing atomic precision,



Scheme 1.1 Atomically precise nanochemistry as a “hub” for nanoscience, inorganic cluster chemistry, gas phase cluster science, and other areas.

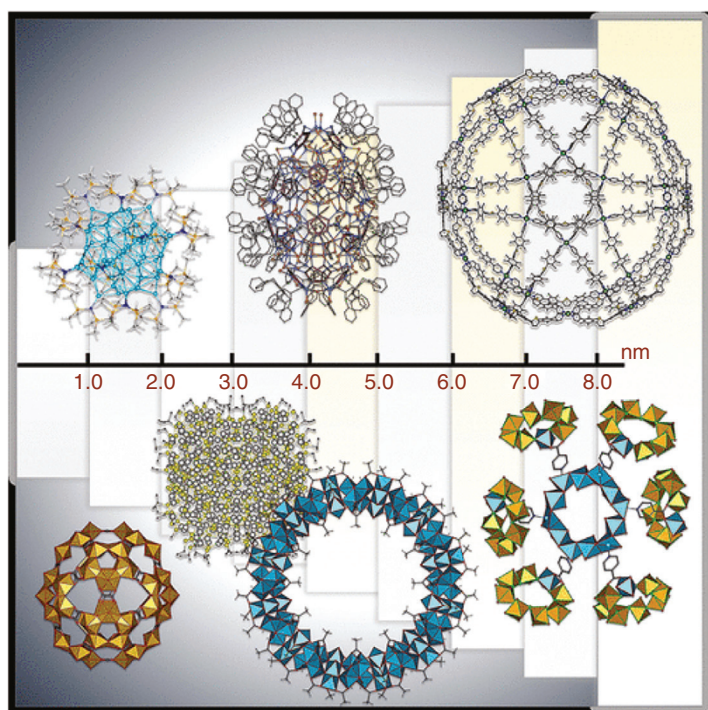


Figure 1.1 Examples of giant structures of nanoclusters and molecular architectures determined by X-ray crystallography. *Source:* Reprinted with permission from [11]. © 2021 American Chemical Society.

those issues can be overcome or at least alleviated, which will enable nanoscience research to reach a new level.

First of all, the polydispersity of nanoparticles (NPs) has long been an issue in nanoscience research. The synthesis of NPs tends to produce particles with a polydispersity (more or less). When the polydispersity is controlled to be better than 15% (e.g. 10 ± 1.5 nm), such NPs are typically called *monodisperse*. Although highly monodisperse NPs (e.g. polydispersity down to 5%) have also been made in some cases (Figure 1.2a/b), these NPs are still not of the same size at the atomic scale. In other words, no two NPs are the same! Therefore, a major dream of nanochemists has long been to synthesize truly uniform NPs (i.e. atomically precise NPs). This dream has now

