Precision Synthesis of Subnanoparticles Using Dendrimers as a Superatom Synthesizer

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ABSTRACT: Classical metal-based nanomaterials come in two prominent types: a mononuclear or multinuclear complex chemically stabilized by organic ligands or a nanoparticle (also called a nanorod, nanosheet, or nanocrystal) physically stabilized by inorganic or polymer supports. Over the last decade, a class of superatoms that lies between these categories of materials has attracted attention because their properties are dramatically different from those typically ascribed to their component elements. Typically the superatoms include a specific, low number of metallic atoms. Because a one-atom difference can alter the properties of these superatoms, their synthesis must be ultraprecise, requiring one-atom resolution.

To date, researchers have only been able to prepare monodisperse superatoms using gas-phase synthesis followed by purification through a flight tube. Though this technique provides monodisperse superatoms, it does not allow researchers to produce them in large quantites. Other researchers have proposed ligand-assisted liquid-phase synthesis as an alternative, but this technique is only useful for a few stable "magic number" clusters. Recently researchers have developed a new approach for the synthesis of superatoms that employs a novel class of molecular templates, which can define the number of metal ions or salts precisely. As a result, researchers can now synthesize nanoparticles or even subnanoparticles successfully. A dendrimer-type template has proven to be especially useful for ultraprecise control of the atomicity of the product, but it works with a full range of metal elements.

In this Account, we highlight recent advances in the precise preparation of metal-assembling complexes using the dendrimer as a template. Next we discuss the selective assembly of subnanoparticles that utilize the dendrimer as a superatom synthesizer. The resulting subnanoparticles are almost monodisperse, and as a result, some of them exhibited distinctive characteristics based on their atomicity. For example, because of the quantum-size effect, the reduction in particle size of TiO_2 and other metal-oxide subnanoparticles led to a significant shift in the band-gap energy. In addition, a miniaturized platinum particle less than 1 nm in diameter showed unexpectedly high catalytic activity for the oxygen reduction reaction (ORR) and other related reactions. Of particular note, in all these examples, this substantial change in their properties arose out of a single-atom difference in the atomicity. These results suggest that next-generation subnanoparticle design could play an important role in new materials and offer an additional palette of physical and chemical properties for new applications.
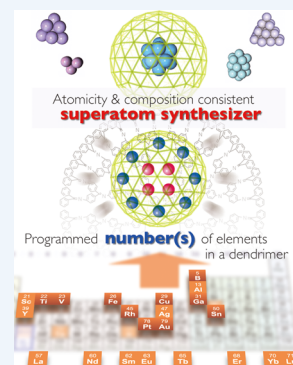
1. INTRODUCTION

Precision synthesis, using a fixed number of atoms, of inorganic fine metal particles with a size of less than 1 nm has rarely been achieved except in the case of extremely stable magic number clusters. Thus, synthesizing such subnanoparticles and identifying their properties are still unexplored territories.

In recent years, a new phenomenon has been uncovered, in that subnanoparticles consisting of up to several tens of metal atoms exhibit totally different characteristics from those of the constituent metal element, as if they were a totally different element. Such extremely small particles are sometimes referred to as "superatoms". For example, it has been reported that small particles consisting of 13 aluminum atoms exhibit the characteristics of a halogen (chlorine) and that particles consisting of 10 gold atoms exhibit the characteristics of platinum.[1−5] The concept of superatoms is attracting attention as a new approach that allows the development of "new elements".[6] At an atom count of approximately 30 or fewer, orbital degeneration occurs, and completely different electronic states emerge each time an atom is removed. Thus, subnanometer particles offer a completely different function-

ality for each discrete atom count, and a diagram classifying the function by a strict atom count must be prepared. Conventional methods are totally unable to address this situation. This highlights the importance of the precisely controlled number of atoms in the particles. Monodisperse subnanometer particles of semiconductors, oxides, and multielement alloys, which have been inaccessible targets in the past, exhibit new hidden functions due to the so-called "quantum size effects".

Conventionally, larger metal nanoparticles have been synthesized by the simple mixing of metallic elements and nucleation with appropriate ligands, surfactants, or supports.[7−10] However, the composition, size, and morphology of the products generally have a wide statistical distribution. This is similar to the case of the random polymerization of polymers, which leads to various degrees of polymerization and composition. When multiple metallic elements are made to react with each other, the composition of each individual particle in the final product often strongly deviates from the
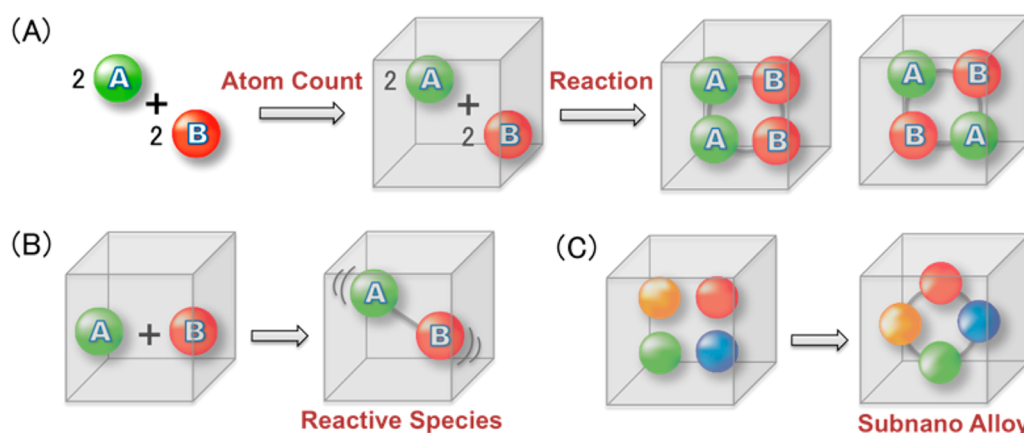
Figure 1. Concept of precision inorganic/metal synthesis. The important roles of nanosynthesizers. (A) Exact definition of the atomicity. (B) Entrapment of the reactive or unstable products. (C) Extension to a multielemental cluster system.
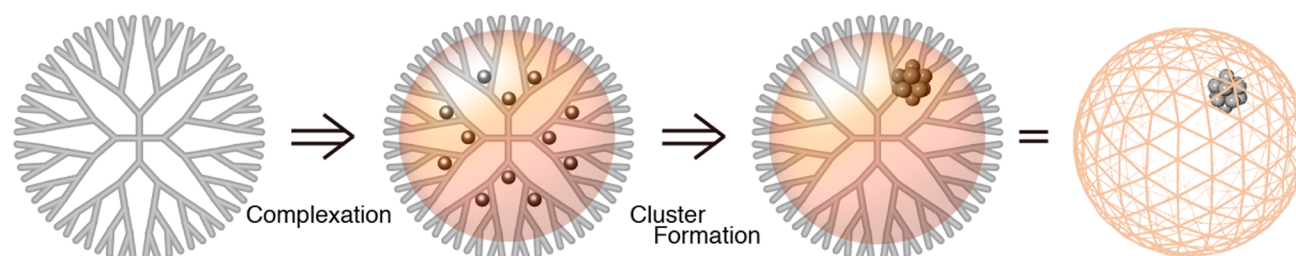

Figure 2. Schematic representation of the precision synthesis producing a fine metal particle by using a dendrimer as the nanosynthesizer.

initial feeding ratio; thus, fine particles of the desired composition cannot be prepared.

