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Keio University

Success in fabricating aluminum superatom substrates
—Development of novel functional nanostructured substrates for chemical conversion and sensors—

Professor Atsushi Nakajima, Project Associate Professor Masahiro Shibuta (at the time of research; currently Associate Professor at Osaka City University), and Assistant Professor Tomoya Inoue *et al.*, have succeeded in fabricating aluminum (Al) superatom^{*1} substrates by size-selectively depositing^{*2} Al nanoclusters which were synthesized in the gas phase on an organic substrate^{*3} pre-decorated with organic molecules, revealing that Al 13-mer superatoms were fixed to the surfaces in a negative ion state.

In order to overcome global environmental problems, it is crucial that a functional nanostructured substrate is developed to facilitate more efficient processes for chemical and energy conversion. Nanocluster superatoms are novel functional nanoscale units which are composed of several to several tens of atoms because nanocluster superatoms exhibit novel physical and chemical properties based on discrete electronic states mimicking that of an atom. However, there had been an intrinsic problem that nanocluster superatoms could not be stabilized on substrates owing to geometric deformations and the change in charge states through a nanocluster-substrate interaction, along with a methodological issue for the synthetic difficulty of efficient generation of nanocluster superatoms.

In this research, anionic Al 13-mer superatoms of Al_{13}^- were synthesized abundantly in a gas phase^{*4} and the Al_{13}^- superatoms were fixed onto a substrate orderly using the organic substrates pre-decorated by organic molecules such as C_{60} . In general, nanoscale aluminum-based materials exhibit extreme chemical reactivity and are instantly oxidized. However, the research group found that the oxidation reactivity rates of Al-superatom substrates could be reduced by about two digits by fabricating ordered assembled-films of Al_{13}^- superatoms. The results can be regarded highly useful in terms of developing functional nanostructured substrates with Al_{13}^- superatoms, leading to the creation of nanostructured functionalities toward the next generation chemical and energy conversions.

The results of this research were published in the academic journal “Nature Communication” on March 14, 2022.

1. Main Points of Research

- Nanocluster superatoms consisting of a specific number of atoms are known as novel functional units in atomic aggregates from several to several tens of atoms.
- The methodologies of synthesizing superatoms had not been established in terms of synthesizing large quantities and non-destructive immobilization on substrates.
- Researchers achieved large scale synthesis of aluminum 13-mer superatoms by a gas-phase

method, and immobilized anionic Al_{13}^- superatoms on well-defined substrates pre-decorated by organic molecules.

- Observations of the electronic states and chemical reactivities revealed that the supported Al_{13}^- superatoms are stably immobilized through substrate interactions associated with pre-decorated electron-donating molecules.

- Researchers expect that ordered functional nanostructures based on superatoms will facilitate the creation of highly efficient chemical transformation catalysts and energy conversion nanomaterials using common elements in the future.

2. Background of Research

“Nanocluster superatoms” (hereinafter simply “superatoms”) consisting of a specific number of atoms are known as novel functional units in atomic aggregates in the order of several to several tens of atoms, and are expected to be functional nanomaterial sources for global society in the next generation. For example, carbon 60-mer (C_{60} ; fullerene) is regarded as one of the representative superatoms, and it has been utilized widely as a material for, among other things, solar cells. The extensive search for new superatoms and the evaluations of their functionalities have been investigated through gas phase syntheses, leading to immobilizing the superatoms on solid substrates. The superatom substrates are expected to be applicable to the chemical catalysts using novel nanostructured materials with inexpensive metal elements and to energy conversion materials exhibiting high photoelectric conversion efficiency.

Above all, the anionic Al_{13}^- superatom, composed of 13 Al atoms and a negative charge, is one of the most studied superatoms, which are greatly stabilized by simultaneous geometric and electronic factors: closely-packed icosahedral structures in which an Al atom are symmetrically surrounded by 12 Al atoms and electron shell closings with the total number of 40 valence electrons (Fig. 1). The latter electronic stability of 40 electrons is attributed to completing electron shells by three valence electrons on each Al atom (39 electrons) together with a charge electron of the anion. Since the electronic feature in Al_{13} is similar to that of a fluorine or chlorine atom, Al_{13} is called a “halogen superatom.”

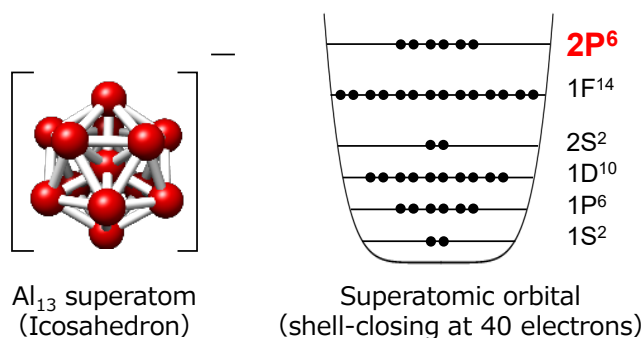


Fig. 1. Geometric and electronic structures of Al 13-mer anion (Al_{13}^- superatom)

In terms of the application of novel functional nanomaterials using superatoms, the methodologies had been required not only for synthesizing superatoms in a large-scale quantity but also for immobilizing superatoms non-destructively on substrates. Specifically, there are a lot of issues with superatom depositions, such as the structural deformation on a substrate surface, aggregation on a surface, and the loss of intrinsic natures of superatoms due to charge transfer between superatoms and the substrate. Furthermore, experts considered it difficult to immobilize Al_{13}^- superatoms on substrates because nanoscale aluminum-based materials exhibit extreme chemical reactivity and are instantly oxidized.