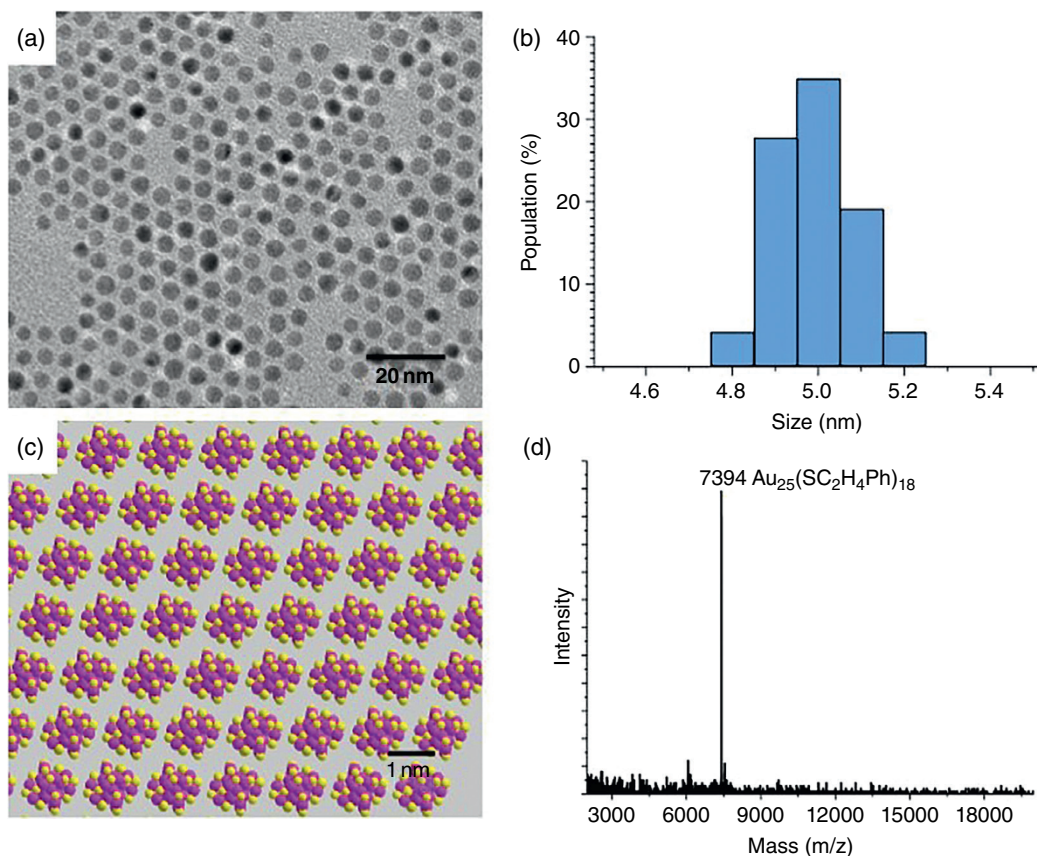


Figure 1.2 Comparison between regular nanoparticles and atomically precise nanoclusters. (a) Monodisperse nanoparticles (average: ~ 5 nm, standard deviation: $\sim 5\%$) imaged by transmission electron microscopy; (b) Typical size distribution (e.g. 5 ± 0.3 nm diameter); (c) Atomically precise $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ nanoclusters (1 nm metal core diameter, $-\text{C}_2\text{H}_4\text{Ph}$ groups are omitted for clarity) assembled in a single crystal; (d) Mass spectrometry characterization of $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$. Source: Reprinted with permission from [12]. © 2014 Springer.

been partially realized in the case of ultrasmall gold NPs of 1–3 nm in size (Figure 1.2c/d) and silver as well [10]. Such atomically precise NPs are often termed as nanoclusters (NCs) in order to differentiate them from the regular NPs. The success in obtaining atomically precise NCs is critically important, because they can serve as models for nanochemists to gain fundamental understanding of some important issues that were previously not feasible to tackle, such as the nanoparticle isomerism, the origin of surface plasmon resonance (SPR), and chemical bonding evolution with size [10].

Second, the surface of NPs often remains poorly controlled in the synthesis and thus poorly understood. Questions on the precise composition of the surface adsorbates (i.e. stabilizers) and how the stabilizers are adsorbed on the particle surface are generally not known for most nanoparticle samples. While transmission electron microscopy (TEM) and various spectroscopy techniques are powerful in characterizing NPs, they often cannot reveal the true composition and bonding structure of the surface. For solution phase NPs, the surface includes the organic stabilizers and the interface to the inorganic core. This organic–inorganic interface (Figure 1.3a) is unfortunately very tough to study, [12, 13] because TEM is ineffective in imaging the particle surface (Figure 1.3b)

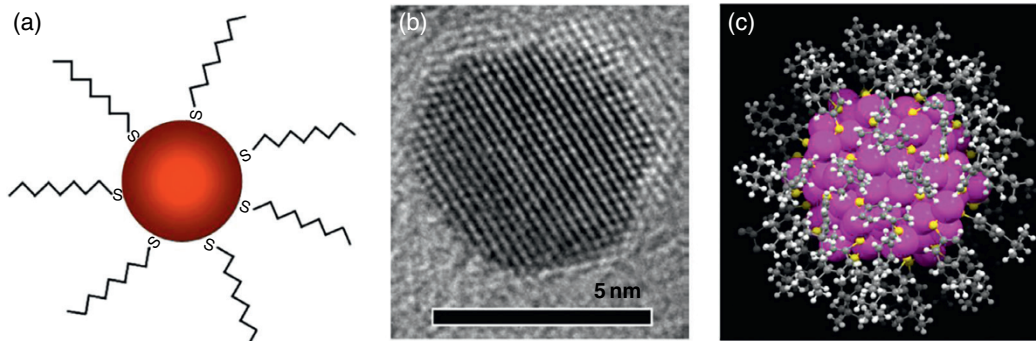


Figure 1.3 Thiolate-protected gold nanoparticles. (a) Cartoon, (b) High resolution TEM image (ligands invisible), (c) X-ray structure of atomically precise $\text{Au}_{246}(\text{SPH-}p\text{-CH}_3)_{80}$ (metal core diameter: 2.2 nm) with both metal atoms and surface ligands visible. *Source:* Adapted with permission from [10, 13]. © 2016 American Chemical Society and American Association for the Advancement of Science.

