Shape-Controlled Synthesis of Pd Nanocrystals and Their Catalytic Applications

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CONSPECTUS

Palladium is a marvelous catalyst for a rich variety of reactions in industrial processes and commercial devices. Most Pd-catalyzed reactions exhibit structure sensitivity, meaning that the activity or selectivity depends on the arrangement of atoms on the surface. Previously, such reactions could only be studied in ultrahigh vacuum using Pd single crystals cut with a specific crystallographic plane. However, these model catalysts are far different from real catalytic systems owing to the absence of atoms at corners and edges and the extremely small specific surface areas for the model systems. Indeed, enhancing the performance of a Pd-based catalyst, in part to reduce the amount needed of this precious and rare metal for a given reaction, requires the use of Pd with the highest possible specific surface area. Recent advances in nanocrystal synthesis are offering a great opportunity to investigate and quantify the structural sensitivity of catalysts based on Pd and other metals. For a structure-sensitive reaction, the catalytic properties of Pd nanocrystals are strongly

dependent on both the size and shape. The shape plays a more significant role in controlling activity and selectivity, because the shape controls not only the facets but also the proportions of surface atoms at corners, edges, and planes, which affect the outcomes of possible reactions. We expect catalysts based on Pd nanocrystals with optimized shapes to meet the increasing demands of industrial applications at reduced loadings and costs.

In this Account, we discuss recent advances in the synthesis of Pd nanocrystals with controlled shapes and their resulting performance as catalysts for a large number of reactions. First, we review various synthetic strategies based on oxidative etching, surface capping, and kinetic control that have been used to direct the shapes of nanocrystals. When crystal growth is under thermodynamic control, the capping agent plays a pivotal role in determining the shape of a product by altering the order of surface energies for different facets through selective adsorption; the resulting product has the lowest possible total surface energy. In contrast, the product of a kinetically controlled synthesis often deviates from the thermodynamically favored structure, with notable examples including nanocrystals enclosed by high-index facets or concave surfaces.

We then discuss the key parameters that control the nucleation and growth of Pd nanocrystals to decipher potential growth mechanisms and build a connection between the experimental conditions and the pathways to different shapes. Finally, we present a number of examples to highlight the use of these Pd nanocrystals as catalysts or electrocatalysts for various applications with structure-sensitive properties. We believe that a deep understanding of the shape-dependent catalytic properties, together with an ability to experimentally maneuver the shape of metal nanocrystals, will eventually lead to rational design of advanced catalysts with substantially enhanced performance.
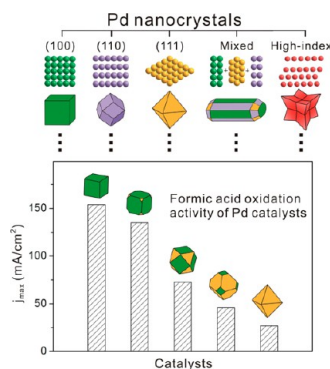
Introduction

Palladium is a key component of many catalysts used in industrial processes and commercial devices.[1] According to a market survey released in 2011,[2] over 60% of Pd was used as a substitute of Pt for oxidizing CO into CO_2 in catalytic converters because of its compatible performance at a substantially lower cost (only 40% of the cost of Pt). Palladium is also of great importance in organic synthesis owning to its catalytic activity for a myriad of carbon−carbon coupling reactions,[3] including those named after Suzuki, Heck, and Negishi who were awarded the 2010 Nobel Prize in Chemistry.[4] In addition, Pd has a strong affinity toward hydrogen and thus holds a niche position for its purification, storage, and detection.[5] Most of these applications require the use of Pd in a finely divided state to enhance its specific activity and thus reduce the loading of this precious and rare metal.

Size and shape are two typical parameters for tailoring the properties of a nanocrystal-based material. While the size determines the specific surface area and the ratio of surface to bulk atoms, the shape controls the facets and thus surface structure of a nanocrystal, as well as the fractions of atoms at corners and edges. As such, shape offers greater versatility than size and other parameters in tuning the catalytic properties of a nanocrystal, especially when the atoms at different facets possess different activities. In recent years, shape control has received the greatest attention in the exploration of noble-metal nanocrystals.[6] To this end, El-Sayed and co-workers reported a solution-phase route to the synthesis of Pt cubes, tetrahedrons, and cuboctahedrons by simply varying the ratio of Pt precursor to sodium polyacrylate.[7] The Pt tetrahedrons showed higher catalytic activity than the Pt cubes for electron-transfer reaction between hexacyanoferrate(III) and thiosulfate ions.[8] This early work clearly demonstrates the importance of controlling the shape of nanocrystals and thus maximizing their performance as catalysts.