As one approach to reduce this statistical factor, a reaction carried out in nanospaces, such as reverse micelles,[11,12] mesoporous materials,[13] or molecular cages,[14] in which metals are assembled, has been considered. These methods just control the size of nanoparticles but not their atomicity by well-defined nanospaces reducing the extent of nanocrystal growth. It is, in principle, very difficult to carry out these reactions while freely controlling the composition of multiple metals and precisely determining the number of metal atoms without any distribution. Ideally, a special molecule is needed in which a fixed number of metal atoms can be accumulated in an isolated reaction field, allowing the numerical control but not the spatial control. That is, metal atoms can be freely assembled at a desired loading ratio in an enclosed space in order to carry out the following nucleation reaction; we refer to such a molecule as a "nanosynthesizer". If we utilized this nanosynthesizer, the precise synthesis of fine metal particles could be achieved (Figure 1). This approach is expected to be effective even for the observation of unstable inorganic intermediates, which could not be isolated in the past, and the synthesis of new alloys.

Although there has been no method available to date to precisely assemble metal atoms, phenylazomethine dendrimers, which the authors discovered, are unique molecules in which the number, location, and percentage of metal atoms can be precisely controlled.[15] They are exactly the type of material that meets the requirements of nanosynthesizers. The unique tree-like dendrimer structure is characterized by the fact that the outer layers have an increasing number of branches; thus the sheltering effect becomes greater. The fact that such molecules can function as capsules also meets the requirements of a

reaction container. We now propose the phenylazomethine dendrimer as a nanosynthesizer (Figure 2) in which dissimilar metal compounds can be assembled and reacted in the desired loading ratio.

2. PREPARATION OF METAL NANOPARTICLES USING DENDRIMERS

In recent years, dendrimers[16−18] have attracted attention as new polymer materials that support nanotechnology. General linear polymers have a molecular weight distribution, and precise nanoscale structural control is difficult by precision synthesis. On the other hand, in the case of dendrimers, control of the molecular size and synthesis of a single molecular weight species are possible by controlling the number of branchings (generations). In addition, functional sites can be selectively introduced at the core, on the main chains, and at the termini. Thus, they are promising polymer materials for the design of precise molecular structures (Figure 3).

Dendrimers are tree-like polymers, first proposed by Tomalia in 1985, and have a structure in which branching is repeated in an orderly manner from the core outward.[18] Dendrimers can be synthesized with molecular weights of over 10000 when they have a high generation number (typically over four generations) and are basically single-molecular-weight materials via a convergent synthetic route. This is important for their use as functional materials. Some commercial dendrimers are currently available, and their applications to functional materials and drug delivery systems have been attempted.[16,17] One interesting characteristic of dendrimers is the "shell effect".[19] In a high-generation (more branching) dendrimer, the molecular chain density of the outer layer becomes extremely high; therefore, mass transfer between the inside and outside of the dendrimer is restricted. With backbones rigid enough to retain
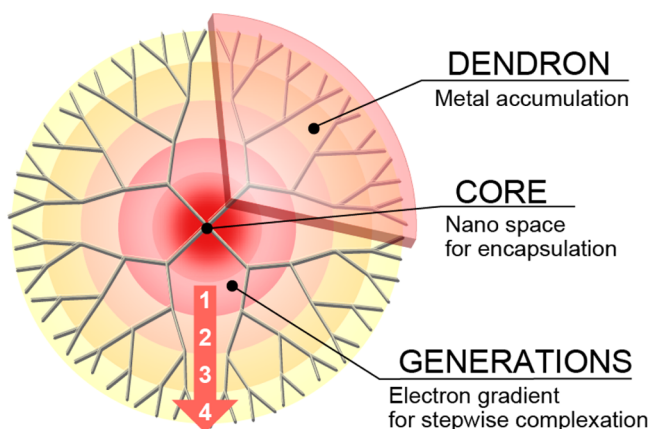
Figure 3. General design of a dendrimer.

the entire morphology, the dendrimer can retain a "dense-shell" configuration with a sufficient inner-nanospace,[20] which might be suitable for some chemical conversions inside.

To produce metal particles in the internal space of a dendrimer, a precursor metal salt is first formed and then chemically reduced (Figure 2). Complex formation between a dendrimer and a metal salt is utilized in order to incorporate the metal salt into the dendrimer. Thus far, a wide variety of dendrimer structures have been reported. Those used in the synthesis of nanoparticles are mostly polyamidoamine-type (PAMAM) dendrimers.[21] This is because a large number of nitrogen atoms are present in the molecular chain, associated with groups such as amines and amides. These have high coordination properties to various metal salts, and modification of the termini is easy.

Crooks et al. first prepared metal nanoparticles with sizes of 1−4 nm by carrying out a chemical reduction after introducing metal ions into a polyamidoamine (PAMAM) dendrimer through a complex formation.[22,23] To convert the precursor metal salt to nanoparticles, reduction using a reducing agent, such as $NaBH_4$, is generally carried out. Esumi et al. demonstrated a reagent-free photochemical reduction to Au nanoparticles,[24,25] having an advantage with respect to the purifications. The size of the metal particles is basically determined by the amount of metal that is incorporated. If multiple metal elements can be simultaneously introduced, it is possible to prepare bimetallic alloy nanoparticles.[26,27] The latest

literature reported finely size-controlled nanoparticles with only a ±10% standard deviation over a 1.5−3.0 nm region.[28,29] Because the molecular weight distribution of dendrimers is very narrow, the statistical distribution of the assembled metal precursors would be minimized versus the case of ordinary macromolecular ligands.

However, the application to subnanoparticles (superatoms) is still difficult because it is necessary to accurately control the amount of incorporated metal during the complex formation. The PAMAM dendrimer contains amines and amides with different coordination properties,[30] and multidentate coordination to metals easily takes place, so accurate control of the amount of metal is not possible. Although several studies have successfully synthesized apparently monodisperse metal subnanoparticles, the equimolar amounts of fed metal precursors for the dendrimer templates are different from the observed atomicity of the resulting particles.[31,32] These results indicated that when a PAMAM dendrimer is used, the average number of metal precursors is properly controlled with relatively narrow deviations, and the aggregation after the nucleation between particles in each encapsulating dendrimer molecule can be prevented. As a result, small nanoparticles can be prepared with narrow size distributions. On the other hand, the number of constituent atoms in the nanoparticle is not strictly controlled. Metal accumulation in the PAMAM dendrimer is entropically perturbed, and the number of accumulated metal ions (complexes) inevitably has a statistical distribution. These multiple coordination sites are averaged and seemingly equivalent, and there is a statistical distribution of the number of metal atoms. Despite their excellent availability developed for nanoparticle synthesis on a single-nanometer scale, it is still very difficult to precisely control the number of metal atoms that constitute a metal subnanoparticle. For strict control, a molecular reactor that can explicitly control the number of accumulated metal atoms is necessary.

3. PRECISE METAL ACCUMULATION ON PHENYLAZOMETHINE DENDRIMER

We have focused on a π-conjugated tree-like structure with a rigid skeleton. Thus, a dendrimer (Figure 4, DPAG4) having a phenylazomethine skeleton containing imine bonds, which function as strong coordination sites for metal ions, was synthesized. Furthermore, it was discovered that metal ions could be arranged at precise locations according to the electron
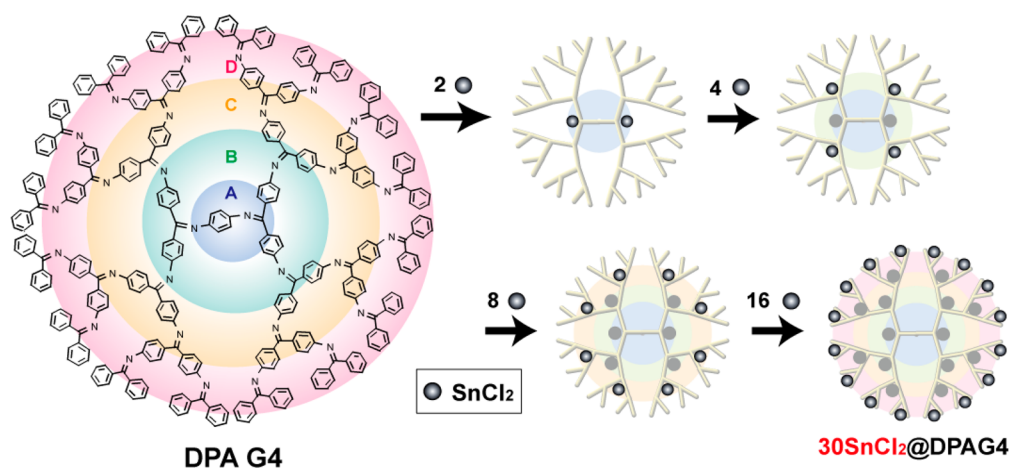

Figure 4. Schematic representation of layer-by-layer stepwise accumulation of metal chloride in phenylazomethine dendrimer (DPAG4).