due to insufficient electron scattering by organics (e.g. light atoms of S, C, N, O, and H). While scanning probe microscopy [14] can readily reveal the surface molecules via van der Waals forces or tunneling currents, unfortunately it is incapable of showing the underlying interface between the inorganic core and surface ligands. In molecular science, many spectroscopic tools have been developed and are very powerful for analyzing molecules, such as nuclear magnetic resonance (NMR), infrared (IR), and Raman scattering, but when they are used for NPs, the polydispersity and heterogeneity of regular NPs make it very difficult (or unreliable) to correlate the NMR/IR/Raman signals with imprecise NPs. Thus, well-defined NPs are critically needed for fundamental research, especially in order to understand the surface composition and structure. By revealing the interfacial bonding between the stabilizers and the underlying inorganic core through X-ray crystallography (XRC) (Figure 1.3c), many fundamental questions could be addressed, such as the nature of active sites in nanocatalysis, charge transfer and catalytic mechanisms, photoluminescence blinking, surface magnetism, self-assembled monolayer (SAM) structure, and nanoparticle assembly mechanisms [10, 13].

Third, conventional NPs often possess various defects in the interior and/or on the surface, which are highly detrimental to many physical and chemical properties, including the stability of NPs, photoluminescence, and charge transport. How to eliminate those defects? Is it possible to create perfect NPs? These questions are of paramount importance in nanoscience research. Thus, new chemistry should be developed to attain atomically precise NPs. Even more exciting is to develop capabilities of tailoring or engineering the NP surface for specific applications, e.g. catalysis and biomedicine. These tasks call for the atomically precise NCs.

Fourth, the mechanisms for shape-controlled synthesis of nanoparticles are still not well understood, such as the nucleation and growth mechanisms. For example, small nanoprisms (<10 nm) were observed as nuclei in the photo- or plasmon-induced transformation of spherical Ag NPs to nanoprisms, [1, 9] but thus far it is not yet clear how the transformation occurs during the nucleation stage [15, 16], nor how the nuclei subsequently grow to larger nanoprisms (e.g. atom by atom in the classical mechanism, particle edge-to-edge fusion [9], or other unknown processes). Considering the important roles of stabilizers, facet-selective binding of stabilizers (or ligands) is often invoked to explain the formation of nonspherical (=anisotropic) nanostructures, but many details are still unknown yet, including how the ligands are bonded to the surface atoms on specific facets such as $\{111\}$ and $\{100\}$ of nanoparticles, and what the bonding geometry is (e.g. terminal vs. bridging bonds). To understand the mechanism for shape control and relevant issues, atomic-level

information for both the nucleation and growth processes is critically needed, in which atomically precise NCs may provide useful hints.

Last but not least, the applications of NPs such as nanocatalysis and nanomedicine require the precise knowledge of the total structure of the NP, not just the core size/shape from TEM analysis. In nanocatalysis, the adsorption of reactant(s) occurs on the surface; thus, without knowing the surface composition and structure, it would not be possible to understand the catalytic mechanism and provide the design principles for efficient catalysts [17]. The same is true in nanomedicine [8]. Upon the nanoparticles (e.g. carrying DNA or drug compounds) being injected into an animal or human body, these nanoparticles first experience interactions with proteins in blood, glutathione in cells, and other types of biomolecules. Knowing the surface of nanoparticles will be critically important and can lead to a fundamental understanding of the biodistribution and pharmacokinetics [18, 19]; hence, precision medicine can be designed.

Beside the research efforts toward atomically precise metal NCs, it is worth noting that the pursuit of atomic precision in semiconductor quantum dot is also emerging [20–22]. In quantum dots, the strong quantum confinement makes the properties extremely sensitive to size variation, thus, precise control over quantum dot size and structural uniformity is very pressing. Efforts toward such goals are underway [22, 23]. In the case of magnetic NPs, the surface disorder often results in electron spin randomization (so-called spin canting), hence, a lower magnetization than the bulk value, but in certain cases an enhanced magnetization was observed [24, 25]. To unravel the mysteries, a precise understanding of the surface atomic structure should be first obtained [26].

To address all the above important issues and many other fundamental ones in nanoscience, atomically well-defined NPs are critically needed. Nanoscientists are thus strongly motivated to develop atomically precise nanochemistry.

