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Nanocrystals

Nanocrystals with Unconventional Shapes—A Class of Promising Catalysts

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Research into noble-metal nanocrystals is stimulated by the fascinating size- and shape-dependent properties of these nanomaterials. Because of their unique and tunable properties, they hold promise for various applications in optics, electronics, information storage, biological labeling, imaging, and surface-enhanced Raman scattering (SERS). Catalysis has also long relied on noble-metal nanocrystals for a wide variety of organic and inorganic reactions.[1] Nanocrystals of noble metals are attractive for use as catalysts because of their high surface-to-volume ratios and high surface energies, which in turn cause their surface atoms to be highly active.[2] So far, they have been used to catalyze many types of reactions including oxidation, cross-coupling, electron-transfer, and hydrogenation.[1,2] In particular, as an active component in catalytic converters, Pt nanocrystals already drastically reduce pollution from automobiles. The use of fuel cells in the future to reduce the dependence on gasoline and the output of greenhouse gases makes it especially significant to manufacture Pt nanocrystals with superb performance for electrocatalysis.[3]

Catalysis requires the use of a noble metal in a finely divided state, where both the size and shape of the nanocrystals are critical parameters that must be controlled to maximize their activity. Shape control could enable the properties of a nanocrystal to be tuned with a greater versatility than can be achieved otherwise. For example, both the reactivity and selectivity of a nanocatalyst can be tailored by controlling the shape, as shape determines the number of atoms located at the edges or corners.[2] Recent work by El-Sayed and Narayanan correlating the catalytic activity of Pt nanocrystals with the number of surface atoms indicates that a large number of edge and corner atoms holds the key to improving their catalytic performance.[2a] Their study was limited to shapes bound only by {111} and {100} facets. In general, high-index planes have a greater density of unsaturated atomic steps, ledges, and kinks which can serve as active sites for breaking chemical bonds. Fundamental studies on the single-crystal surfaces of bulk Pt have shown that high-index planes exhibit much higher catalytic activity than common, stable, low-index planes, such as {111} and {100}.[4] If one can create shapes with high-index surface facets, the catalytic activity can be further enhanced. Hence, it is clear that maximization of high-index surfaces and abundant corner and edge sites should be the criteria for selection of an excellent nanocatalyst.

However, the common shapes of face-centered cubic (fcc) metals are enclosed by {111} and {100} facets and contain a low percentage of corner and edge sites (see Figure 1). These shapes are a result of the minimization of surface energy. Surface energies corresponding to different crystallographic facets usually increase in the order $\gamma_{\{111\}} < \gamma_{\{100\}} \leqslant \gamma_{\{110\}} \leqslant \gamma_{\{hkl\}}$, where $\{hkl\}$ represents high-index facets, with at least one h, k, and l equal to two or greater.[5] Because facets with high surface energies usually grow much faster than others, they are eliminated from the crystal surface during growth; that is, low-index facets are enlarged at the expense of high-index facets. As dictated by thermodynamics (i.e., the Wulff construction[6]), atoms in a vacuum are expected to nucleate and grow into cuboctahedrons enclosed by {111} and {100} facets to minimize the total surface energy.[6,7] In solution-phase synthesis, capping agents or impurities can change the

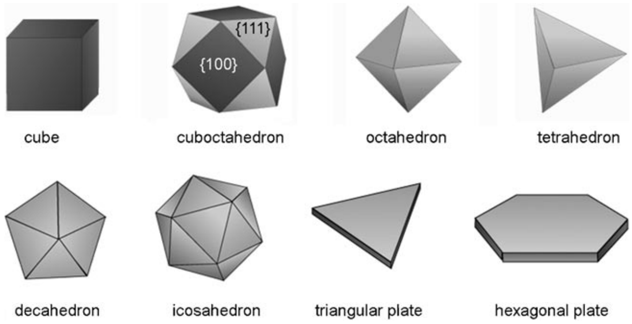

Figure 1. Conventional shapes of face-centered cubic (fcc) metals whose surface is enclosed by {100} and/or {111} facets. Black and gray colors represent the {100} and {111} facets, respectively.