3. Content of Research and Results

◆ Surface immobilization of size-selected Al nanoclusters

This research group developed a gas-phase nanocluster generation apparatus (nanojima®),^{*5} enabling the synthesis of nanoclusters in a vacuum with large quantities and achieved massive synthesis of pure Al_{13}^- superatoms reaching 1 billion to 10 billion ions per second. Using the nanocluster source under soft-landing conditions while controlling the collisional energy to a substrate, Al_{13}^- superatoms are non-destructively deposited as a monolayer onto a substrate surface in a few hours.

Specifically, to realize the anionic charge state of Al_{13}^- superatoms on a substrate, the highly ordered organic substrate pre-decorated by coronene derivative molecules (HB-HBC)^{*6} was used as an electron-donor (*p*-type) organic substrate. For comparison, the organic substrate pre-decorated by an electron-acceptor (*n*-type) C_{60} was prepared for the substrate, and the electronic states and chemical reactivities were evaluated when Al_{13}^- superatoms were deposited on each organic substrate.

◆ The stability of Al 13-mer anion (Al_{13}^- superatoms)

The Al_{13}^- superatom substrates were fabricated by the deposition of Al_{13}^- on the pre-decorated by *n*-type (C_{60}) or *p*-type (HB-HBC) organic molecules in a well-ordered manner, and the Al_{13}^- substrates were transported to an X-ray photoelectron spectroscopy (XPS)^{*7} apparatus while keeping ultra-high vacuum conditions, where the charge state and chemical reactivity were evaluated. The oxidation state of the Al atom in Al_{13}^- superatoms deposited on *n*-type C_{60} organic substrate was +3 state (Fig. 2a bottom), showing that Al_{13} immediately reacted after the deposition of Al_{13}^- superatoms with residual gas like oxygen or water molecules even under ultra-high vacuum conditions. In fact, XPS spectra negligibly changed with further oxygen gas dosing (Fig. 2a top), indicating that Al_{13} were easily oxidized at the deposition onto *n*-type C_{60} substrate (Fig. 2b).

On the other hand, the oxidation state of Al atom in Al_{13}^- superatoms deposited on *p*-type HB-HBC organic substrate was metallic 0 valent state (Fig. 2c bottom), showing that individual Al_{13}^- superatoms were immobilized on the substrate monodispersely without oxidations. Moreover, in terms of the electronic state of *p*-type HB-HBC substrate, HB-HBC molecules were positively charged by donating an electron to Al_{13} . The results show that, as well as halogen elements like fluorine and chlorine atoms, halogen superatoms of Al_{13} were electronically stabilized on a *p*-type HB-HBC substrate as Al_{13}^- superatoms (Fig. 2d). The behavior can be rationalized by the local interactions between superatoms and the substrate while controlling the charge state (cation or anion) by pre-decorating appropriate organic molecules with respect to optimizing the properties of the substrate. This study could reveal a new strategy for designing organic substrates to create a functional substrates using superatoms as building blocks for nanostructured units.

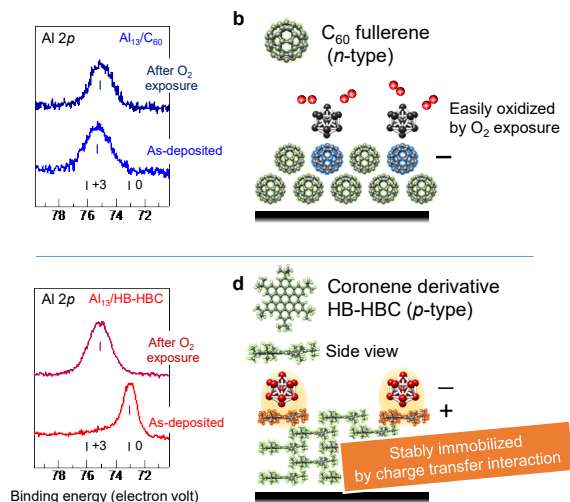


Fig. 2. XPS spectra for Al 2*p* (a, c) and schematic images of Al₁₃⁻ superatoms supported on an organic surface (b, d)

◆ Specific stability of Al₁₃⁻ superatoms

To examine the specific stability of Al₁₃⁻ superatoms on substrates, Al nanoclusters with a different number of constituent atoms (Al_{*n*}⁻; *n* is the number of constituent atoms, *n* = 7-24) were similarly synthesized and deposited on *p*-type HB-HBC organic substrates. The oxidative reactivities on each size of Al_{*n*}⁻ were evaluated by XPS measurements for Al_{*n*}⁻ nanocluster substrates before and after oxygen molecule exposure. In terms of the oxidative reactivities in Fig. 3, Al₁₃⁻ superatoms are about two digits more stable than other size Al_{*n*}⁻ nanoclusters. Thus, the size-selective deposition of Al_{*n*}⁻ nanoclusters with nanojima® apparatus enables us to reveal the importance of a specific number of atoms (13 Al atoms in this research) on a substrate including the local interaction between superatoms and the molecular substrate.