1.1.2 Motivations from Inorganic Chemistry Research

The cluster state is also of wide interest in the inorganic chemistry field. Understanding the chemical bonding pattern in the cluster state and the pattern evolution with increasing size has long been a central task. Since the early twentieth century, research in inorganic chemistry has led to the production of metal clusters (typically in ligand-protected form) and also boron clusters, Zintl clusters, and metal-oxo nanoclusters. There is strong interest in pushing up the size of such clusters.

Boron cluster research was pioneered by Stock in the 1910s [27] and has significantly expanded the concept of chemical bonding [28]. In contrast to classical covalent bonds in which two electrons are shared by two atoms or centers (denoted “2c-2e,” so-called Lewis pair [29]), multicenter bonding such as 3c-2e [30] was introduced for boron clusters. In addition, the concept of three-dimensional (3D) aromaticity was also put forth [31, 32], which is in contrast with the 2D case, i.e. Hückel aromaticity. Such aromaticity rules have been widely applied in later research in different areas.

The Zintl cluster research was initiated by Zintl in the 1930s [33], such as As_7^{3-} and Sb_7^{3-} in liquid ammonia. A striking feature is that Zintl clusters are bare (without the need of ligand protection in solution phase) [34]. Larger sizes are such as $[\text{As}@_{12}\text{Ni}_{12}@_{20}\text{As}_{20}]^{3-}$, [35] $[\text{Au}_8\text{Pb}_{33}]^{6-}$, and $[\text{Au}_{12}\text{Pb}_{44}]^{8-}$ [36]. Understanding the electronic structure of Zintl clusters and the size evolution is of particular interest [34, 37]. Several theories, such as the Zintl-Klemm concept [38], were developed in early work. The Wade-Mingos electron counting rules from the polyhedral borane clusters were later introduced into the Zintl cluster field. The concepts of aromaticity and multicenter delocalized bonding [32, 39], as well as the superatom electronic picture, [37d, 40] have all been applied to Zintl clusters.

Another line of inorganic cluster chemistry involves the metal-oxo chemistry or polyoxometalate clusters (POM), which also features atomic precision [41]. The POMs are closely relevant to

the corresponding metal oxide in terms of composition and structure, [42] thus, atomically precise POMs can serve as molecular or nanoscale models for metal oxides, such as Ti-oxo NCs for modeling TiO_2 and Ce-oxo for CeO_2 . Using the Ti-oxo cluster (TOC) system as an example, the inorganic Ti—O core is coordinated by organic or inorganic ligands. In early work, a hydrolysis product of titanium tetraethoxide was identified by XRC to be $[\text{Ti}_7\text{O}_4(\text{OEt})_{20}]$ in 1967 [43]. Since then, many TOCs have been reported, such as Ti_{42} , Ti_{44} , and Ti_{52} [44–46]. Their structures can be controlled, such as spherical cages, rings or wheels, and many types of dense structures [41]. In addition to monometallic TOCs, there are also bimetallic ones with doped ions being main group ions, transition metal ions, and lanthanide ions [41]. The incorporation of Ag clusters into TOCs is quite appealing, such as the $\text{Ag}_{14}@\text{Ti}_{16}$ -oxo nanocluster [47].

Finally, metal coordination-based supramolecular chemistry has also moved toward the nanoscale by creating ever-larger nanostructures, such as wheels/rings, cages, and polyhedrons, as well as tubular architectures [11]. The construction of large and exquisite molecular architectures calls for new development of nanochemistry [48].

1.1.3 Motivations from Gas Phase Cluster Research

The field of gas phase cluster science has moved from small sizes (several to a dozen atoms in earlier research) to larger sizes in the current efforts [49]. Since the 1960s, intense research on gas phase clusters has been carried out, including inert-gas-element clusters (e.g. xenon clusters, Xe_n), metal clusters (e.g. Na_n clusters), carbon clusters (C_n), water clusters ($[\text{H}_2\text{O}]_n$), and many other types [50]. The Xe_n cluster research led to an important insight into the structural stability of clusters, i.e. the formation of icosahedral packing structures, such as the one-shelled Xe_{13} , two-shelled Xe_{55} , and three-shelled Xe_{147} [51]. These are called the *geometric magic numbers*, and the atomic shell closing endows high stability to the clusters.

