



Title of Project : On-demand synthesis of sub-nano hybrid alloy particles based on the periodic table

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【Purpose and Background of the Research】

Sub-nano particles have long been known as clusters in the field of physical chemistry (Fig.1). However, as a chemistry in the gas phase, it has not yet reached a material that can be freely synthesized. Due to laser evaporation, the number of atoms cannot be controlled and particles with any number of atoms are generated. Beside only a very small amount can be obtained. On the other hand, in recent years, synthetic methods of particles by strongly protecting them with a ligand such as alkanethiol has also been reported. However, it is limited to isolate magic number clusters with stable atomic numbers. With these synthesis methods, it is very difficult to perform precise synthesis by expanding to multiple elements and freely controlling the heteroatomic composition. Moreover, until now, there is currently no theoretical design for obtaining desired hybrid alloy particles.

This research aims to create atomically accurate sub-nano-sized hybrid alloy particles. ¹⁾

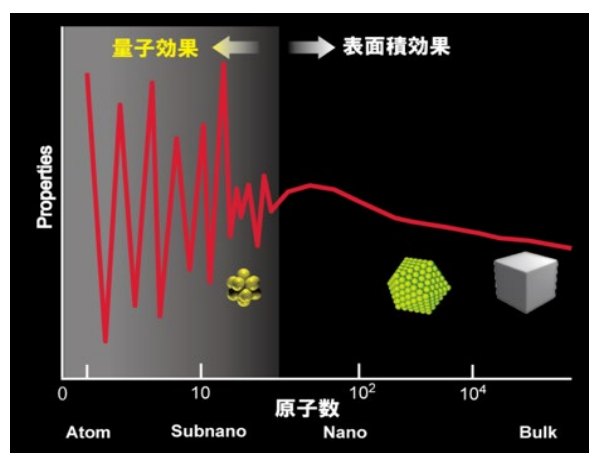


Fig. 1 Differences in physical properties between nano and sub-nano regions (the properties of the sub-nano region change depending on the number of atoms)

【Research Methods】

We have succeeded in developing phenylazo- methine dendrimers with a dendritic structure as a precision metal accumulation molecule. We discovered the unique multi-step radial complexation of metal salts, and established the world's first method (atomhybrid) to

integrate the number of atoms and the elemental composition ratio with atomic accuracy (Fig.2). For the first time, by this method, we have succeeded in synthesizing a sub-nano hybrid alloy containing 6 kinds of elements. In addition, the periodicity of the sub-nanoparticles based on the results of many sub-nanoparticles is discovered and we proposed it as the periodic table of the sub-nanoparticles. We aim to create sub-nano-sized hybrid alloy particles based on our unique method and periodic table. ²⁾

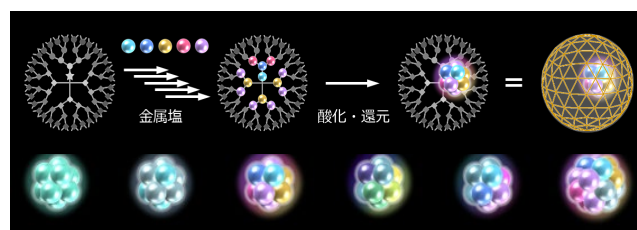


Fig. 2 Synthesis of superatom / sub-nanoalloy particles by dendrimer

【Expected Research Achievements and Scientific Significance】

This proposal is to anticipate the trend toward the sub-nano region, which has begun to start in the world, and to challenge the creation of desired sub-nano size alloy particles. It will be possible to explore sub-nano materials as solid chemistry on the substrate, not in the conventional vacuum. It will open up a new field of material chemistry, and it is expected that new materials will be created for highly active catalysts, super heat-resistant alloy particles, etc.

【Publications Relevant to the Project】

- 1) Takamasa Tsukamoto, Tetsuya Kambe, Takane Imaoka, Kimihisa Yamamoto, Modern cluster design based on experiment and theory, *Nat. Rev. Chem.* 2021, 5, 338-347.
- 2) Kimihisa Yamamoto, Takane Imaoka, Makoto Tanabe, Tetsuya Kambe, New Horizon of Nanoparticle and Cluster Catalysis with Dendrimers, *Chem. Rev.* 2020, 120, 1397-1437.

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