Pure Metal Clusters with Atomic Precision for Nanomanufacturing

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Abstract
Advances in cluster science have enabled the preparation of atomically precise metal clusters with one to a hundred atoms under controllable expansion conditions. After introducing typical gas-phase cluster preparation and reaction apparatuses, this work summarized recent progress in preparing pure metal clusters of single-atom resolution, including neutral and ionic ones, with typical examples of Al, V, Nb, Fe, Co, Ni, Rh, Pt, Ag, Cu, and Pb. With the development of soft-landing deposition technology, the size-selective pure metal clusters with strict atomic precision and predictive property will benefit nanomanufacturing down to atomic and near-atomic scales. This work serves as a modest motivation to stimulate the interest of scientists focusing on interdisciplinary subjects.

Keywords Metal cluster · Gas phase · Cluster assembly · Deposition · Printing

1 Introduction
Atomic clusters are a new type of matter that bridges the gap between atoms and the nanoscale and exhibits well-defined structures and atomically precise size and composition. Cluster investigations help further understand the micro-mechanisms of nano-catalysis and the structure–function relationship of nanomaterials. Significant research was performed to explore the potential applications of these materials, such as in catalysis, chemo-sensing, bioimaging, biomedicine, optics, quantum computing, and solid-state memory [1–8]. Over the past decades, extensive progress has been made in the preparation of naked metal clusters [9–14] and ligand-protected metal clusters [15–21]. Advances have also been achieved in probing their structural stability, reactivity, and properties [22–27]. Studies on the structural stability of clusters and the preparation of condensed-phase metallic nanomaterials or quantum dots with highly tunable properties by cluster assembly or soft-landing deposition [28] for various applications [29, 30] are of great importance.

Micro-dispensing, electrospray deposition, robotic printing, stamping, ink jet deposition, and ion soft-landing are the main techniques for the preparation of solid-supported metal clusters. Among these, the soft-landing deposition of selected metal clusters onto various supports has made substantial progress in the past decades and provided a new way to elucidate interface interactions and improve the selectivity and efficiency of catalytic reactions [31–39]. For example, Cooks et al. [40–44] prepared protein microarrays by soft-landing mass-selected ions on specific spots of a moveable target [45]. Palmer et al. [46] studied the physical vapor deposition of metal atoms onto cryogenically cooled supports with simultaneous co-condensing argon and developed a preparation method for the colloidal suspensions of the physically deposited clusters. Vajda and coworkers [47–50] and Laskin, Johnson, and coworkers [51] conducted many investigations to determine the size effect of supported clusters for chemical reactions [24]. Heiz [52–55] and Landman [56] revealed a dramatic size dependence in the deposition of mass-selected gold clusters on supports for hydrogenation and oxygen reduction reactions. Nakajima [57] studied the deposition of silicon and metal-doped silicon metal clusters. Song and Wang [58, 59] dedicated efforts to improve the preparation process at the macro scale and examined the size-dependent properties of supported clusters. The
development of soft-landing technologies helps further understand the mechanisms of nanomaterials and nanomanufacturing down to atomic and near-atomic scales.

Controllable preparation is the prerequisite for well-resolved metal clusters. However, this condition is challenging because naked nanometals are often reactive in the presence of trace contamination, which largely affects the formation of pure metal clusters (instead of metal oxides or carbides). In general, cluster sources based on magnetron sputtering (MagS) and laser vaporization (LaVa) are dominantly applied for the efficient preparation of gas-phase metal clusters. For these cluster sources, nucleation and growth can be controlled by adjusting the buffer gas pressure and monomer concentration that depends on the ablation laser density or MagS power. In particular, the local space (namely, the waiting room) preceding the nozzle plays a key role in cluster formation.