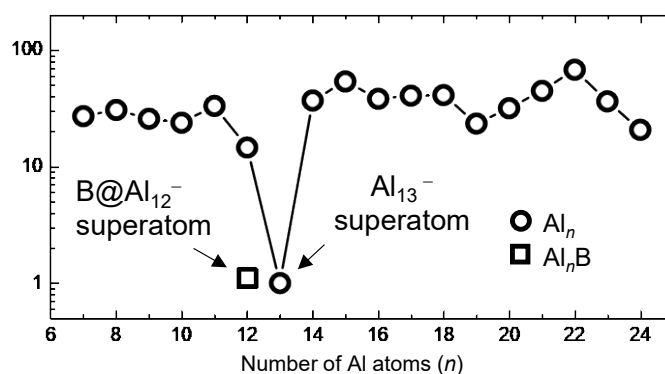


Fig. 3. The relative reactivity of supported Al nanoclusters against oxygen molecules showing the specific stabilities of Al₁₃⁻ and B@Al₁₂⁻ superatoms.

◆ Specific stability of boron encapsulating Al superatoms

The Al₁₃⁻ superatoms are geometrically stabilized by a closely-packed icosahedral structure in which 12 Al atoms symmetrically surround a central Al atom (Al@Al₁₂ structure, @ means encapsulation, [Fig. 1]). In this study, the geometric stability was examined by substituting the central Al atom for a boron (B) atom, which belongs to the same group in the periodic table, because a smaller B atom was anticipated to enhance the geometric packing. B@Al₁₂⁻ superatoms were generated using Al targets mixed with B elements and deposited on *p*-type HB-HBC substrate. The reactivity measurements against oxygen molecules showed that B@Al₁₂⁻

superatoms exhibit high chemical stability equal to or better than that of Al_{13}^- superatoms and that the B atom was encapsulated by the surrounding Al_{12} atoms. With respect to superatom formation, a method of combining different elements can widen the synthesizable superatoms and the controllability of chemical stability, while the number of constituent atoms is only a parameter for a single element nanocluster. In addition to Al_{13}^- superatoms, the formation stable B@Al_{12}^- superatoms will be important milestones for creating functional nanomaterials using superatoms.

4. Future Developments

This study in a bottom-up approach has successfully paved the road to utilize Al_{13}^- superatoms generated in the gas phase for functional nanomaterials, together with generating the know-how on supporting substrates with ordered organic substrate. Moreover, the finding of binary B@Al_{12}^- superatoms is promising in the exploration of research for novel functional nanostructures based on Al based superatoms. Future research involving the interdisciplinary study of superatoms and surface science based on this study is expected to pave the way for previously inconceivable next-generation functionalities of ordered nanostructure substrates that facilitate the creation of more efficient chemical transformation catalysts and energy conservation nanomaterials using common elements.

5. Special Notes

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<Terms>

※1 superatoms

One of nanoclusters in which atomic aggregates enhance a rational property mimicking a single atom in spite of aggregates of more than a few to tens of atoms.

※2 depositing

Immobilization of the nanoclusters or nanoparticles on the surfaces of solid or powder by adhesion.

※3 organic substrate

Highly-ordered substrate in which organic molecules are assembled as a thin film by vacuum vaporization to decorate a base substrate such as graphite.

※4 gas phase synthesis

The method for synthesizing chemical species with ions or plasma in an inert gas such as helium. Since the chemically pure species are generated under solvent-free conditions, low impurities are contaminated, and the method is applicable to synthesizing nanostructured species consisting of highly reactive metal elements. By combining a mass-selection technique, it is possible to deposit nanoclusters (included superatoms) onto a substrate for preparing atomically precise nanocluster assemblies.

※5 gas-phase nanocluster generation apparatus (nanojima®)

The apparatus for synthesizing pure nanoclusters without ligands efficiently in a gas phase with high power impulse magnetron sputtering (HiPIMS) method. Coupled with the deposition apparatus, nanoclusters can be deposited on substrates or powders in a non-destructive and monodisperse manner. The apparatus is called nanojima® by the trademark registration of ayabo Co. Ltd.

※6 HB-HBC

Hexa-*tert*-butyl-hexa-*per*-hexabenzocoronene (C₆₆H₆₆) is one of the polycyclic aromatic hydrocarbons and a planar organic molecule which act as a *p*-type organic semiconductor.

※7 X-ray photoelectron spectroscopy (XPS)

A spectroscopic method to measure the composition of sample material and the chemical binding environments of constituent elements by measuring the energy of photoelectrons emitted from X-ray irradiation for a sample.

Details of Journal Article

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