Recently, the solution-phase approach has emerged as a powerful and highly versatile tool for shape-controlled synthesis of nanocrystals made of noble metals such as Ag, Au, Pd, Pt, and Rh.[6] For Pd, many different shapes have been achieved by manipulating the thermodynamics or kinetics involved in nanocrystal growth.[9] When the growth is under thermodynamic control, the product will have the lowest surface energy. In this case, the capping agent plays a critical role in determining the product's shape by altering the order of surface energies for different facets via selective adsorption and thus their growth rates.[10] In contrast, the product of a kineticall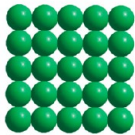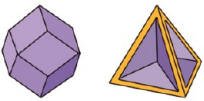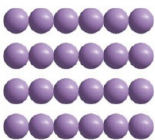y controlled synthesis can drastically deviate from the thermodynamically favored structure; notable examples include nanocrystals with high-index facets or concave surfaces.[11] In this Account, we begin with a brief discussion of mechanistic understanding and experimental control for shape-controlled synthesis of Pd nanocrystals. We then examine the catalytic properties of Pd nanocrystals enclosed by different facets for reactions including Suzuki coupling, hydrogenation, oxygen reduction, and formic acid oxidation.
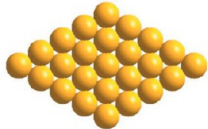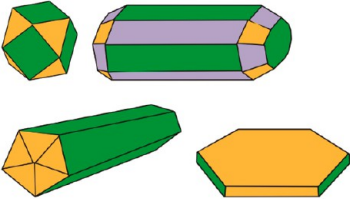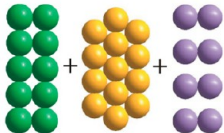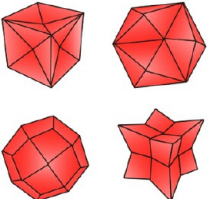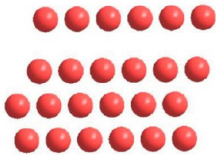
Shape-Controlled Synthesis of Pd Nanocrystals

The past decade has witnessed the successful synthesis of Pd nanocrystals in a rich variety of shapes, which can be divided into five groups according to the types of facets exposed on the surface (Table 1).[9] Similar to Ag,[22] we found that the shape of a Pd nanocrystal is also determined by the internal structure (i.e., single-crystal, single-twinned, or multiple-twinned) of the seed and the growth rates of different crystallographic planes. In general, the three different types of seeds can all exist in a synthesis. Introducing an oxidative etchant such as Cl^-/O_2[18] or blocking oxidative etching with citric acid or citrate ions[16] is an effective means to enrich seeds with a specific internal structure and thus control the final shape of Pd nanocrystals. A capping agent controls the shape of a nanocrystal by changing the order of free energies associated with different crystallographic planes and thereby their relative growth rates.[12] The growth pattern of different crystallographic planes can also be altered by manipulating the reaction kinetics to generate Pd nanocrystals enclosed by high-index facets or with concave surfaces.

Solution-phase synthesis of Pd nanocrystals is typically conducted in air by reducing a Pd precursor in the presence of a stabilizer such as poly(vinyl pyrrolidone) (PVP). Since the reaction solution also contained halide ions (such as Cl^-) from the precursor, nanocrystals with twin defects (e.g., decahedron and icosahedron) could hardly survive due to oxidative etching.[18] By taking advantage of this selectivity in etching, single-crystal seeds could be obtained as the dominant species. To this end, we have synthesized Pd cuboctahedrons in ethylene glycol containing Na_2PdCl_4 and PVP at 110 °C.[18] In the initial stage, the sample contained both cuboctahedrons and multiply twinned particles. As the reaction proceeded, all the twinned particles disappeared due to the oxidative etching caused by O_2 and Cl^-, while the number of Pd cuboctahedrons steadily increased with time. Figure 1A,B shows TEM and HRTEM images of Pd cuboctahedrons 8−10 nm in size and enclosed by a mix of {100}

TABLE 1. Palladium Nanocrystals with Different Shapes That Have Been Reported in Literature

Nanocrystals with different shapes	Exposed facets	Atomic arrangements	References
	{100}		12, 13
	{110}		14, 15
	{111}		16, 17
	Mixed facets	+ +	18, 19
	High-index facets		20, 21

and {111} facets. The selective dissolution of twinned particles by oxidative etching was also observed in the water-based synthesis.[23]