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density gradient (electron gradient) on the imine nitrogen atoms of the respective generations. The degree of the gradient was surprisingly high, and a difference in the basicities (K_a) of the respective imine nitrogen groups on the neighboring layers is about 2 orders of magnitude.[33] Thus, the synthesis of a precise organic−metal hybrid material has become possible. This material is totally different from the conventional material in which metal ions and polymers are simply statistically mixed.

When stannous chloride ($SnCl_2$) was gradually added to phenylazomethines, a spectral change due to coordination with the imine nitrogen atoms was observed.[15] Based the observed variation, complex formation at a quantitative ratio of about one-to-one was confirmed. The UV−vis titration with a fourth-generation phenylazomethine dendrimer exhibited a gradual spectral change accompanying four isosbestic points in turn (Figure 5). If it were a random metal coordination with the
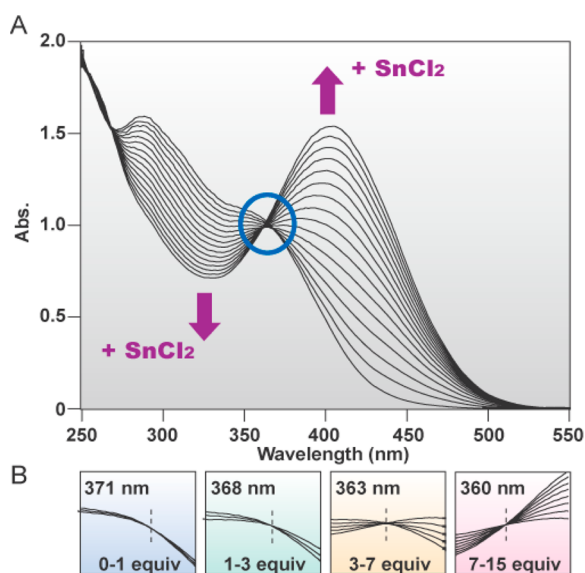

Figure 5. (A) UV−vis absorption spectra of DPAG4 upon the stepwise addition of $SnCl_2$. (B) Four independent isosbestic points appeared in turn indicating the stepwise complex formation.

imine sites, only one isosbestic point would be expected. The presence of four isosbestic points suggests that the complex formation proceeds in four steps. Furthermore, the added amounts until the switching were in perfect agreement with the number of imine nitrogen atoms in generations 1−4 of the dendrimer. Thus, metal ions are accumulated in a stepwise manner from the inner layer to the outer layer (Figure 4). Contrary to the common sense that complex formation by a multidentate ligand randomly takes place, this behavior reflects the electron gradient on the imines. Thus, coordination takes place in an orderly manner, and if the complex formation in a generation nearer the core is not completed, the next complex formation does not begin in the outer generations. This stepwise complex formation was verified by several methods such as the shift in the redox potential, fluorescence quenching, TEM, and partial chemical reduction of the skeleton, in addition to titration experiments combined with UV−vis absorption spectroscopy.[15,34] During this phenomenon, the statistical distribution is minimized when metal salt atoms completely fill the respective layers of the dendrimer (2, 6, 14, and 30 for dendrimer **1**). Thus, when 6 equiv of metal salt is added, for example, the six metal salt atoms fill the first layer

and the second layer in the equilibrium state of most dendrimer molecules. This unique multistep radial complex formation is an important phenomenon, in which a fixed number of metal atoms can be arranged at fixed locations within the dendrimer.

If this principle is expanded, it is possible to change the accumulation order by programming the electronic contribution of the dendrimer by chemical modification. The number of accumulated metal atoms is determined by the number of branch sections (dendrons) of the dendrimer and the accumulation order. Therefore, phenylazomethine dendrimer derivatives with one-substituted to four-substituted cores were synthesized (Chart 1). The respective dendrimers can form stepwise radial complexes. However, some dendrimers with an increased flexibility resulted in a distortion of the stepwise complexation,[35] suggesting the significant importance of the conformational shape persistence. The rigidity is a significant advantage against the conventional dendrimer ligands (e.g., PAMAM dendrimer) in terms of the numerical control for the accumulation. In particular, a dendrimer in which one phenyl group of the tetraphenyl core is replaced with a pyridine ring is used for the synthesis of a subnanoparticle with 13 metal atoms, namely, a magic number cluster.[36] Thus, far, different specific numbers of metal assembly were established by utilizing the metal accumulation method. This is particularly important for the case of 10−50 atoms, which are difficult to control using conventional gas-phase and liquid-phase methods.
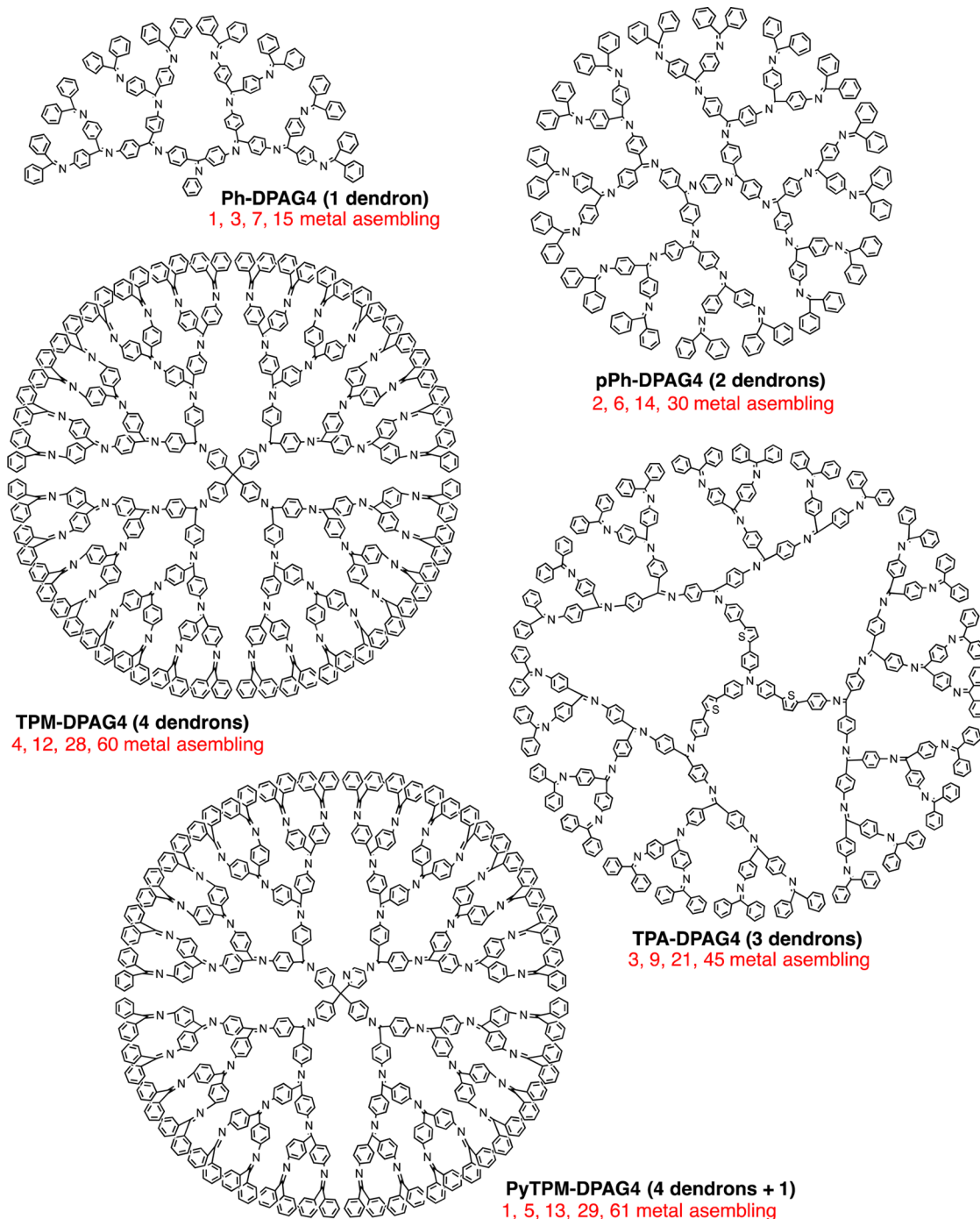
In addition to tin, a similar multistep complex formation with imines has been observed for the coordination of other metal salts such as $FeCl_3$, $AuCl_3$, VCl_3, $GaCl_3$, $CuCl_2$, and $PtCl_4$.[37−39] Thus, multielement heterometal accumulation into a quad-layered assembly has been realized by the precise accumulation of a fixed number of molecules in each layer, for example, two ferric chloride molecules in the first layer, four gallium chloride molecules in the second layer, eight gold chloride molecules in the third layer, and 16 stannous chloride molecules in the fourth layer (Figure 6).