In the 1980s, research on gas phase Na_n clusters led to another important concept, that is, the electron shell closing of $1S\ 1P\ 2S\ 1D\ \dots$, with notable sizes of Na_8 , Na_{34} , Na_{58} , and Na_{92} (so-called superatoms because of the atomic-like orbitals in such clusters) [52]. Much work has also been done on gas phase gold clusters, [53, 54] and theoretical computations on the 2D to 3D structure transition (Figure 1.4) [55, 56]. To investigate the evolution of the superatom electronic shell picture, larger sized NCs should be pursued. As the size boundary moves up, the cluster science indeed merges with nanoscience. Preparation of clusters in gas phase with hundreds of atoms per core has been pursued in recent years, [49] although major effort is still required in the pursuit of atomic precision.

Carbon clusters (or fullerenes) are one of the significant areas in gas phase cluster research [57, 58]. Fullerenes are typically produced using the electric arc discharge or thermal chemical vapor deposition (CVD) method. From the initial discovery of C_{60} in 1985, a variety of sizes have been reported, with smaller ones such as C_{20} , C_{24} , C_{28} , C_{32} , C_{36} and larger ones such as C_{70} , C_{80} , C_{82} , C_{108} and even up to C_{540} [59]. The size-dependent structure, electronic, and optical properties of C_n are under active investigation, and the cage structure of C_n clusters is particularly appealing for encapsulating atoms, molecules, and clusters of few-atom in size, forming endohedral clusters [60]. New additions to the nanocarbon family also include the atomically precise graphene nanoribbons (GNR) [61] and some other forms.

1.1.4 Motivations from Other Areas

The concept of atomic precision is also critically important in solid-state materials. A variety of solid-state materials are being intensively pursued in the field of materials science, such as the low dimensional materials (2D van der Waals materials, stacked 2D materials, etc.) and quantum

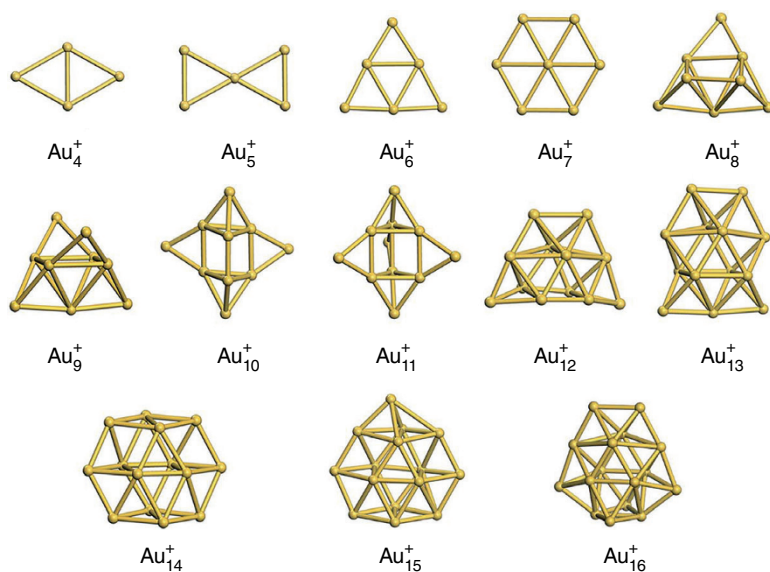


Figure 1.4 Computed structures of bare cationic Au_n^+ clusters and 2D to 3D structural transition. Source: Reprinted with permission from [55]. © 2019 Royal Society of Chemistry.

materials. Precise control over the edge and topology is of vital importance for controlling the functionality, and heteroatom doping (e.g. doped WS_2) also calls for atomic precision strategies [62].

In the semiconductor industry, silicon chips have moved toward the few-nm regime, in which precise control of the film quality and interface has become a major issue in order to prevent electrical leak in the few-nm transistors [63]. This calls for atomically precise fabrication strategies, which is vital in advancing toward the 1-nm transistor technology.

1.2 Types of Nanoclusters Covered in This Book

Intense efforts in the past years have led to success in synthesizing Au, Ag, Cu, Pt, Pd, Rh, Al, Fe, Co, and Ni nanoclusters, as well as alloys. The obtained atomically precise nanoclusters can serve as new models or platforms for solving many issues of structure and bonding evolution, and thus enable significant progress in nanoscience research.