Once the internal structure (e.g., single-crystal) of a seed is fixed, the final shape taken by the nanocrystal will be determined by the relative growth rates of different crystallographic planes, and the facets with a slower growth rate will be expressed more on the surface. A capping agent can change the relative growth rates of different crystallographic planes via chemisorption and thus control the shape of a nanocrystal. For example, PVP can selectively passivate {100} rather than {111} facets of Ag to slow down their growth rate, resulting in the formation of a nanocube from a single-crystal seed.[22] However, small molecules or ions seem to work the best as capping agents for Pd nanocrystals. We found that citric acid or citrate ions could selectively stabilize the {111} facets and thus favor the formation of Pd nanocrystals enclosed by {111} facets.[17] In this case, Pd

octahedrons enclosed by {111} facets were produced by heating an aqueous solution containing Na_2PdCl_4, PVP, and a relatively low concentration of citric acid (e.g., 28 mM) at 90 °C for 26 h (Figure 1C). Different from citric acid or citrate ions, Br^- ions could selectively adsorb onto the {100} facets of Pd nanocrystals and thus stabilize these facets during growth.[12] As such, Pd nanocubes enclosed by {100} facets were produced in the presence of Br^- ions as a capping agent.[24] The synthesis of Pd nanocubes was typically conducted in an aqueous solution containing Na_2PdCl_4, PVP, and different amounts of KBr and KCl at 80 °C for 3 h, with ascorbic acid as a reducing agent.[25] The addition of halide species such as Br^- and Cl^- also alters the size of resultant Pd nanocubes by formation of complexes with Pd^{2+} ions and thus retardation of the reduction kinetics. As shown in Figure 1D, Pd nanocubes of 6 nm in size were formed with the addition of 4 mM KBr and 226 mM KCl. When the concentration of KBr was substantially increased to 458 mM, the
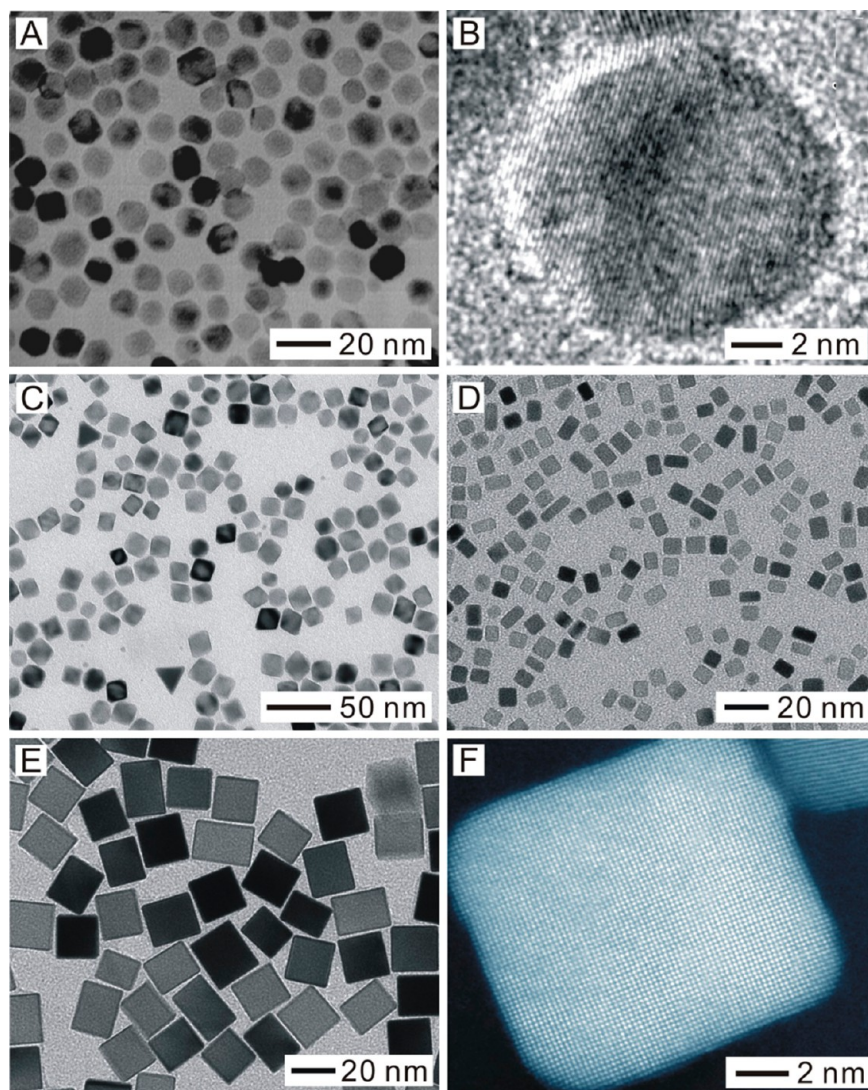
FIGURE 1. (A) TEM and (B) HRTEM images of Pd cuboctahedrons that were obtained by a polyol synthesis in a mixture containing PVP and Na_2PdCl_4 at 110 °C.[18] (C) TEM image of Pd octahedrons that were obtained by heating an aqueous solution containing Na_2PdCl_4, citric acid, and PVP at 90 °C for 26 h.[17] (D, E) TEM images of Pd nanocubes with different sizes that were prepared in an aqueous solution containing Na_2PdCl_4, PVP, ascorbic acid, and different concentrations of KCl and KBr: 6-nm cubes with 4 mM of KBr and 226 mM of KCl and 18-nm cubes with 458 mM of KBr.[25] (F) A typical HAADF-STEM image of the Pd nanocube.[24]

