Shape- and Size-controlled Synthesis of Tetrahedral Pd Nanoparticles Using Tetranuclear Pd Cluster as Precursor

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Structurally well-defined tetrahedral Pd nanocrystals were obtained by a simple stabilizer- and reductant-free synthesis method using a tetranuclear Pd cluster as a precursor. The Pd tetrahedral nanoparticles were successfully immobilized on the surface of a solid support maintaining not only their size but also their shape.

Metal nanoparticles have become an attractive class of materials for both academic and industrial areas because of their unique chemical and physical properties, which are attributed to their size and shape.[1] Much attention has been paid to the size-controlled synthesis of metal nanoparticles, and some mechanistic insights into their growth kinetics have been obtained.[2] On the other hand, shape-controlled synthesis of some metal nanoparticles have been continuously developed by various methods.[3] Noble metals are known to form cubooctahedral- or icosahedral-type spherical nanoparticles, while other morphologies such as cubes and tetrahedra are rare.[4] Nanoparticles with specific morphologies can be applied to catalysts and optical, electronic, and magnetic devices. In particular, controlling the particle shape and the atomic arrangement of the crystal planes constituting the particle surface is essential to furthering our understanding of the phenomena in terms of catalytic performance and to enable further design of highly functionalized catalysts for new types of chemical transformations such as face-selective reactions.[5]

Here, we present a new and simple technique for constructing Pd tetrahedral-shaped nanoparticles with a high crystallinity. To the best of our knowledge, this is the first example of structurally well-defined tetrahedral-shaped Pd nanocrystals. The Pd tetrahedra were successfully immobilized on the surface of a solid support maintaining not only their size but also their shape. Among the transition metals, Pd compounds are one of the most useful catalysts for organic syntheses. Therefore, we consider that our studies on the shape evolution of Pd nanoparticles will make strong contributions to new designs of well-defined nanoscale metal catalysts and also to our understanding of conventional metal catalytic performances.

In general, use of both reductants and stabilizers, such as capping polymers and surfactants, is essential in chemical reduction methods for the formation of metal nanoparticles. Our synthesis method for obtaining the tetrahedral-shaped Pd nanoparticles is simple. Tetranuclear Pd(I) carbonyl acetate cluster complex, $Pd_4(CO)_4(OAc)_4 \cdot 2AcOH$ (PCA),[6] was adopted as a precursor for the synthesis of these specific nanocrystals. PCA (0.020 g) was stirred in *N*,*N*-dimethylacetamide (DMA 1.0 mL) at room temperature in air. The originally yellow solution gradually turned light brown over several minutes and finally to homogeneous dark brown. A TEM image of the resultant solution obtained after 5 min reveals that the majority (≈70%) of the Pd nanoparticles consisted of triangular nanoparticles with an edge length of 6.0 ± 0.7 nm.

The Pd nanoparticles were easily immobilized on the surface of TiO_2 by stirring a mixture of PCA and TiO_2[7] in DMA at room temperature. After 50 min, a blue-gray solid (TiO_2-supported Pd nanoparticles; Pd: 6.2 wt %) was separated by filtration from a colorless supernatant, which indicates the quantitative formation of the Pd nanoparticles. HR-TEM and FE-SEM images of these TiO_2-supported Pd nanoparticles are shown in Figure 1. Pd triangular nanoparticles were found to be uniformly distributed over the TiO_2 surface without aggregation and were stable in air for several months at room temperature. The HR-TEM image shows that each Pd nanoparticle was a single crystal with high crystallinity and exhibited clear atomic lattice fringe. The lattice spacing of 0.22 nm corresponds to the {111} plane of the face-centered cubic Pd. The FE-SEM image revealed the three-dimensional crystal structure of the Pd nanoparticles; the Pd particles with triangular outline showed the tetrahedron enclosed with four {111} crystal planes, not a flat prism.[8] The tetrahedron had the same order of edge length, i.e., 6.4 ± 1.2 nm, as those obtained without TiO_2, as described above. Notably, the Pd tetrahedra were formed at an initial stage even in the presence of TiO_2 support, and then, they were immobilized on the TiO_2 surface maintaining not only their size but also their specific structure.

Furthermore, the size of the Pd tetrahedra can be tuned by adjusting the reaction time. As well as by the above method, larger nanocrystals were easily immobilized on the TiO_2 surface by injection of TiO_2 into the Pd colloidal solution after 70 min of aging,[9] as shown in Figure 2. In this case, Pd nanocrystals with an increased edge length of 15 ± 2.5 nm were immobilized

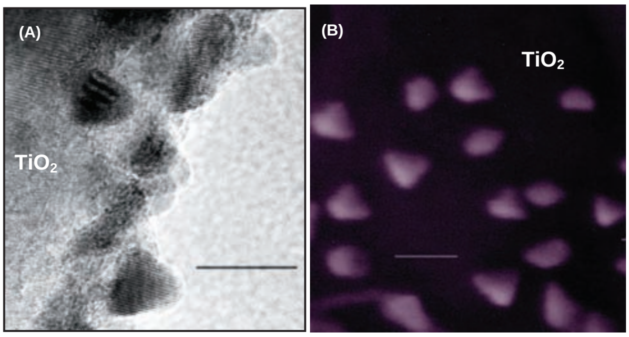

Figure 1. (A) HR-TEM and (B) FE-SEM images of tetrahedral-shaped Pd nanoparticles immobilized on the TiO_2 (scale bar = 10 nm).