In addition to its effective preparation, mass spectrometry is one of the most common and powerful tools that can analyze clusters simply by measuring the ion abundance relative to mass-to-charge ratios [60–62]. Mass spectrometry techniques, including customized quadrupole mass spectrometry, time-of-flight mass spectrometry (TOFMS), ion-trap mass spectrometry, tandem quadrupole TOFMS (Q-TOFMS), and Fourier transform ion cyclotron resonance system, have been widely used for gas-phase metal cluster studies. Here we summarized the efforts devoted to preparing gas-phase pure metal clusters based on the two source types. We also present several examples of the well-resolved mass spectra of a few typical metals, including Al, V, Nb, Fe, Co, Ni, Rh, Pt, Ag, Cu, and Pb, and the prospect of nanomanufacturing micro materials down to atomic and near-atomic scales.

2 Experimental Methods

Figure 1a displays the diagram of the customized ReTOFMS system with a self-developed deep ultraviolet (DUV) laser system (abbreviated as DUV-TOFMS) for the optional ionization of neutral species. This instrument involves a self-made LaVa source coupled with a downstream flow tube reactor (~60 mm), which allows for efficient cluster preparation and multiple gas collisions [63–66]. The reactants and product ions pass through a skimmer and are then directed into the second chamber where they are orthogonally accelerated by five plate-electrodes woven with gold wires. The materials are pushed back by a multiplate reflector and collected by a microchannel plate detector. The ion signal is recorded by a digital storage oscilloscope. This integrated system is efficient for the preparation of neutral and ionic clusters and for the study of their gas-phase reactivity with high-resolution mass spectrometry.

A MagS source has the advantages of high efficiency and continuous flow [67–69] and operates under highly controllable parameters to achieve tunable cluster size distribution. Figure 1b shows a MagS source in combination with a customized triple quadrupole mass spectrometer (TQMS) and a 1-m-long multiple-ion laminar flow tube (MIFT) reactor [70, 71]. Pure metal clusters can be formed with the MagS source under proper sputtering conditions and are driven out of the source chamber due to the pressure difference in the flow tube (e.g., ~0.7 vs. ~3 Torr) controlled by a large Roots blower (490 rpm, 510 m³/h). In the absence of electric field constraint, sufficient gas collisions under such a system provide a reliable strategy for probing stable and unstable species. The whole instrument is mounted on a moveable aluminum–alloy shelf, and all the chambers can be separated independently.

3 Results and Discussion

3.1 Main Group Metal Clusters

Figure 2 presents the typical mass spectra of anionic, cationic, and neutral aluminum clusters produced by the LaVa source. Anion aluminum clusters $\text{Al}_n^- (n = 7–37)$ that will fit with a Gaussian distribution (e.g., centered at $\text{Al}_{15}^-/\text{Al}_{20}^-$) are relatively easy to prepare at proper experimental
conditions. By comparison, neutral clusters often show high mass abundance for \( n = 1, 2 \). This finding is consistent with previous studies \([72, 73]\). In addition to mass distribution, the formed clusters are subjected to size-dependent stability. In particular, \( \text{Al}^+_7, \text{Al}^-_{13}, \) and \( \text{Al}^-_{23} \) magically correspond to the closed electronic shells of 40 and 70 valence electrons \([74, 75]\). This phenomenon is rationalized using the Clemenger–Nilsson ellipsoidal shell model, which considers an effective single-particle potential based on a harmonic oscillator (valid for small clusters). In this model, 2, 8, 20, 40, 70, and 112 correspond to magic numbers. The magic numbers of stable aluminum clusters differ from those of the sodium clusters. Early experimental studies on sodium clusters identified 8, 20, 40, and 58 to be the magic numbers that simply fit with the energy-level occupation for square-well potentials (with 2, 8, 20, 40, 58, 68, 90, and 92 at a sequence of closed shells for 1s, 1p, 1d2s, 1f2p, 1g, 2d, 1h, and 3s, respectively) \([76]\). As an intermediate of these two potentials, a phenomenological Woods–Saxon potential (identical to the self-consistent Kohn–Sham potential) has been widely applied for the empirical jellium model \([76–78]\) and successfully predicted the magic numbers in diverse metal clusters.