size of Pd nanocubes was increased to 18 nm (Figure 1E). We also studied the surface structure of Pd nanocubes by high-angle annular dark-field scanning TEM with subangstrom resolution. As shown in Figure 1F, the as-synthesized nanocubes contained several types of defects such as adatom islands and steps on the {100} facets due to the involvement of two-dimensional nucleation and growth.[24]

Seeded growth, in which newly formed atoms are added onto the surface of preformed seeds, offers a simple, versatile, and powerful approach to the synthesis of nanocrystals with controlled shapes by skipping the complicated, unknown nucleation process. In a recent study, we used this method to grow Pd nanocrystals with controlled shapes and different proportions of {100} and {111} facets on the surface in high yields (Figure 2).[26] By varying the ratio of precursor to seed, the nanocrystals evolved from cubes into truncated cubes, cuboctahedrons, truncated octahedrons, and octahedrons due to faster growth along ⟨100⟩ directions relative to ⟨111⟩ directions. In this synthesis, formaldehyde played an important role in the evolution of Pd polyhedrons with different shapes by selectively binding to the {111} facets.

Palladium nanocrystals enclosed by {110} facets have been rarely explored because the {110} facets have the highest surface energy among the low-index facets. Recently, Xu and co-workers reported a versatile method for
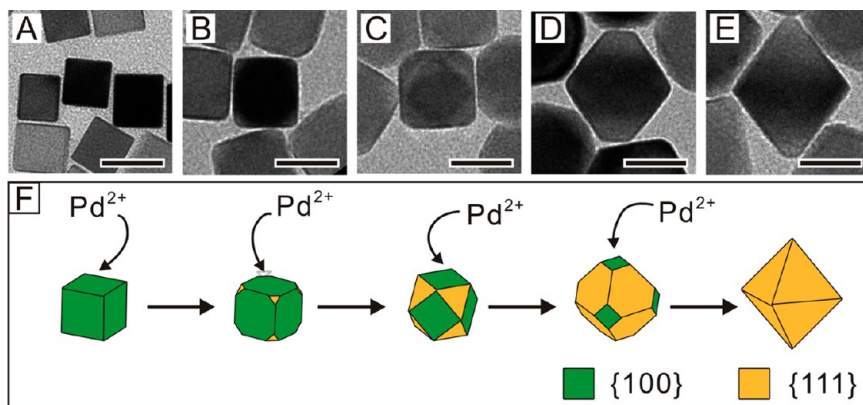
FIGURE 2. TEM images of Pd polyhedrons grown on Pd cubic seeds at different amounts of Na_2PdCl_4: (A) 0, (B) 5.8, (C) 8.7, (D) 17.4, and (E) 29.0 mg. (F) A schematic showing how continuous growth on the {100} planes led to the transformation of a Pd cube bound by {100} facets into an octahedron enclosed by {111} facets.[26]

the synthesis of Pd nanocrystals with a number of shapes including rhombic dodecahedrons, cubes, and octahedrons by reducing H_2PdCl_4 with ascorbic acid in an aqueous solution containing cetyltrimethylammonium bromide (CTAB), KI, and Pd cubic seeds.[14] These Pd nanocrystals were formed by varying the concentration of KI and reaction temperature. Relatively high temperatures and medium KI concentrations favored the formation of Pd rhombic dodecahedrons encased by 12 {110} facets. In addition, Zheng and co-workers reported the synthesis of tetrahedral and trigonal bipyramidal nanocrystals of Pd with concave surfaces using a solvothermal process in the presence of formaldehyde.[15] The concave surface, mainly enclosed by {110} facets, was a result of fast growth along a combination of ⟨100⟩ and ⟨110⟩ directions of a tetrahedral seed. The formaldehyde was supposed to dramatically retard the growth rate of a Pd seed along ⟨111⟩ directions by selectively capping the {111} facets and thus promoting the formation of concave tetrahedrons.