This book is intended to provide an overview of the progress in atomically precise nanochemistry with a focus on inorganic nanostructures, including metals (e.g. Au, Ag, Cu, Ni, Rh), Zintl clusters, Ti-oxo nanoclusters, and carbon clusters, as well as catalytic application and assembly of NCs into functional materials. On a note, other types (e.g. Pd_n , [64] Pt_n , [65] Al_n [66] and cerium-oxo NCs [42], metallo-rings and wheels [11], supramolecular cages/polyhedrons/capsules [11, 48], and DNA-templated Au_n and Ag_n NCs [67, 68]) are not covered due to the limitations of the book. Semiconductor NCs [20–23] are also not covered.

Among the chapters, atomically precise metal NCs (Au, Ag, Cu, Ni, Rh) and their catalytic applications are discussed in Chapters 2–10. Some other types of NCs, including endohedral metallofullerenes (EMF), GNRs, Zintl clusters, and Ti-oxo nanoclusters, are presented in Chapters 11 to 14. Finally, Chapters 15 and 16 are devoted to the assembly of metal NCs (Au, Ag, Cu), including their incorporation into metal organic frameworks (MOFs) toward the fabrication of assembled functional materials.

1.2.1 Atomically Precise Metal Nanoclusters (Au, Ag, Cu, Ni, Rh)

In recent years, atomically precise metal NCs have been intensely pursued. Such NCs may be divided into three types:

- i) *Coinage metals*, including Au, Ag, Cu, and alloys, which are primarily motivated by the elegant optical properties of such elements in the form of NCs (*c.f.* their larger counterparts – plasmonic NPs in the 3–100 nm range exhibiting distinct SPRs in the visible and near-infrared wavelength range),
- ii) *Platinum group metals*, including Pd, Pt, Rh, and alloys, which are mainly motivated by their excellent catalytic properties, and
- iii) *Magnetic metals*, such as Fe, Co, Ni, and alloys, which are primarily motivated by the size-dependent magnetism from the cluster state to the bulk metals.

Among the types of atomically precise metal NCs protected by various types of ligands (e.g. phosphines [69, 70], thiolates [71, 72], alkynyls [73], carbenes [74], halides [75], and Stibine [76]), the gold-thiolate (Au-SR) system is perhaps the most extensively studied one (Figure 1.5). Its larger counterparts (i.e. plasmonic Au NPs of 5–100 nm) have been widely studied in the past decades and explored in numerous applications. The success in atomically precise gold-thiolate NCs (tens to hundreds of gold atoms per core) will help explain the regular NPs in terms of the latter's surface structure, assembly, and catalytic mechanism, as well as many other fundamental aspects [10, 77].

In this book, Chapter 2 by Xie's group summarizes the progress in total synthesis of gold NCs, including the control over size, structure, composition and ligand engineering, and Chapter 3 by Wu's group reviews the advances in the synthesis, characterization, and application of gold NCs with a focus on the categorization of structural series. The structures of metal NCs constitute the basis for understanding the functionality and stability of NCs. A theoretical perspective on the structure evolution and structural design of $\text{Au}_n(\text{SR})_m$ NCs is provided by Xu and coworkers (see Chapter 4). Among the applications of Au NCs, catalysis (e.g. electrocatalytic water splitting and CO_2 reduction) is summarized in Chapter 5 by Lee's group, and theoretical simulations on the electrocatalysis mechanisms are given in Chapter 6 by Tang's and Jiang's groups.

While a large body of research focuses on gold NCs, there has also been substantial progress in Ag NCs (reviewed in Chapter 7 by Zhu's group), Cu NCs (Chapter 8 by Bakr's group), Ni NCs (Chapter 9 by Hayton's group), and Rh and its alloy NCs (Chapter 10 by Femoni's group). Some selected crystal structures of these metal NCs are shown in Figure 1.6.

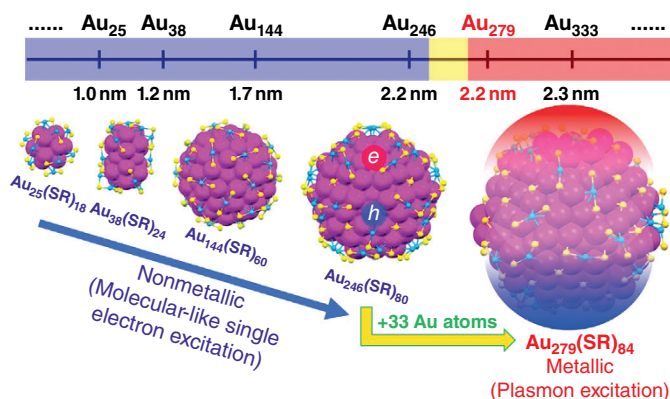


Figure 1.5 Atomically precise gold nanoclusters with the transition from nonmetallic Au_{246} to metallic Au_{279} . Source: Reprinted with permission from [77]. © 2021 The Authors (Jin and Higaki).