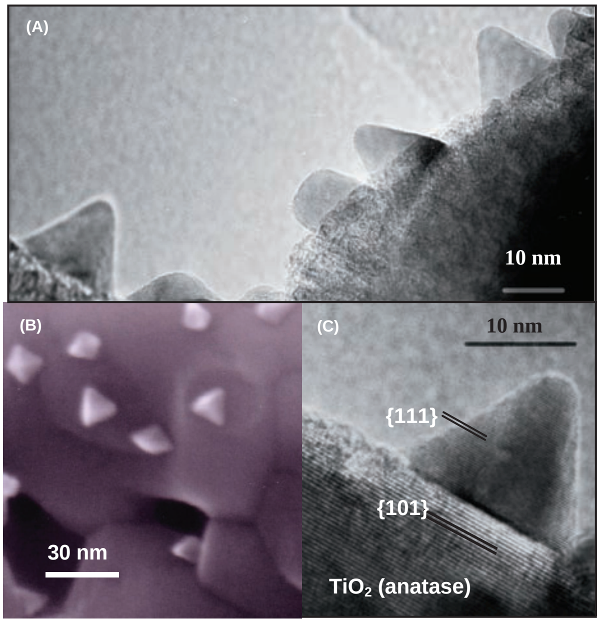

Figure 2. (A) TEM, (B) FE-SEM, and (C) HR-TEM images of larger Pd tetrahedra immobilized on the TiO$_2$ surface.

on the surface of TiO$_2$. Specific diamond-shaped nanoparticles, twinned tetrahedra, also appeared together with the single tetrahedra.

TiO$_2$ (anatase) was the best support among the various metal oxides used, such as TiO$_2$ (rutile), Al$_2$O$_3$, and SiO$_2$,[10] probably owing to the unique affinity of TiO$_2$ toward Pd nanoparticles.[11] HR-TEM images show that the {111} planes of Pd tetrahedra were well united with the {101} lattice plane of TiO$_2$ anatase and the Pd tetrahedra were stable on the surface (Figure 2C). A particle size could be controlled by seeded growth method, in which the precursor is added to grow the seeds to the larger sized particles.[12] In contrast, our method can control the particle size by adjusting the reaction time on the basis of spontaneous particle growth followed by the Ostward ripening where large crystals are made to grow even larger at the expense of small nanocrystals.[13]

Using this simple one-step synthesis method, uniquely shaped Pd nanocrystals with only a {111} facet were obtained without the use of any reductants or stabilizers. Moreover, this novel morphology was stable both in colloidal suspension and on the support. Concerning the nucleation mechanism in the synthesis of Pt tetrahedra,[4a,b] Miyake et al. have reported that the reduction rate of Pt^{4+} ions might markedly affect the shape of the Pt nuclei and that a slow reduction of Pt^{4+} ions favored the formation of tetrahedral nuclei.[14] In the current process, use of a PCA precursor is crucial for directing the intrinsic shape of the nanocrystals;[15] initially, a structural transition of PCA (Pd$_4$ square clusters) might occur producing Pd$_4$ tetrahedral clusters[6] with a relatively slow reduction rate (Pd$^+$ → Pd^0),[16] followed by the Pd$_4$ tetrahedral clusters growing into Pd tetrahedron seeds, which act as building blocks enabling the growth of the larger supertetrahedral nanocrystals with only a {111} facet.

In summary, we present a method for controlling the shape and size of Pd nanoparticles by utilizing a simple stabilizer-free reduction technique. The controlling factors that are responsible for the shape and catalytic properties of nanocrystals are currently under investigation. Our synthesis method has a great potential for enabling further advanced research into catalysts and other nanoscale devices.

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9 After 70 min, the resulting colloidal solution, in the absence of TiO$_2$, mainly contained large tetrahedral nanoparticles ($\approx$70%) with an edge length of around 15 nm.

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15 When the reaction was performed under Ar, nanoparticles with irregular shapes were formed. O$_2$ plays an important role in constructing the Pd tetrahedral shape. Under the same reaction conditions, Pd nanoparticles were not formed from Pd(OAc)$_2$, PdCl$_2$, and other Pd precursors in place of PCA.

16 The reduction of Pd$^+$ ions in the starting complex PCA might be initiated by releasing the ligands such as CO and OAc.

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