4. FINE METAL OXIDE PARTICLES DISPLAYING QUANTUM SIZE EFFECTS

Even for metal particles without a band gap, the semiconducting properties may be displayed when they are miniaturized to nanometer sizes. For example, fluorescence emission, not plasmon emission, was observed for the metal nanoparticles of gold, platinum, and silver, which intrinsically display no fluorescence.[31,32,40] Such behavior can be explained by the quantum size effects, which take place when particle sizes enter the nanometer to subnanometer range. Here, the degeneracy of the electronic levels is lifted, so that they become split, and the bands are quantized. Thus, the quantum size effects can be realized by the precise control of the number of constituent metal atoms.

Titanium oxide (TiO_2) has been attracting attention as an optical functional material for applications such as photocatalysis, and the possibility of a size dependence of its optical properties is a subject of considerable interest. Although titanium oxide is the most well-known semiconducting material, its distinct quantum size effect has not been confirmed. Quantum size effects have been difficult to experimentally confirm because TiO_2 fine particles easily aggregate and have a large size dispersion. On the other hand, the semiempirical effective mass approximation method predicts the appearance of quantum size effects in titanium oxide for particle sizes of less than 1 nm. With DPA as a

Chart 1

Ph-DPAG4 (1 dendron)
1, 3, 7, 15 metal asembling

pPh-DPAG4 (2 dendrons)
2, 6, 14, 30 metal asembling

TPM-DPAG4 (4 dendrons)
4, 12, 28, 60 metal asembling

TPA-DPAG4 (3 dendrons)
3, 9, 21, 45 metal asembling

PyTPM-DPAG4 (4 dendrons + 1)
1, 5, 13, 29, 61 metal asembling

molecular reactor, TiO_2 nanoparticles were synthesized and their spectral characteristics were examined.[41] A single titanium−acetylacetone complex $(Ti(acac)Cl_3)$ forms a 1:1 adduct at each imine site of the DPA. Thus, the stoichiometric accumulation of a fixed number of titanium metal atoms is possible. In this way, the precise synthesis of subnanometer-sized particles is possible (Figure 7).

Dilute solutions of dendrimer complexes, in which 6, 14, and 30 equiv of $Ti(acac)Cl_3$ were accumulated, were then cast on mica substrates. TiO_2 was then formed in the dendrimers by hydrolysis in a HCl atmosphere (Figure 7). Because the dendrimer itself is an organic compound, it can be removed by decomposition following an annealing/ozone treatment. In this

way, nanodots consisting of TiO_2 particles with sizes of less than 1 nm are formed on the substrate. TEM and atomic force microscopy (AFM) confirmed that the particles produced using this method had about the size predicted by the crystal molecular model. By use of a dendrimer as the molecular reactor, synthesis of the smallest reported titanium oxide particles was thus achieved. In contrast, in a control sample produced without a dendrimer, aggregated particles with sizes of 2−3 nm were observed (Figure 8).

The UV−vis absorption spectra revealed that the bandgap of the TiO_2 nanoparticles showed a particle-size dependence. As the number of Ti atoms that constitute a nanoparticle changes from 30 to 14 to 6, the UV−vis absorption edge shifts to
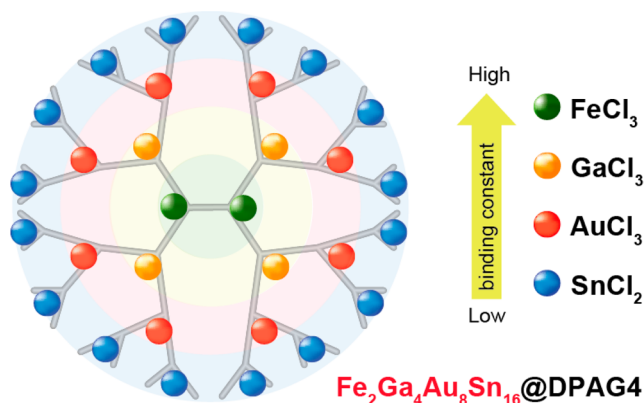
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Figure 6. Layer-by-layer precise heterometal accumulation of four-component metal salts.

shorter wavelengths. The bandgap increases from 3.2 to 4.05 eV as the particle size decreases from 1.2 ± 0.2 to 0.7 ± 0.1 nm. Thus, quantum size effects have been confirmed for the first time in titanium oxide (Figure 9).

5. SYNTHESIS OF SUBNANOMETER PLATINUM PARTICLES

Metal surfaces can act as platforms for a range of catalytic reactions. If metal particles are miniaturized, the fraction of surface atoms in the particles drastically increases. For icosahedral or face-centered cubic Pt nanoparticles, the number of atoms in a particle with 10 shell layers is 3871, and the particle size is 5.8 nm. The percentage of surface atoms is about 25%. For a Pt particle with five shell layers, the number of atoms is 561, and the percentage of surface atoms is about 45%. However, for a particle made up of a single shell layer, the number of atoms is 13, the particle size is 0.8 nm, and the percentage of surface atoms is 92%. This means that 12 atoms out of 13 atoms are exposed. However, the surface reactivity of very small particles is extremely high, and aggregation very easily takes place. In order to prevent this, surface protection is necessary, for example, by using micelles. However, a disadvantage of this is that the active surface becomes consumed by the protective agent with the resulting loss of catalytic activity. In an ideal nanoparticle catalyst, the nanoparticles themselves are protected by cage-like molecules with few contacts, and the activity is maintained by easy penetration of a substrate through the gaps in the protecting material. The molecular structure of a dendrimer thus makes it quite suitable for use as a molecular reactor having such a function (Figure 2).

In fact, nanoparticle catalysts of dendrimer-protected metallic elements, such as Pd,[24,42−44] Pt,[45,46] and Rh,[47] and their alloys[48] have been reported, and each shows unique characteristics.

For example, if a complex in which platinum(IV) chloride is accumulated in a phenylazomethine dendrimer with tetraphenylmethane as the core is used as a precursor, nanoparticles with a strictly controlled number of platinum atoms can be synthesized (Figure 2).[49] Like other metal chlorides, $PtCl_4$ forms 1:1 complexes with the imine groups of DPA. Platinum nanoparticles can be prepared by reducing this metal-accumulated complex using a $NaBH_4$ solution. Based on TEM observations of nanoparticles synthesized by accumulating 12, 28, and 60 platinum atoms, the corresponding particle sizes were 0.9, 1.0, and 1.2 nm, respectively (Figure 10).

