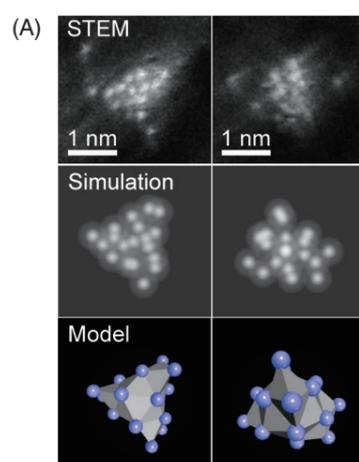


Structure of the Most Catalytically Active Platinum Cluster (Pt₁₉)

Structures of platinum metal subnanoparticles exhibiting significant catalytic activity for oxygen reduction reaction were studied by transmission and in-situ fluorescence mode XAFS in the electrochemical condition. In combination with other structural studies (HAADF-STEM, ESI-TOF-MS, DFT calculation), it was revealed that a common structural motif (atomic edge) was indicated as the highly active sites. We now describe that the structure and catalytic activity of these metal clusters are completely different from those of larger nanoparticles, and are quite sensitive to the atomicity because their structure strongly depends on the total atomicity.

Platinum nanoparticles are one of the most important materials for catalytic applications. Higher surface-to-volume ratio is desirable because the catalytic reaction takes place only at the nanoparticle surface. In principle, all atoms in a particle appear on the surface when the particle diameter is smaller than 1 nm. However, most previous studies indicated a dilemma that very small platinum nanoparticles lose their catalytic activities. The reason for this deactivation has been thought to be changes in the surface adsorption property caused by the different electronic property (*d*-band center) or different surface index profiles.

What is the structure of these platinum “subnanoparticles”? The structure of larger particles contains the face-centered-cubic (*fcc*) lattice which is easily determined by the X-ray diffraction method. However, the subnanoparticle does not exhibit such diffraction because the periodic lattice no longer exists. It has been found that the structure becomes amorphous due to the disappearance of the lattice pattern. With respect to catalytic applications, this change is unfavorable because the catalytic site is mainly related to specific surface indexes such as (100) or (111). This is thought to be another reason why very small nanoparticles are not suitable for catalytic applications. However, recent advances in single-atom catalysis clearly suggest that the lattice is not a requirement for efficient catalysis. Surprisingly, the science of subnanoparticles – an intermediate species between the nanoparticle and the single atom – is still a frontier at present.



We have developed a method of synthesizing metal subnanoparticles using a dendrimer reactor [1, 2]. This method allows the preparation of “one-atom” precise subnanoparticles based on the stoichiometric assembly of metal-complex precursors within a nanospace acting as a nano-size reactor [3]. In the case of platinum subnanoparticle synthesis, PtCl₄ is used for the precursor material, which could be reduced by NaBH₄ as a reducing agent. The reduced subnanoparticles produced within the dendrimer reactor have been determined by HAADF-STEM (high-angle-annular-dark-field scanning transmission electron microscope) observation or ESI-TOF-MS (electrospray-ionization time-of-flight mass spectrum). The HAADF-STEM observations indicated that the particle size is monodisperse. The atomicity of a subnanoparticle completely agreed with the equivalent amount of [PtCl₄]/[dendrimer]. When the equivalent was 12, only Pt₁₂ was formed.

Recently, our study revealed that Pt₁₉ is the best catalyst for the oxygen reduction reaction [4]. Although an increase of the equivalent to 19 resulted in a slight deviation from the monodisperse composition, the main product was still Pt₁₉ and the standard deviation was still ca. 1 atom. Direct observation of Pt₁₉ by aberration-corrected HAADF-STEM indicated the formation of a triangle-shaped subnanoparticle, which was predicted by a DFT calculation (Fig. 1).

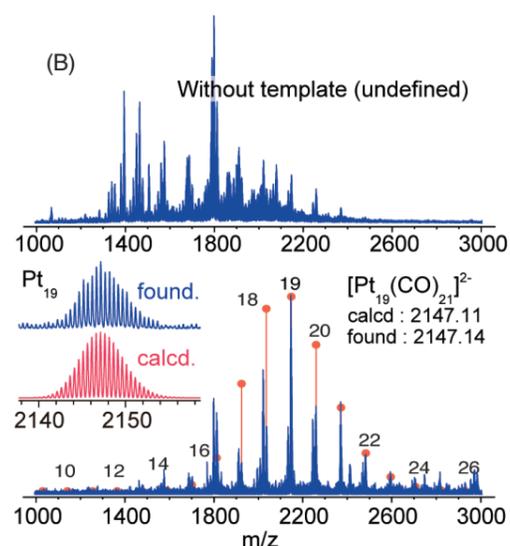


Figure 1: (A) High resolution HAADF-STEM images of a Pt₁₉ particle with the calculated model and simulated image, (B) ESI-TOF-MS of Pt₁₉ measured after the protection by carbonyl ligand (CO). The mass spectrum without any size control is also shown.