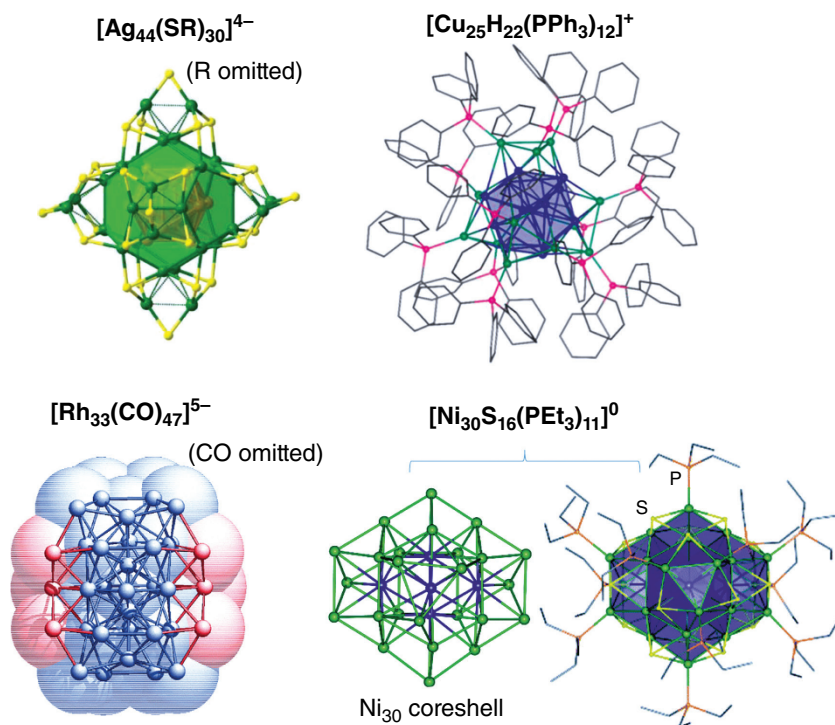


Figure 1.6 Examples of atomically precise Ag, Cu, Rh, and Ni nanoclusters with metal–metal bonding. Source: Adapted from Chapters 7–10.

The types of metal NCs that are discussed in Chapters 2–10 contain a certain number of delocalized valence electrons of metal atoms, such as 2e, 8e, 18e, 20e, 34e, 40e, 58e, 70e, and 92e. These so-called electronic magic numbers are closely relevant to the stability and properties of the NCs. Unlike the zero valent Au, Ag, Pt, Pd, and Rh NCs – which can even be in negative (e-rich) states for Rh atoms [78], Cu NCs tend to be in Cu(I) state or have low numbers of core valence electrons, such as 2e in the NCs of $[\text{Cu}_{25}\text{H}_{22}(\text{PPh}_3)_{12}]^+$ [79], $[\text{Cu}_{13}\{\text{S}_2\text{CN}^n\text{Bu}_2\}_6(\text{CCPh})_4]^+$ [80], $\text{Cu}_{14}(\text{C}_2\text{B}_{10}\text{H}_{10}\text{S}_2)_6(\text{CH}_3\text{CN})_8$ [81], and $[\text{Cu}_{61}(\text{S}^t\text{Bu})_{26}\text{S}_6\text{Cl}_6\text{H}_{14}]^+$ [82]. However, upon introducing heterometal dopants, the valence electron number could be raised, such as the 10e $[\text{Pt}_2\text{Cu}_{34}(\text{PET})_{22}\text{Cl}_4]^{2-}$ [83a] and the 67e $[\text{Cu}_{43}\text{Al}_{12}](\text{Cp}^*)_{12}$ [83b].

Historically, chemists have long been interested in counting the valence electrons, such as the organic aromaticity rule of $4n + 2$ (π electrons) put forth by Hückel in 1931, and the Wade-Mingos electron counting rules for boron and metal clusters [38, 39] developed in the 1970s, the superatom electron counts [52] in the 1980s, and so on. More discussions on the counting of cluster valence electrons are provided in Section 1.3.2.