In the past decades, the structure and stability of heavy metal clusters have been widely studied. The global annual production of lead has reached a few thousand million tons, and lead chemistry study is important for battery application. For this metal, we prepared pure cationic clusters \( \text{Pb}^+_n \) \((n = 1–13)\) with a MagS source and studied the gas-phase reactivity with \( \text{CH}_3\text{I} \). As shown in Fig. 3, the nascent \( \text{Pb}^+_n \) clusters displayed a near-Gaussian distribution, and the reactivity of these cationic \( \text{Pb}^+_n \) clusters with \( \text{CH}_3\text{I} \) exhibited strong size dependence \([79]\). \( \text{Pb}_n\text{I}^+ \) was the dominant product for \( \text{Pb}^+_1-4 \), but this material was not observed for \( \text{Pb}^+_n \) \((n > 4)\). Relative to the Pb-I bonding, the Pb-Pb interatomic interactions were strengthened with the increasing number of Pb atoms. In contrast to those of \( \text{Pb}^+_1-4 \) clusters, the reactions of \( \text{Pb}^+_n \) \((n > 4)\) with \( \text{CH}_3\text{I} \) showed insurmountable transition state energy barriers.

### 3.2 Platinum Group Metal Clusters

Platinum group metals are widely used as catalysts for many reactions. Figures 4a–c present the typical mass spectra of \( \text{Rh}^{\pm,0}_n \) clusters \([80]\) produced by the laser ablation of a rotating and moving rhodium disk under a helium atmosphere. The abundances of anionic rhodium clusters \( \text{Rh}^-_n (n = 5–33) \) and neutral \( \text{Rh}^+_n (n = 4–22) \) fitted well with Gaussian distribution, and the cations \( \text{Rh}^+_n (n = 3–31) \) fitted well with Rayleigh distribution. We also obtained clean and well-resolved clusters for the other Pt group metals. Figure 4d shows an example of the anionic \( \text{Pt}^-_n (n = 3–25) \) clusters, which can also be fitted by a Gaussian curve. By reacting \( \text{Pt}^-_n \) with different gas molecules and conducting comprehensive theoretical calculations, we discovered the unexpected stability of \( \text{Pt}^-_n \) \((n = 3–25)\). This feature is associated with the
all-metal β-aromaticity and superatom–atom bonding nature (Pt6@Pt4) in mimicking methane [81].

3.3 Magnetic Metal Clusters

Cobalt, iron, and nickel are the most important metals used as magnetic materials. We studied the size-dependent stability and reactivity of cationic Fe, Co, and Ni clusters using the DUV TOFMS instrument. Figure 5 shows the typical mass spectra of the cationic Fe

\[ \text{Fe}_n^+ \] \( (n = 1–35) \), Co

\[ \text{Co}_n^+ \] \( (n = 1–33) \), and Ni

\[ \text{Ni}_n^+ \] \( (n = 4–50) \) clusters produced by the LaVa source. Most of these clusters readily reacted with oxygen to produce diverse oxides but displayed competitive multiple reaction channels when reacting with acetylene. At the relatively low partial pressure of the acetylene gas, the Fe

\[ \text{Fe}_n^+ \], Co

\[ \text{Co}_n^+ \], and Ni

\[ \text{Ni}_n^+ \] clusters reacted with acetylene and were dominated by dehydrogenation; however, at high acetylene concentrations, the cyclotrimerization of acetylene to benzene became the dominant reaction channel [82].