In addition to their capping effect for {111} facets of Pd nanocrystals, citric acid or citrate ions could also block oxidative etching and thus promote the formation of multiply twinned seeds.[16] As such, the population of multiply twinned seeds could be controlled by varying the extent of oxidative etching associated with citric acid or citrate ions.[17] Reducing the amount of citric acid favored the formation of Pd octahedrons enclosed by eight {111} facets (Figure 1C). In contrast, Pd decahedrons were obtained when the amount of citric acid was increased (Figure 3A). In addition, the growth of Pd nanocrystals was also sensitive to the concentration of Na_2PdCl_4 precursor used in the synthesis. Generally, a lower concentration of the precursor means a slower growth rate for the nanocrystals and thus smaller size. Reducing the concentration of Na_2PdCl_4 (e.g., by 20%) with other parameters

being kept the same gave icosahedrons as the major product (>80%, Figure 3B). This result is consistent with the fact that icosahedrons are usually stable at small sizes and decahedrons at medium sizes.[27] The HRTEM image (Figure 3C) taken from an individual icosahedron clearly revealed a multiple twinned structure with a 3-fold axis oriented parallel to the electron beam. The twin structure of Pd nanocrystals was also controlled by the amount of Br^- ions added during the synthesis. The addition of Br^- ions can retard the reduction of Pd^{2+} ions via the formation of $[PdBr_4]^{2-}$. At a slow growth rate, there was enough time for twinned seeds to grow into pentagonal nanorods or right bipyramids through atomic addition. Figure 3D shows the TEM image of a sample that was prepared by increasing the amount of Br^- ions with all other parameters being kept the same as those for the synthesis of Pd nanocubes.[13] Obviously, Pd nanocrystals with various shapes including cubes, bipyramids, and pentagonal rods coexisted in the product.

Compared with the use of a capping agent, kinetic control may represent a simpler and more powerful route to the synthesis of noble-metal nanocrystals with high-index facets on the surface. The growth kinetics is controlled by manipulating the rate at which atoms are added to the surface of a seed. In practice, a kinetically controlled synthesis can be achieved by substantially slowing the reduction rate. For example, Pd plates with both top and bottom faces covered by the {111} facets were generated with commercially available PVP as a reducing agent in an aqueous solution containing Na_2PdCl_4 (Figure 4).[28] The weak reduction power was derived from the hydroxyl end groups of PVP. The reduction kinetics could be manipulated by varying the molar ratio of PVP to Na_2PdCl_4 and the molecular weight of PVP. Hexagonal Pd plates were favored at low molar ratio
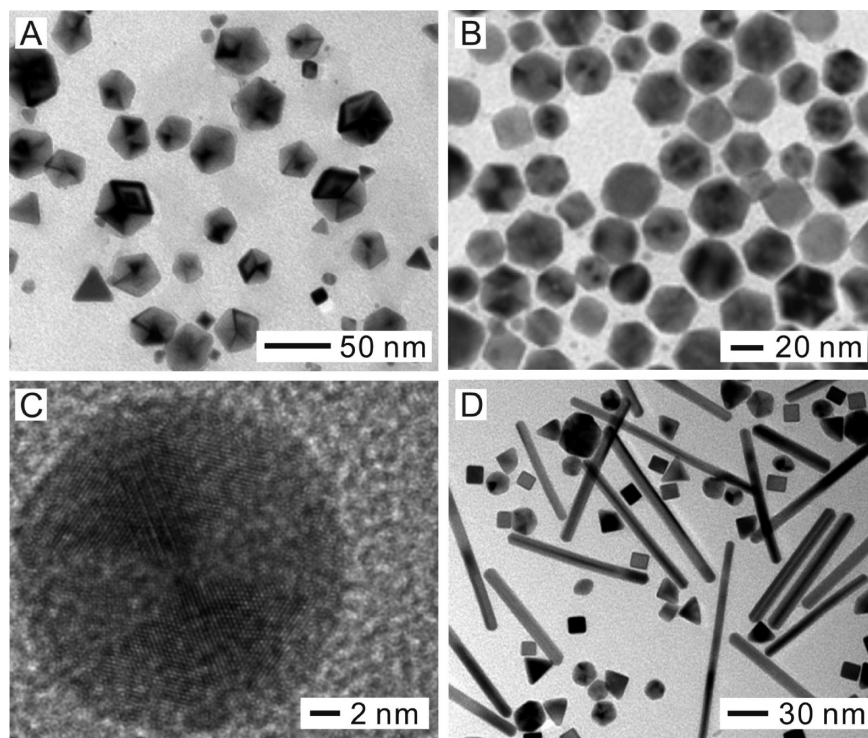
FIGURE 3. (A) TEM image of Pd decahedrons that were obtained by heating 11 mL of an aqueous solution containing 17.4 mM Na_2PdCl_4, 84 mM citric acid, and 87 mM PVP at 90 °C for 26 h. (B) TEM image of Pd icosahedrons prepared under the same conditions as in panel A except that the concentrations of Na_2PdCl_4 and PVP were reduced to 5.8 and 29 mM, respectively.[17] (C) HRTEM image of an individual icosahedron.[16] (D) TEM image of Pd cubes, bipyramids, and pentagonal rods that coexisted in a synthesis involving 57 mg of Na_2PdCl_4, 105 mg of PVP, 60 mg of ascorbic acid, and 980 mg of KBr at 80 °C.[13]