Extended X-ray absorption fine structure (EXAFS) spectra showed that the Pt–Pt coordination number is quite low as expected from the particle size of less than 1 nm. It was also confirmed by XPS that the electronic states of the nanoparticles are slightly more deficient in d electrons compared with the bulk platinum.

Evaluation of the oxygen reduction catalytic activity of platinum nanoparticles was carried out by rotating disk voltammetry (RDV). The catalytic activity increased in proportion to the mass of the catalyst loaded on the electrode surface (Figure 11). It was possible to estimate the activity per unit catalyst weight from the slope of the straight line. It was found that the catalytic activity improves with the decreasing nanoparticle size. Surprisingly, the previously accepted notion was disregarded since it was clarified that the smallest nanoparticles with 12 platinum atoms exhibited a 13 times higher catalytic activity than a conventional commercial carbon-supported platinum fine particle catalyst (particle size 2−4 nm) (Figure 11). Thus, the highest catalytic activity is obtained for particles with a little over 10 platinum atoms, which overturns the common belief that the optimum particle size in an oxidation−reduction catalyst for fuel cells is 3−5 nm.

6. ONE-ATOM CONTROL IN SUBNANOPARTICLES: AN IMPACT ON THE CATALYTIC ACTIVITY

Of particular importance is that the high activity cannot be explained only by the advantage due to an increased surface-to-volume ratio of Pt_{12} versus Pt_{28} or larger particles. Finding this unexpectedly high catalytic activity of Pt_{12} has lead us to reveal its geometric and electronic structures. What is the structure of the Pt_{12} subnanoparticle? It has been well characterized that the bulk crystal and the larger nanoparticles (∼2 nm) of platinum have a face-centered-cubic (FCC) close-packed structure.[50,51] If the size approaches 1 nm, the icosahedral close-packed structure becomes preferential.[52,53] For the Pt_{13} particle, as a stable magic number cluster, the highly symmetric icosahedral geometry was characterized by an X-ray crystallographic analysis.[54] Every Pt atom in Pt_{13} is a prerequisite of the highly symmetric structure. Therefore, Pt_{12} should have a completely dissimilar structure from the larger ones. To experimentally elucidate this, we also synthesized a Pt_{13} subnanoparticle by the
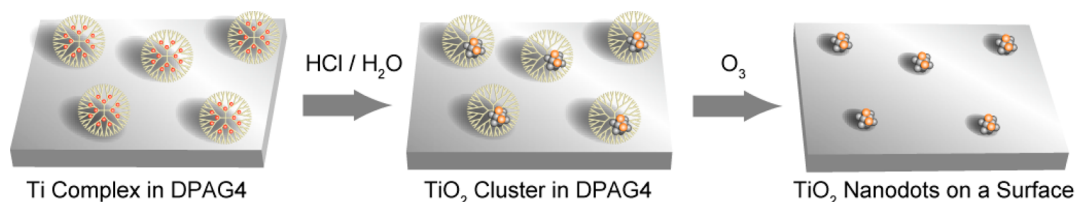

Figure 7. Preparation of subnanometer TiO_2 particles on a surface using a dendrimer as the template by successive hydrolysis and template removal.
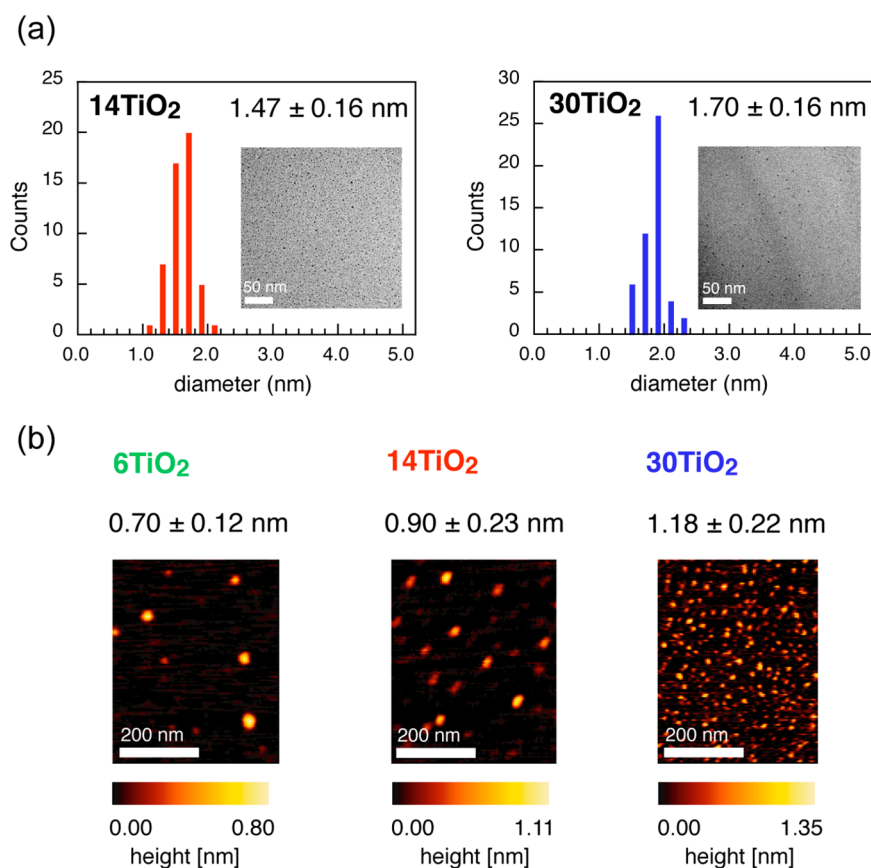
(a)

(b)

6TiO$_2$ **14TiO$_2$**   **30TiO$_2$**

0.70 ± 0.12 nm   0.90 ± 0.23 nm   1.18 ± 0.22 nm

Figure 8. (a) TEM and (b) AFM images of the titanium oxide nanoparticles ($[TiO_2]_6$, $[TiO_2]_{14}$, and $[TiO_2]_{30}$) synthesized by a thermolysis method using the dendrimer reactor from the corresponding metal assembling complexes under different stoichiometric conditions.
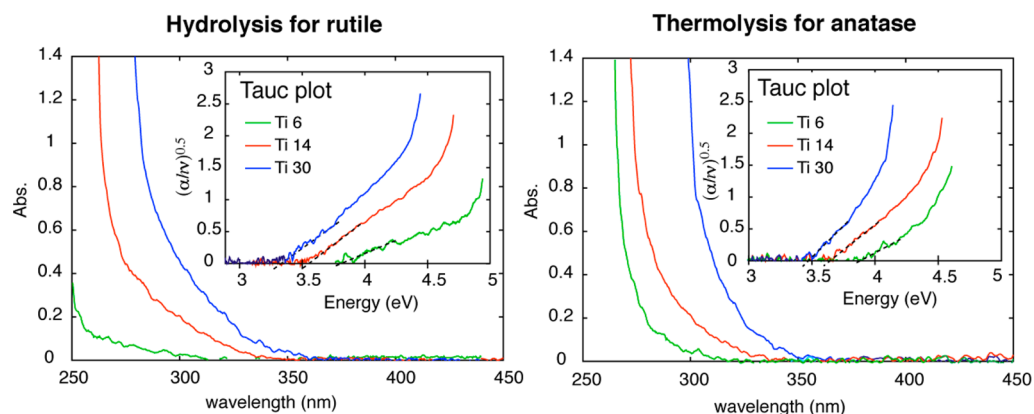

Figure 9. UV−vis absorption spectra of TiO$_2$ nanoparticles with different sizes and different preparation methods measured on an optical waveguide. The insets show Tauc plots of these samples exhibiting their bandgap energies.

same strategy but using a special dendrimer template for the magic number Pt$_{13}$ cluster.[36]

The as-synthesized Pt$_{12}$ and Pt$_{13}$ particles were surprisingly monodispersed. The ESI-TOF-mass spectroscopic analysis of the carbonyl-protected particles showed that this synthetic technique allows a one-atom precision synthesis (Figure 12), and each particle (Pt$_{12}$ and Pt$_{13}$) can be selectively synthesized. Indeed, the previous ligand-assisted synthesis of monodispersed metal particles was available only for a stable species with a magic number of the metal atoms composed of one cluster. Against this synthesis, the most important advantage of the superatom synthesizer approach is the applicability to non-magic number species, which could never be synthesized by the

other method. The applicability of the previous method only depends on its own stability of the target subnanoparticle. In sharp contrast, the template method can be applied to a variety of precise metal-assembling structures in which the metal chlorides completely fill the respective layers of the dendrimer.