For these metals, we also prepared the anionic clusters and compared their reactivity with that of a few chemicals. The neutral and anionic ones appeared relatively inert while reacting with nitrogen, and the cationic Co

\[ \text{Co}_n^+ \] clusters reacted with multiple N₂ to form diverse adducts. One exception is the octahedral superatom Co

\[ \text{Co}_6^+ \], which survived the reactions with dinitrogen due to its unique stability. In addition, a
few cobalt cluster complexes showed significant mass abundances. One of them is Co$_5$N$_6$$^+$, which was identified as a typical superatomic complex. These superatoms and superatomic complexes embody the previously proposed concept of special and general superatoms [83].

Taking advantage of our self-made DUV TOFMS that has ps-pulsed laser ionization and is free of fragmentation, we prepared well-resolved neutral Co$_n$ ($n = 1–30$) metal clusters as shown in Fig. 6a. Given that the ionization energies of the neutral Co$_n$ clusters are smaller than the single-photon energy of 177.3-nm-deep ultraviolet laser (except Co atoms), the ps-pulsed laser bears unique advantages for efficient single-photon ionization. For these well-resolved Co$_n$ ($n \leq 30$) clusters, we comprehensively studied their reactions with oxygen (Fig. 6b). An extremely stable cluster Co$_{13}$O$_8$ emerged in the spectra and showed dominant mass abundance upon the introduction of sufficient oxygen reactant (Fig. 6c). Furthermore, this Co$_{13}$O$_8$ cluster showed a cubic structure with remarkable cubic aromaticity. We also studied the reactions of pure Ni$_n$$^{\pm}$ clusters with O$_2$ and found magic clusters Ni$_{13}$O$_8$$^{\pm}$ with a body-centered cubic structure similar to that of Co$_{13}$O$_8$ [84]. This class of oxygen-passivated metal clusters contain a perovskite-like cubic structure and are named “metalloxocubes,” which are an ideal candidate for genetic materials due to the advantages of the cubic building blocks and the stability within inorganic aromaticity [85, 86].

### 3.4 VB Group Metal Clusters

Extensive studies have illustrated the chemistry of group VB transition metals. Figure 7 plots the mass spectra of neutral vanadium and anionic niobium clusters produced and detected by DUV TOFMS. Taking advantage of the DUV laser ionization and our experiences in preparing metal clusters, we observed the well-resolved mass distribution of neutral V$_n$ ($n = 1–42$) clusters, as shown in Fig. 7a. The reactions of neutral V$_n$ clusters with water revealed the prominent stability of superatomic V$_{10}$ (insert of Fig. 7a) and V$_{16}$ [87]. We also prepared niobium clusters, with the typical spectrum of anionic Nb$_n$$^-$ ($n = 5–64$) clusters displayed in Fig. 7b. Owing to its unique electron configuration ([Kr]4d$^4$5s$^1$), Nb is more active than other VB transition metals V ([Ar]3d$^3$4s$^2$) and Ta ([Xe]4f$^{14}$5d$^3$6s$^2$). Niobium shows diverse oxidation states ranging from $-1$ to $+5$; however, the Nb-Nb bond energy is up to 513 kJ/mol (V-V bond at 269.3 kJ/mol), which is convenient for the formation of niobium clusters. As shown in Fig. 7b, the Nb$_n^-$ clusters generated from the LaVa source exhibited a Gaussian-like curve with $n$ up to 60.

We investigated the reactions of the Nb$_n^-$ clusters with oxygen in the flow tube reactor and found concentration-dependent reaction channels that involve the addition of oxygen, which coexists with O$_2$ etching and growth channels to form various Nb$_n$O$_m^-$ products [88]. We also observed a highly selective product, Nb$_{11}$O$_{15}^-$, which dominated the

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Fig. 6 a Representative size distribution of the neutral Co$_n$ ($n = 1–30$) clusters. A sketch of the instrument showing the sampling and reaction method. b, c Mass spectra of the Co$_n$ clusters after reacting with different amounts of O$_2$ in the flow tube.