of PVP to Na_2PdCl_4 and high molecular weight of PVP owing to the relatively slow reduction rate (Figure 4A and the inset). In contrast, triangular plates were obtained as the dominant product (Figure 4B and the inset). Obviously, both the hexagonal and triangular plates were derived from seeds with stacking faults at a slow reduction rate (Figure 4C). Similar Pd plates have also been synthesized by introducing $FeCl_3$ and HCl into a polyol synthesis.[29] The oxidative etching caused by Fe(III) species and O_2/Cl^- greatly slowed the reduction rate and thus induced the formation of thin plates.

We also found that the syntheses for cuboctahedrons (Figure 1A) and cubes (Figure 1C) could facilitate anisotropic overgrowth when a stronger reducing agent or higher temperature was involved. In this case, Pd cuboctahedrons could evolve into nanorods with a truncated octagonal cross-section along one ⟨100⟩ direction when ascorbic acid was replaced by ethylene glycol in an aqueous solution containing Br^- ions.[12] As shown in Figure 5A, a large number of Pd nanorods with an average aspect ratio of 8 were generated through anisotropic overgrowth. The HRTEM images (Figure 5B,C) clearly show well-resolved fringes with the same orientation, indicating that the Pd nanorod was a

single crystal bounded by a mix of {100}, {110}, and {111} facets. Similarly, Pd nanocubes could be elongated along one of the axes to form nanobars with aspect ratios higher than one by increasing temperature from 80 to 100 °C (Figure 5D,E).[24] Localized oxidative etching,[12] in which the adsorbed Br^- ions on one of the faces of a seed were removed to create an active site for atomic addition, was previously proposed to explain the anisotropic growth. Our later work indicated that oriented attachment might also played a role in promoting the anisotropic growth via particle coalescence along one direction to minimize the surface area.[24] Our most recent work on the face-selective growth of Ag on Pd cubic seeds suggested another plausible mechanism to account for the formation of Pd nanorods and nanobars through preferential overgrowth under kinetic control.[30]