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order of free energies of {111} and {100} facets through their interaction with the metal surface, and thus other single-crystal shapes (including octahedron, cube, and tetrahedron) become favorable in terms of surface energy.[8–10] Alternatively, twin defects—a single atomic layer in the form of a mirror plane—may also be formed in small crystals. The extra strain energy caused by twinning is more than compensated by a reduction in surface energy achieved by maximizing the surface coverage of {111} facets.[11] These twinned nanocrystals are usually decahedral and icosahedral with a small surface area.[12] In addition to these shapes, the nanocrystals covered by {111} and {100} facets could have a platelike morphology (including triangular, hexagonal, and circular) whose top and bottom faces are {111} facets. The formation of plates usually involves stacking faults or twin defects to induce their anisotropic growth. Although the total surface energy of plates is relatively high owing to the internal strain and large surface area, they can be produced with high yields through kinetic control.[13] To date, the synthesis of fcc metal nanocrystals of Pt, Ag, Pd, and Au with these conventional shapes has been accomplished through a variety of synthetic methods.[7–10,12,13]

A number of unconventional shapes covered by high-index facets have been observed in minerals of noble metals. The mineralogist Victor Goldschmidt (1853–1933) listed four typical single-crystal shapes with high-index surfaces in his classic reference book “*Atlas der Krystallformen*”: tetrahexahedron covered by {*hk*0}, trapezohedron by {*hkk*}, trisoctahedron by {*hhl*}, and hexoctahedron by {*hkl*} (see Figure 2, $h > k > l$).[14] For example, the tetrahexahedron (THH) with O_h symmetry is bound by 24 high-index planes of {*hk*0}, which can be considered as a cube with each face capped by a square-based pyramid. Although THHs are generally unfamiliar to the nanomaterial community, they are common forms in minerals of Au as well as Ag and Cu. In 1973, a fine THH was discovered in the Morro Velho gold mine at Nova Lima, Brazil.[15] Later, notably fine single-crystal and twinned THHs were also found in the Zapata gold mine in Venezuela.[15] These shapes are covered by high-index surfaces and display a large number of edges and corners, making them ideal candidates for catalysis. However, it is a challenge to synthesize nanocrystals with these unconventional shapes because of their relatively high surface energy.

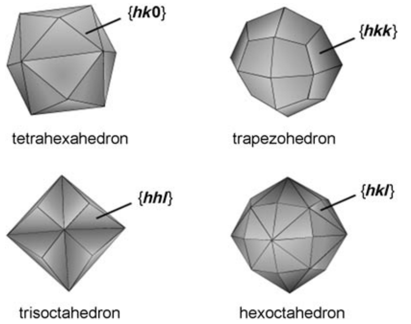

Figure 2. Unconventional shapes of fcc metals whose surface is enclosed by high-index facets. The Miller indices {*hkl*} obey the order $h>k>l$.

Recently, a breakthrough in the synthesis of nanocrystals with high-index surfaces was achieved by Sun, Wang, and coworkers,[16] who generated THH nanocrystals of Pt by applying a square-wave potential (a pulse sequence that alternates between reducing and oxidizing potentials at a rate of 10 Hz) on 750 nm diameter polycrystalline Pt spheres (deposited on a substrate of glassy carbon) in the presence of ascorbic acid and sulfuric acid (Figure 3). In their synthesis, the size (Heywood diameter) of THH nanocrystals could be tailored from 20 nm to 240 nm by varying the number of cycles of square-wave treatment. These THH nanocrystals were enclosed by {730}, {210}, and/or {520} facets, as revealed by high-resolution transmission electron microscopy. It is very surprising that these high-energy surfaces, which include numerous dangling bonds and atomic steps, could be stable at the nanoscale in this case, even when the temperature was increased to 800 °C.