In combination with the EXAFS analysis, we obtained information about the structures of each compound. The structure of Pt$_{13}$ prepared by this method was proven to be icosahedral. This cluster-valence electron (CVE) determined by an ESI-TOF-mass measurement completely agreed with that of the previous value,[54] and a fitting result of the EXAFS data supported this idea. Therefore, how about Pt$_{12}$? The calculated valence electrons (CVE = 154) for such a 12-nuclear cluster
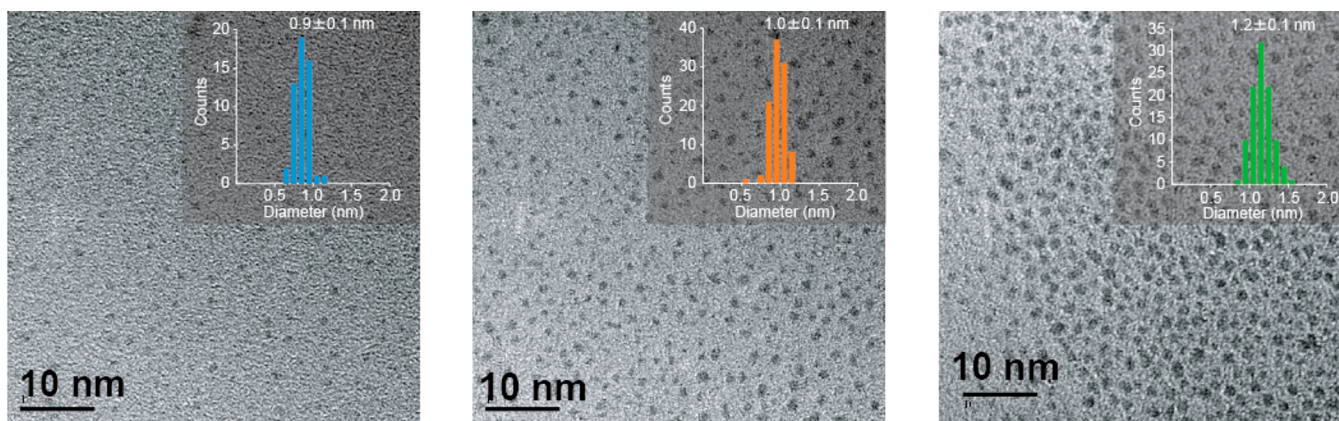
Figure 10. TEM images of precision-synthesized platinum nanoparticle catalysts: Pt_{12} (left), Pt_{28} (middle), Pt_{60} (right). The insets show histograms of their particle size distribution.
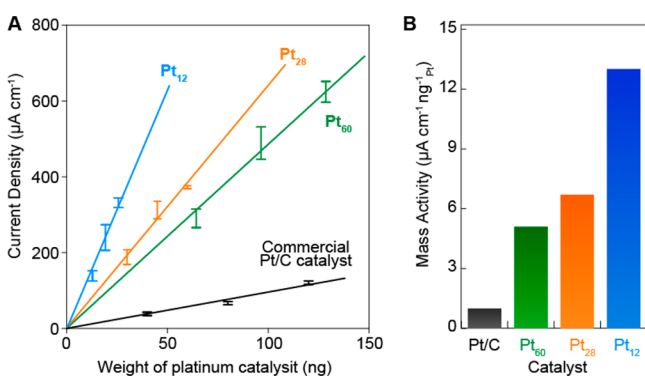

Figure 11. Comparison of kinetic limiting currents (left) and the catalytic performances normalized by the weight of platinum (right) for different size nanoparticle catalysts.
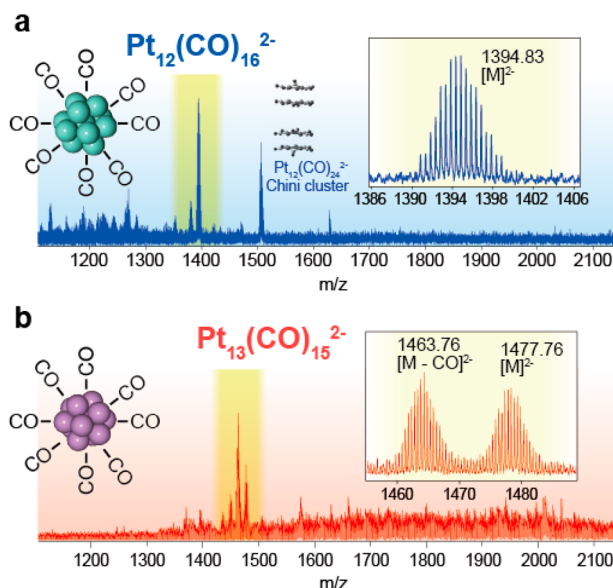

Figure 12. Negative mode ESI-TOF mass spectra of the as-synthesized (a) Pt_{12} and (b) Pt_{13} particles in their carbonyl-protected form. Insets are the enlargements in the target mass ranges. From the isotope patterns, these species are characterized as divalent anions. Reprinted with permission from ref 55. Copyright 2013 American Chemical Society.

have never been previously reported to the best of our knowledge. The EXAFS data also indicated a structure different from that for Pt_{13}. One possible Pt_{12} structure predicted by a DFT calculation satisfying these structural analysis results was quite distorted from the highly symmetric icosahedron of Pt_{13}.[55]

Not only the structures but also the catalytic activities of Pt_{12} and Pt_{13} were not alike. Surprisingly, the oxygen reduction catalytic activity of Pt_{12} was ca. 2.5-fold higher than that of Pt_{13}, although the difference in the composition was only one platinum atom per a dozen of the atoms comprising one subnanoparticle. In the fuel-cell research community, a common notion was that a platinum nanoparticle smaller than the best one with ca. 3 nm diameter has a lower catalytic activity. Even now, we can say that this common notion is still alive above 1 nm. However, within a subnanometer scale, a structure-specific activity may occasionally break the rule. A typical example is the present Pt_{12} subnanoparticle. In general, larger nanoparticles have a substantial size distribution, which would lead to an averaged functional property of the particles. Subnanoparticles with a very narrow size distribution might be mainly composed of a particle with a specific formula. If the formula only allows an odd particle structure, many kinds of surface facets would appear in some cases. The case of Pt_{12} was nothing short of this specific instance.