We also demonstrated the facile synthesis of Pd concave nanocubes through preferential overgrowth on Pd cubic seeds under kinetic control.[21] The reaction kinetics was controlled by lowering the concentration of Na_2PdCl_4 and KBr or increasing the concentration of ascorbic acid, with Br^- ions as a capping agent to stabilize the {100} facets. Our characterizations confirmed the formation of Pd concave
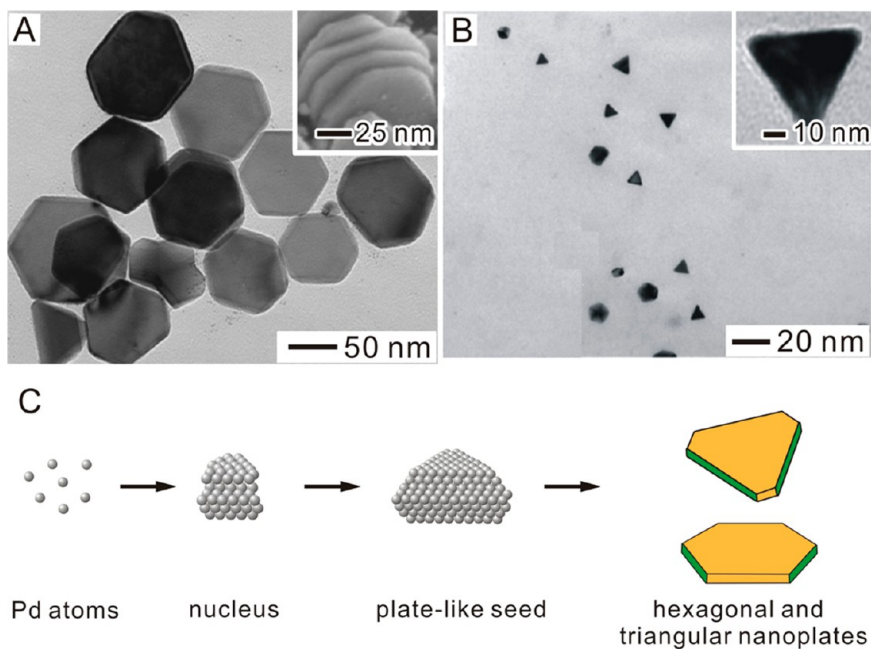
FIGURE 4. (A) TEM image of Pd hexagonal plates prepared in an aqueous solution by reducing Na_2PdCl_4 with PVP. The PVP had an average molecular weight of 55 000, and its molar ratio (in terms of repeating unit) to Na_2PdCl_4 was 5. (B) TEM image of Pd triangular plates prepared in an aqueous solution by reducing Na_2PdCl_4 with PVP. The PVP had an average molecular weight of 10 000 and its molar ratio to Na_2PdCl_4 was 15. The insets show images at higher magnifications.[28] (C) A proposed mechanism for the formation of Pd hexagonal and triangular plates.

nanocube enclosed by 24 high-index {730} facets via preferential overgrowth at corners and edges of a cubic seed along the ⟨111⟩ and ⟨110⟩ directions (Figure 6). Compared with the kinetically controlled synthesis of Pd plates at a slow reduction rate, fast reduction (e.g., increasing the concentration of ascorbic acid) seems to facilitate the kinetic control in this synthesis. This difference can be attributed to the two different ways for atoms to be added to the surface of a seed depending on the absence or presence of a capping agent, which was thoroughly discussed in our recent review.[11]

Catalytic Applications

Palladium is a fantastic catalyst for a wide variety of reactions, where the activities are highly sensitive to the facets expressed on the surface of a Pd nanocrystal and thus its shape. The availability of Pd nanocrystals with many different shapes offers a great opportunity to systematically investigate the structure sensitivity in an effort to maximize the catalytic performance and thereby reduce its loading in a catalyst.

Removal of PVP. For solution-phase synthesis of Pd nanocrystals, PVP is commonly used as a colloidal stabilizer. Even with extensive washing and centrifugation, a trace amount of PVP may still remain on the surface. The residual PVP can block the active sites due to a strong binding to the Pd surface and prevent reactants from reaching the surface.

It is desired to have the PVP removed under mild conditions to avoid structural changes to the surface.