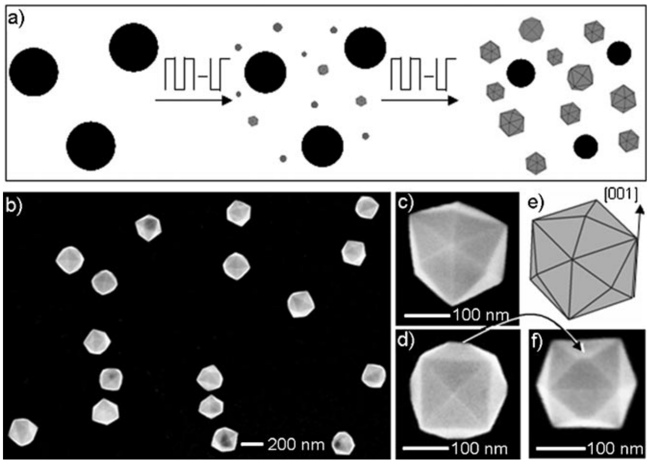

Figure 3. a) Electrochemical preparation of Pt tetrahexahedrons (THHs) from nanospheres. Under the influence of the square-wave potential, Pt THHs can nucleate and grow at the expense of spherical particles. b) Low-magnification SEM image of the Pt THHs. c, d) High-magnification SEM images of a Pt THH nanocrystal along different orientations, clearly showing the THH shape. e) Geometrical model of an ideal THH. f) High-magnification SEM image of a Pt THH nanocrystal, showing the imperfect vertices as a result of the unequal size of the neighboring facets. The arrow indicates imperfect vertices as a result of the unequal sizes of neighboring facets. (Adapted from Ref. [16] with permission. Copyright 2007, American Association for the Advancement of Science (AAAS).)

It was proposed in their work that the electrochemical treatment was vital to the formation of high-index surfaces. In the synthesis, the adsorption and desorption of oxygen on Pt occurs at the alternating steps of positive and negative potentials, respectively. This electrochemical treatment increases the chance that oxides or hydroxides will form on the surface of the nanocrystal, an important difference compared to other synthetic methods. As high-index facets contain many dangling bonds and atomic steps, the surface Pt atoms can easily form Pt–O bonds with oxygen. This surface binding is reversible so that there is no structural change during an electrochemical cycle. In contrast, {111} and {100} facets are so smooth that oxygen atoms diffuse into the lattice and replace Pt atoms. After the oxygen atoms are desorbed from the lattice, the ordered surface structure will be destroyed. As a result, only the high-index surfaces are able to survive after the electrochemical treatment.

This mechanism can explain why high-index facets can be enlarged on the surface of the nanocrystals through the electrochemical treatment. However, it cannot be responsible for the superior stability of the reaction products at a temperature as high as 800 °C. We believe that oxides or hydroxides on high-index surfaces, which can readily form during electrochemical treatment, might be the answer. Adsorption of these impurities could significantly alter the surface energy of Pt and make the THH shape energetically favorable. Another possibility is that ascorbic acid and other chemical species are preferentially adsorbed onto the high-index facets through their dangling bonds or on atomic steps, and thus reduce the surface energy of those facets. The alternation of surface energy seems to be the most important reason for the unusual stability of these unconventional shapes.

As predicted, the Pt THHs far surpassed nanoparticles of Pt with no shape control in terms of catalytic activity. The Pt THHs were up to 200 % more efficient per unit surface area than commercial 3.2 nm diameter Pt/C catalyst (E-TEK Inc.) for the oxidation of ethanol, and up to 400 % more efficient for the oxidation of formic acid. In many cases, the surface atoms of nanocatalysts are so active that their size and shape changes during the catalytic reaction. In the case of Pt THHs, their unusual chemical stability allows them to preserve their shape after catalysis and to be recycled for further catalytic reactions. This unusual stability also deserves further investigation.

Over the past decade, the field of metal nanocrystal research has seen a great revival as a result of the potential of shape control. Shape control has endowed the research community with the power to precisely tailor the catalytic, optical, electronic, and magnetic properties of metal nanocrystals. The current research by Sun, Wang and co-workers opens an exciting avenue for the development of new shapes with relatively high surface energies. The obstacle to form nanocrystals with high-energy facets, once thought impossible, has now been pushed aside by this new electrochemical process. This discovery inspires us to further purse the use of unconventional synthetic methods or even extreme conditions to generate exotic shapes. The feasibility of constructing unconventional nanocrystals for different metals with this electrochemical approach presents a very promising avenue for future research.

One final issue that has not been addressed thus far is the size effect of these nanocatalysts. The smallest size (diameter) of Pt THHs identified by scanning electron microscopy (SEM) was around 20 nm.[16] As compared with the size of commercial Pt catalysts (≈ 3.2 nm), this new structure is at least six times larger, so the overall catalytic activity per unit weight of Pt is actually lower. In the future, one should expect that the research community will drive these high-energy nanoparticles to much smaller sizes for even higher catalytic efficiency.[17] As Feldheim suggested,[18] another approach to putting this work into practical applications is to replace some Pt atoms by oxygen atoms, which should both enhance the reactivity and reduce the cost of the raw material.

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