On the other hand, there are also many Au(I), Ag(I), and Cu(I) NCs that have no free valence electrons, such as the anion-templated Cu(I) and Ag(I) NCs. While these systems are not the focus of this book, some Cu(I) and Ag(I) NCs are discussed in Chapter 8 and 16, respectively. In Chapter 8, Dong et al. provides a very systematic summary of the syntheses of Cu(I) and Cu(0) NCs, whereas Chapter 16 by Wang and Zang focuses on the assembly of Ag(I) NCs for framework materials, and Chapter 15 by Mandal's and Sun's groups summarizes the assembly of Au and Ag NCs into 3D and 2D crystals.

1.2.2 Endohedral Fullerenes and Graphene Nanoribbons

Nanocarbon has many types, including the fullerenes (C_n), EMFs, carbon nanotubes, graphene quantum dots, and nanoribbons. Some of them are in atomically precise forms, such as fullerenes and endohedral fullerenes, as well as certain GNRs.

Since the discovery of C_{60} , carbon clusters have long been of major interest to chemists, physicists, and materials scientists owing to the unique cage structure, superconductivity, and other unprecedented functionalities [57–60]. In this book, Chapter 11 is devoted to the endohedral fullerenes (Figure 1.7). Chen's group has summarized recent progress in EMFs with a monomer, dimer, and even cluster enclosed in the carbon cage, forming metallofullerenes and clusterfullerenes, and the new properties are discussed, such as optical absorption, electrochemical, and magnetic properties, as well as the chemical reactivity. Charge transfer from the enclosed metal atom to the fullerene cage may result in different isomeric fullerene structures. In the case of two metal atoms enclosed, metal–metal interactions (including bonding and non-bonding) lead to interesting phenomena. The inclusion of more atoms gives rise to clusterfullerenes, such as the enclosing of metal nitride (e.g. Sc_3N), oxide (Dy_2O), sulfide (Sc_2S), carbide (M_2C_2 , where M = metal), and carbonitride (Sc_3CN) clusters. The configuration of the enclosed few-atom cluster may be rigid (e.g. M_3N) or flexible (e.g. M_2C_2), and the enclosed cluster may also transfer a certain number of valence electrons to the fullerene cage.

Fullerenes and doped ones exhibit rich optical absorption peaks in the visible to near-infrared (NIR) range. The different metal-cage interaction and electron transfers greatly affect the energy distribution of molecular orbitals of endohedral fullerenes and thus their optical absorption spectra. There are also rich electrochemical properties of endohedral fullerenes, and both the first oxidation and first reduction potentials can be largely varied by the metal atoms in the cage.

In addition to the zero-dimensional (0D) C_n clusters with spherical or spheroidal shape, atomically precise 2D GNRs are also of major interest (Figure 1.8). Chapter 12 by Yamada and Hayashi summarizes some recent progress in the on-surface synthesis of GNRs and bandgap engineering toward transistor applications.

1.2.3 Zintl Clusters

Zintl cluster research constitutes an important branch in the field of inorganic chemistry. Previous work focused on the main group elements such as Ge, Pb, and Sb. Recent efforts have also investigated transition metals (Figure 1.9), for example, Dehnen's group carried out a series of work on endohedral Zintl clusters such as $[Th@Bi_{12}]^{4-}$, $[Co@Sn_6Sb_6]^{3-}$, and double-metal centered $[Co_2@Sn_5Sb_7]^{3-}$ [34]. Sun's group recently obtained large sized $[Au_8Pb_{33}]^{6-}$ and $[Au_{12}Pb_{44}]^{8-}$ with gold kernels and lead shells [36]. Chapter 13 by Sun and coworkers have summarized some recent

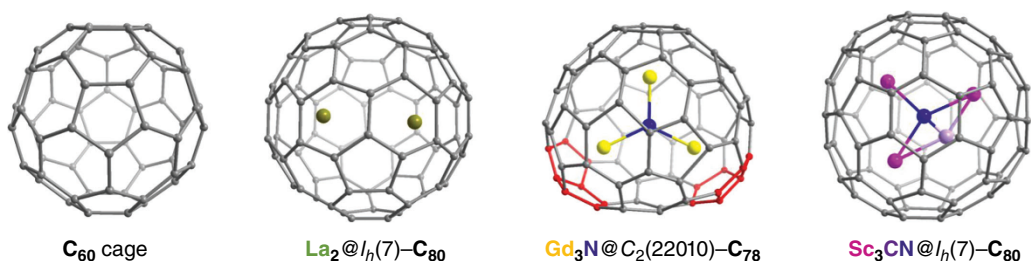


Figure 1.7 Structures of C_{60} and some endohedral fullerenes (the letter colors code the elements).

Source: Adapted from Chapter 11.