7. CONCLUSIONS

The precise synthesis of inorganic nanoparticles with a controlled number of metal atoms was achieved using a nanosynthesizer in which a precise number of metal complexes can be accumulated. This approach is extremely general and is applicable, in principle, to all metallic elements that can be accumulated in the dendrimer. Although this report dealt only with titanium oxide and platinum, it is expected that the proposed method in the future will be applied to the synthesis of a variety of superatoms. It has already been reported that by controlling the composition ratio of the iron–rhodium heteroparticles, a much higher hydrogenation–reduction catalytic activity was achieved than that for the Wilkinson complex catalyst or rhodium-only particles.[48]

In this Account, it was reported that the properties of platinum and titanium oxide subnanoparticles are strongly influenced by their particle size, so that they can be considered to be a type of superatom. Furthermore, since there are 67 naturally occurring metallic elements, an enormous number of

combinations is possible. Therefore, precision inorganic metal syntheses using a phenylazomethine dendrimer derivative as a nanosynthesizer are expected to lead to the creation of a large number of as-yet-unknown inorganic functional materials and open up the field of nanomaterials.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Bergeron, D. E.; Roach, P. J.; Castleman, A. W.; Jones, N. O.; Khanna, S. N. Al Cluster Superatoms as Halogens in Polyhalides and as Alkaline Earths in Iodide Salts. *Science* **2005**, *307*, 231−235.

(2) Reimers, J. R.; Wang, Y.; Cankurtaran, B. O.; Ford, M. J. Chemical Analysis of The Superatom Model for Sulfur-Stabilized Gold Nanoparticles. *J. Am. Chem. Soc.* **2010**, *132*, 8378−8384.

(3) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. A Unified View of Ligand-Protected Gold Clusters as Superatom Complexes. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 9157−9162.

(4) Walter, M.; Moseler, M.; Whetten, R. L.; Häkkinen, H. A 58-Electron Superatom-Complex Model for the Magic Phosphine-Protected Gold Clusters (Schmid-Gold, Nanogold) of 1.4-nm Dimension. *Chem. Sci.* **2011**, *2*, 1583.

(5) Häkkinen, H. Atomic and Electronic Structure of Gold Clusters: Understanding Flakes, Cages and Superatoms from Simple Concepts. *Chem. Soc. Rev.* **2008**, *37*, 1847−1859.

(6) Castleman, A. W., Jr.; Khanna, S. N. Clusters, Superatoms, and Building Blocks of New Materials. *J. Phys. Chem. C* **2009**, *113*, 2664−2675.

(7) Bruix, A.; Rodriguez, J. A.; Ramírez, P. J.; Senanayake, S. D.; Evans, J.; Park, J. B.; Stacchiola, D.; Liu, P.; Hrbek, J.; Illas, F. A New Type of Strong Metal−Support Interaction and the Production of H$_2$ through the Transformation of Water on Pt/CeO$_2$(111) and Pt/CeO(X)/TiO$_2$(110) Catalysts. *J. Am. Chem. Soc.* **2012**, *134*, 8968−8974.

(8) Gotoh, K.; Hashimoto, H.; Kawai, R.; Nishina, Y.; Fujii, E.; Ohkubo, T.; Itadani, A.; Kuroda, Y.; Ishida, H. Arrangement and Dispersion of Rh and Pt Atoms on Graphene Oxide Sheets. *Chem. Lett.* **2012**, *41*, 680−682.

(9) Liang, Y.; Li, Y.; Wang, H.; Dai, H. Strongly Coupled Inorganic/Nanocarbon Hybrid Materials for Advanced Electrocatalysis. *J. Am. Chem. Soc.* **2013**, *135*, 2013−2036.

(10) Mostafa, S.; Behafarid, F.; Croy, J. R.; Ono, L. K.; Li, L.; Yang, J. C.; Frenkel, A. I.; Cuenya, B. R. Shape-Dependent Catalytic Properties of Pt Nanoparticles. *J. Am. Chem. Soc.* **2010**, *132*, 15714−15719.

(11) Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A. Chemistry and Properties of Nanocrystals of Different Shapes. *Chem. Rev.* **2005**, *105*, 1025−1102.

(12) Cushing, B. L.; Kolesnichenko, V. L.; O'Connor, C. J. Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles. *Chem. Rev.* **2004**, *104*, 3893−3946.

(13) Kónya, Z.; Puntes, V. F.; Kiricsi, I.; Zhu, J.; Ager, J. W.; Ko, M. K.; Frei, H.; Alivisatos, P.; Somorjai, G. A. Synthetic Insertion of Gold Nanoparticles into Mesoporous Silica. *Chem. Mater.* **2003**, *15*, 1242−1248.

(14) Suzuki, K.; Sato, S.; Fujita, M. Template Synthesis of Precisely Monodisperse Silica Nanoparticles within Self-Assembled Organometallic Spheres. *Nat. Chem.* **2009**, *2*, 25−29.

(15) Higuchi, M.; Tsuruta, M.; Chiba, H.; Shiki, S.; Yamamoto, K. Control of Stepwise Radial Complexation in Dendritic Polyphenylazomethines. *J. Am. Chem. Soc.* **2003**, *125*, 9988−9997.

(16) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. About Dendrimers: Structure, Physical Properties, and Applications. *Chem. Rev.* **1999**, *99*, 1665−1688.

(17) Fischer, M.; Vögtle, F. Dendrimers: From Design to Application − A Progress Report. *Angew. Chem., Int. Ed.* **1999**, *38*, 884−905.

(18) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. A New Class of Polymers: Starburst-Dendritic Macromolecules. *Polym. J.* **1985**, *17*, 117−132.

(19) Hecht, S.; Fréchet, J. M. Dendritic Encapsulation of Function: Applying Nature's Site Isolation Principle from Biomimetics to Materials Science. *Angew. Chem., Int. Ed.* **2001**, *40*, 74−91.

(20) Ballauff, M.; Likos, C. N. Dendrimers in Solution: Insight from Theory and Simulation. *Angew. Chem., Int. Ed.* **2004**, *43*, 2998−3020.

(21) Bronstein, L. M.; Shifrina, Z. B. Dendrimers as Encapsulating, Stabilizing, or Directing Agents for Inorganic Nanoparticles. *Chem. Rev.* **2011**, *111*, 5301−5344.

(22) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. Dendrimer-Encapsulated Metal Nanoparticles: Synthesis, Characterization, and Applications to Catalysis. *Acc. Chem. Res.* **2001**, *34*, 181−190.

(23) Scott, R. W. J.; Wilson, O. M.; Crooks, R. M. Synthesis, Characterization, and Applications of Dendrimer-Encapsulated Nanoparticles. *J. Phys. Chem. B* **2005**, *109*, 692−704.

(24) Esumi, K.; Isono, R.; Yoshimura, T. Preparation of PAMAM− and PPI−Metal (Silver, Platinum, and Palladium) Nanocomposites and Their Catalytic Activities for Reduction of 4-Nitrophenol. *Langmuir* **2004**, *20*, 237−243.

(25) Esumi, K.; Matsumoto, T.; Seto, Y.; Yoshimura, T. Preparation of Gold−Gold/Silver−Dendrimer Nanocomposites in The Presence of Benzoin in Ethanol by UV Irradiation. *J. Colloid Interface Sci.* **2005**, *284*, 199−203.

(26) Chung, Y.-M.; Rhee, H.-K. Dendrimer-Templated AgPd Bimetallic Nanoparticles. *J. Colloid Interface Sci.* **2004**, *271*, 131−135.

(27) Scott, R. W. J.; Datye, A. K.; Crooks, R. M. Bimetallic Palladium-Platinum Dendrimer-Encapsulated Catalysts. *J. Am. Chem. Soc.* **2003**, *125*, 3708−3709.

(28) Myers, V. S.; Weir, M. G.; Carino, E. V.; Yancey, D. F.; Pande, S.; Crooks, R. M. Dendrimer-Encapsulated Nanoparticles: New Synthetic and Characterization Methods and Catalytic Applications. *Chem. Sci.* **2011**, *2*, 1632−1646.

(29) Anderson, R. M.; Zhang, L.; Loussaert, J. A.; Frenkel, A. I.; Henkelman, G.; Crooks, R. M. An Experimental and Theoretical Investigation of the Inversion of Pd@Pt Core@Shell Dendrimer-Encapsulated Nanoparticles. *ACS Nano* **2013**, *7*, 9345−9353.