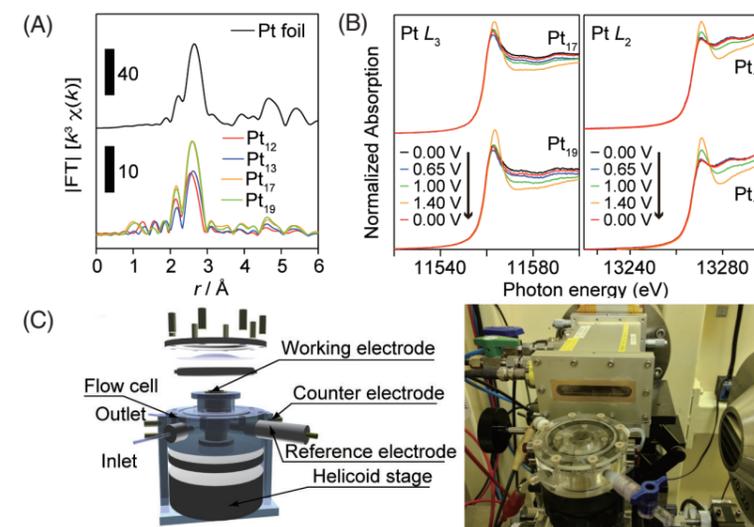


Figure 2: (A) Fourier transforms of the Pt-L₃ EXAFS by transmission mode measurements of Pt₁₂, Pt₁₃, Pt₁₇, Pt₁₉ and Pt-foil. (B) Pt-L₃ and -L₂ XANES spectra of Pt₁₇ and Pt₁₉ by fluorescence mode measurements taken in the *in-situ* electrochemical condition. The applied potential was changed between 0.00 V and 1.40 V vs. Ag/AgCl by the measurements. (C) A conceptual diagram and photograph of the *in-situ* cell.

X-ray absorption fine structure (XAFS) analysis provides access to the structural information of non-crystalline compounds. As noted earlier, metal subnanoparticles are diffraction-silent. Therefore, XAFS is the only analysis technique providing atomic-scale structural information. Pt-L₃ extended X-ray absorption fine structure (EXAFS) analysis of these platinum subnanoparticles elucidated that these compositions still have metal–metal bonds of which the average distance (2.74 Å) is slightly shorter than that of the corresponding bulk metal (2.77 Å). The subnanoparticles with different atomicities (Pt₁₂, Pt₁₃, Pt₁₇ and Pt₁₉) were not so different in terms of the metal–metal distances, suggesting that the electronic and bonding characters are almost identical. A small difference in the coordination number was confirmed, reflecting the difference in particle size (Fig. 2A).

It is curious that the catalytic activities of oxygen reduction reaction were significantly different between the platinum subnanoparticles with different atomicities despite the similar structures and electronic states. The highest activity was observed at Pt₁₉, exhibiting more than three times higher activity than that of Pt₁₃ as the stable “magic-number” cluster [4]. One possible reason is the difference in stability between the active and stable subnanoparticles. If Pt₁₉ was changed to other species during the catalysis, the difference could be explained. To confirm this assumption, *in-situ* XAFS measurement under the electrochemical condition was carried out (Fig. 2B, 2C). When the higher potential was applied to Pt₁₉, the Pt-L₃ and -L₂ XANES exhibited an obvious increase of the white line, suggesting oxidation. It is important to note that this XANES spectral change was reversible. When the applied potential was returned to 0 V vs. Ag/AgCl where platinum becomes a zero-valent metal, the initial XANES spectrum reappeared. This

fact negates the explanation that the apparent catalytic activity was controlled by the subnanoparticle stability. It was confirmed that the intrinsic activities of the subnanoparticles differ with the atomicity.

The DFT calculation and HAADF-STEM suggested that the subnanoparticles with different atomicity have a specific surface structure, which was quite different from that of the bulk surface such as Pt(111) or Pt(100). It was indicated that sharp V-shaped edges act as highly active sites for oxygen reduction reaction due to the suitable oxygen-binding energy.

The present result suggests that the character of subnanoparticles is quite different from that of the larger analogues and is strongly dependent on the atomicity. From this fact, it is predicted that the addition of second and third metals to the subnanoparticles might provide more significant modulation of properties than those of larger bimetallic or trimetallic alloy nanoparticles. These investigations are currently under way.

REFERENCES

- [1] K. Yamamoto, T. Imaoka, W.-J. Chun, O. Enoki, H. Katoh, M. Takenaga, A. Sonoi, *Nat. Chem.* **1**, 397 (2009).
- [2] K. Yamamoto and T. Imaoka, *Acc. Chem. Res.* **47**, 1127 (2014).
- [3] T. Imaoka, H. Kitazawa, W.-J. Chun, S. Omura, K. Albrecht and K. Yamamoto, *J. Am. Chem. Soc.* **135**, 13089 (2013).
- [4] T. Imaoka, H. Kitazawa, W.-J. Chun and K. Yamamoto, *Angew. Chem. Int. Ed.* **54**, 9810 (2015).

BEAMLINES

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