Fig. 7 Mass spectra of a neutral V$_n$ ($n = 1–42$) clusters and b anionic Nb$_n^-$ ($n = 5–64$) clusters generated by DUV TOFMS.
mass spectra under the suitable gas flow rate of intermediate O2. DFT calculations unveiled the special stability of Nb11O15− cluster within D5h symmetry and under protection by 15 Nb–O–Nb bridges. Despite being a cluster anion, the cluster shell of Nb11O15− is almost electronically neutral. However, the net atomic charge on the center Nb atom is around −1, and the shielding effect consequently restricts the electrostatic interactions with other molecules. Meanwhile, the delocalized 11c-2e multicenter bonds endowed remarkable superatomic characteristics to the Nb@Nb10 core, as shown in Fig. 8 [88], accompanied by an extremely large energy release in Nb11O15 formation. The HOMO–LUMO gap (142.8 kJ/mol) is appropriately smaller than that of Nb2O5, thus further indicating its potential application as cluster-genetic materials for Nb-related semiconductors.

3.5 Coinage Metal Clusters

In recent years, coinage metal (Au, Ag, and Cu) nanoclusters have been widely studied, and a variety of ligand-protected metal nanoclusters with high catalytic activity and photoluminescence have been synthesized [89–91]. The features of the s-band of coinage metals are close to the density of states of Group IA metals, indicating their comparable electronic structures with group alkali metals; however, these transition metals exhibit properties related to d-d electronic activity [92]. The general principles of the formation of coinage metal clusters and their stabilization mechanism in the gas phase must be studied. Despite their small bond energy (Cu–Cu bond at 201 kJ/mol; Ag–Ag at 162.9 kJ/mol; Au–Au at 226 kJ/mol), coinage metals bear relatively high sputtering rates and readily form metal clusters. Figure 9a presents the mass spectrum of cationic Agn+ clusters generated by the MagS source, and b and c anionic Agn− and Cun− clusters by the LaVa source and method, we prepared pure copper cluster anions Cun− (n = 7–37) as shown in Fig. 9c. Cun− clusters appeared similarly inert while reacting with a few small molecules such as NO, CO, and O2. The results highlighted the remarkable stability of the open-shell cluster Cu18−, which is comparable with that of the closed-shell clusters Cu17− and Cu19 [95]. The unpaired electron on the SOMO of Cu18− is mainly contributed by the copper atom in the central Cu atom with a charge of −1.06 |e|, thus implying the endohedral structure (Cu−@Cu17) with electrostatic shielding and electron transfer restriction during the reaction with the chemicals of electron acceptor.

4 Summary and Perspective

Gas-phase naked metal clusters provide an ideal model for studying catalytic activity, electronic and magnetic properties, and atomically precise reaction mechanisms. Although the preparation of pure metal clusters of tunable size distribution has been elucidated, challenges remain in this field, especially for some metals with a weak metal–metal bonding
or readily reacting with trace amounts of contamination. Metal cluster studies revealed the possibility of tailoring the unique properties of subnano metals, thus prompting the development of precise chemistry and benefiting atomically precise nanomanufacturing. In the future, the importance of metal cluster catalysis and cluster-genetic materials will be recognized. As a result, cluster soft-landing deposition, assembly, and printing will be adopted for the design of catalysts and functional materials at atomic and near-atomic scales.

Surface spectroscopy has been applied to study the electron transfer between the support and metal clusters (e.g., gold clusters on MgO) [55] and will progress with further research on supported metal clusters, especially the development of extended X-ray absorption fine structure spectroscopy [96]. In addition, the rapid development of electron microscopes, such as spherical aberration microscopes and cryo-electron microscopes, could bring significant contributions to cluster characterization. Advancements on cluster theory from the viewpoints of physics and chemistry [97], including superatom theory [98–104], will provide insights into the most primitive mechanism of nucleation and cluster formation and serve as a scientific basis for cluster-genetic materials and atomically precise manufacturing.

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Conflict of interest The authors declare no conflicts of interest.

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