(30) Ottaviani, M.; Bossmann, S.; Turro, N.; Tomalia, D. A. Characterization of Starburst Dendrimers by the EPR Technique. 1. Copper Complexes in Water Solution. *J. Am. Chem. Soc.* **1994**, *116*, 661−671.

(31) Zheng, J.; Petty, J. T.; Dickson, R. M. High Quantum Yield Blue Emission from Water-Soluble Au_8 Nanodots. *J. Am. Chem. Soc.* **2003**, *125*, 7780−7781.

(32) Tanaka, S.-I.; Miyazaki, J.; Tiwari, D. K.; Jin, T.; Inouye, Y. Fluorescent Platinum Nanoclusters: Synthesis, Purification, Characterization, and Application to Bioimaging. *Angew. Chem., Int. Ed.* **2011**, *50*, 431−435.

(33) Yamamoto, K.; Higuchi, M.; Kimoto, A.; Imaoka, T.; Masachika, K. Novel Functional Groups with Fine-Controlled Metal Assembling Function. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 349−355.

(34) Imaoka, T.; Tanaka, R.; Arimoto, S.; Sakai, M.; Fujii, M.; Yamamoto, K. Probing Stepwise Complexation in Phenylazomethine Dendrimers by a Metallo-Porphyrin Core. *J. Am. Chem. Soc.* **2005**, *127*, 13896−13905.

(35) Imaoka, T.; Tanaka, R.; Yamamoto, K. Investigation of a Molecular Morphology Effect on Polyphenylazomethine Dendrimers; Physical Properties and Metal-Assembling Processes. *Chem.—Eur. J.* **2006**, *12*, 7328−7336.

(36) Kitazawa, H.; Albrecht, K.; Yamamoto, K. Synthesis of a Dendrimer Reactor for Clusters with a Magic Number. *Chem. Lett.* **2012**, *41*, 828−830.

(37) Takanashi, K.; Fujii, A.; Nakajima, R.; Chiba, H.; Higuchi, M.; Einaga, Y.; Yamamoto, K. Heterometal Assembly in Dendritic Polyphenylazomethines. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1563−1572.

(38) Enoki, O.; Imaoka, T.; Yamamoto, K. One-Step Synthesis of A Platinum Nanoparticle with Carbon Materials Using a Phenylazomethine Dendrimer as a Template. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 621−626.

(39) Yamamoto, K.; Kawana, Y.; Tsuji, M.; Hayashi, M.; Imaoka, T. Additive-Free Synthesis of Poly(phenylene oxide): Aerobic Oxidative Polymerization in a Base-Condensed Dendrimer Capsule. *J. Am. Chem. Soc.* **2007**, *129*, 9256−9257.

(40) Zheng, J.; Dickson, R. M. Individual Water-Soluble Dendrimer-Encapsulated Silver Nanodot Fluorescence. *J. Am. Chem. Soc.* **2002**, *124*, 13982−13983.

(41) Satoh, N.; Nakashima, T.; Kamikura, K.; Yamamoto, K. Quantum Size Effect in TiO_2 Nanoparticles Prepared by Finely Controlled Metal Assembly on Dendrimer Templates. *Nat. Nanotechnol.* **2008**, *3*, 106−111.

(42) Chechik, V.; Crooks, R. M. Dendrimer-Encapsulated Pd Nanoparticles as Fluorous Phase-Soluble Catalysts. *J. Am. Chem. Soc.* **2000**, *122*, 1243−1244.

(43) Diallo, A. K.; Ornelas, C.; Salmon, L.; Ruiz Aranzaes, J.; Astruc, D. "Homeopathic" Catalytic Activity and Atom-Leaching Mechanism in Miyaura−Suzuki Reactions under Ambient Conditions with Precise Dendrimer-Stabilized Pd Nanoparticles. *Angew. Chem., Int. Ed.* **2007**, *46*, 8644−8648.

(44) Ooe, M.; Murata, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. Dendritic Nanoreactors Encapsulating Pd Particles for Substrate-Specific Hydrogenation of Olefins. *Nano Lett.* **2002**, *2*, 999−1002.

(45) Huang, W.; Kuhn, J. N.; Tsung, C.-K.; Zhang, Y.; Habas, S. E.; Yang, P.; Somorjai, G. A. Dendrimer Templated Synthesis of One Nanometer Rh and Pt Particles Supported on Mesoporous Silica: Catalytic Activity for Ethylene and Pyrrole Hydrogenation. *Nano Lett.* **2008**, *8*, 2027−2034.

(46) Ye, H.; Crooks, R. M. Electrocatalytic O_2 Reduction at Glassy Carbon Electrodes Modified with Dendrimer-Encapsulated Pt Nanoparticles. *J. Am. Chem. Soc.* **2005**, *127*, 4930−4934.

(47) Nakamula, I.; Yamanoi, Y.; Yonezawa, T.; Imaoka, T.; Yamamoto, K.; Nishihara, H. Nanocage Catalysts-Rhodium Nanoclusters Encapsulated with Dendrimers as Accessible and Stable Catalysts for Olefin and Nitroarene Hydrogenations. *Chem. Commun.* **2008**, 5716−5718.

(48) Nakamula, I.; Yamanoi, Y.; Imaoka, T.; Yamamoto, K.; Nishihara, H. A Uniform Bimetallic Rhodium/Iron Nanoparticle Catalyst for the Hydrogenation of Olefins and Nitroarenes. *Angew. Chem., Int. Ed.* **2011**, *50*, 5830−5833.

(49) Yamamoto, K.; Imaoka, T.; Chun, W.-J.; Enoki, O.; Katoh, H.; Takenaga, M.; Sonoi, A. Size-Specific Catalytic Activity of Platinum Clusters Enhances Oxygen Reduction Reactions. *Nat. Chem.* **2009**, *1*, 397−402.

(50) Chen, C.-C.; Zhu, C.; White, E. R.; Chiu, C.-Y.; Scott, M. C.; Regan, B. C.; Marks, L. D.; Huang, Y.; Miao, J. Three-Dimensional Imaging of Dislocations in a Nanoparticle at Atomic Resolution. *Nature* **2013**, *496*, 74−77.

(51) Wang, Z. W.; Palmer, R. E. Mass Spectrometry and Dynamics of Gold Adatoms Observed on the Surface of Size-Selected Au Nanoclusters. *Nano Lett.* **2011**, *12*, 91−95.

(52) Barreteau, C.; Desjonquères, M. C.; Spanjaard, D. Theoretical Study of the Icosahedral to Cuboctahedral Structural Transition in Rh and Pd Clusters. *Eur. Phys. J. D* **2000**, *11*, 395−402.

(53) Rodriguez, A.; Amiens, C.; Chaudret, B.; Casanove, M.-J.; Lecante, P.; Bradley, J. S. Synthesis and Isolation of Cuboctahedral and Icosahedral Platinum Nanoparticles. Ligand-Dependent Structures. *Chem. Mater.* **1996**, *8*, 1978−1986.

(54) Femoni, C.; Iapalucci, M. C.; Longoni, G.; Zacchini, S.; Zarra, S. Icosahedral Pt-Centered Pt_{13} and Pt_{19} Carbonyl Clusters Decorated by $[Cd_5(\mu\text{-}Br)_5Br_{5-x}(solvent)_x]^{x+}$ Rings Reminiscent of the Decoration of Au-Fe-CO and Au-Thiolate Nanoclusters: A Unifying Approach to Their Electron Counts. *J. Am. Chem. Soc.* **2011**, *133*, 2406−2409.

(55) Imaoka, T.; Kitazawa, H.; Chun, W.-J.; Omura, S.; Albrecht, K.; Yamamoto, K. Magic Number Pt_{13} and Misshapen Pt_{12} Clusters: Which One is the Better Catalyst? *J. Am. Chem. Soc.* **2013**, *135*, 13089−3095.