Ultraviolet−ozone (UVO) cleaning has been used to produce clean surfaces while keeping the morphology of nanocrystals intact. This method is based on a combination of UV light and ozone at room temperature to eliminate organic adsorbates via the formation of volatile species through a photosensitized oxidation process. We recently evaluated the effect of PVP removal by UVO treatment on the morphology and catalytic behavior of Pd nanocubes on carbon.[31] The removal of PVP was monitored by XPS, XRD, SEM, and in situ attenuated total reflection infrared spectroscopy (ATR-IR). The ATR-IR spectroscopy showed that all the peaks associated with PVP (e.g., the fingerprint region of $1250-1800$ cm^{-1}) had a fast and homogeneous decay during the first 30 min of UVO treatment, together with the rising of a new band at 1900 cm^{-1}, probably due to the CO derived from decomposition of PVP. After 3 h of UVO treatment, PVP was completely removed, as confirmed by XPS analysis. The SEM and XRD measurements further revealed that the shape, size, distribution, and composition of the Pd nanocubes were all retained even after 6 h of UVO treatment. The UVO-treated Pd nanocubes on a carbon support were then tested as a catalyst for the hydrogenation of acetylene, showing a 4-fold increase of activity over that of PVP-covered nanocubes. This result confirmed that UVO
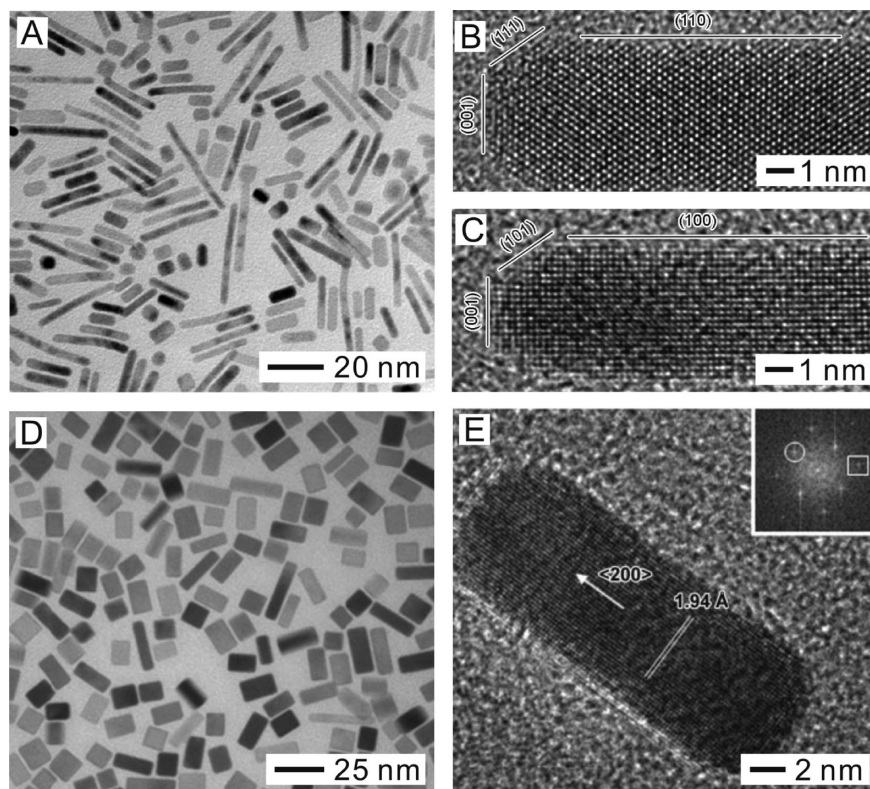
FIGURE 5. (A) TEM and (B, C) HRTEM images of Pd nanorods with a truncated octahedral cross-section that were prepared in a mixture of 72.7% ethylene glycol and 27.3% water in the presence of KBr at 120 °C for 3 h.[12] (D) TEM and (E) HRTEM images of Pd nanobars prepared in an aqueous solution containing PVP, Na_2PdCl_4, KBr, and ascorbic acid at 100 °C. The inset shows the corresponding Fourier transform patterns.[24]

cleaning was a useful technique for removing organic adsorbates with high efficiency and good preservation of morphology.

Suzuki Coupling. Carbon−carbon coupling plays an important role in the synthesis of complex molecules to be used as pharmaceuticals and fine chemicals.[3] The Suzuki coupling (i.e., Pd-catalyzed cross-coupling of aromatic or vinyl halides with boranes, boronic acids, or esters) offers a number of attractive features including commercial availability of reactants, mild reaction conditions, high product yields, and environmentally friendly conditions. Owning to the presence of atomic steps and kinks with low coordination sites in high densities, Pd nanocrystals with concave surfaces are attractive as catalysts for Suzuki reaction. Recently, we demonstrated the synthesis of Pd concave nanocubes (Figure 6) enclosed by high-index {730} facets through preferential overgrowth on the corners and edges of Pd cubic seeds.[21] Their catalytic activity was then evaluated for Suzuki coupling by reacting phenylboronic acid with iodobenzene to generate biphenyl. For the Pd concave nanocubes, 99% of iodobenzene was converted into biphenyl after 20 min, whereas only 38% conversion yields were achieved for conventional Pd nanocubes. The turnover frequency (TOF) of the

concave nanocubes was 3.5 times higher than that of the conventional nanocubes. This result indicates that the concave nanocubes hold great promise for Suzuki coupling thanks to their high-index facets.

Structure Sensitivity of Alkynol Hydrogenation. Alkynol hydrogenation plays an important role in bulk and fine chemical production, and it shows structure-sensitive activity or selectivity over Pd-based catalysts. We recently examined the structure sensitivity of Pd octahedrons, cubes, and cuboctahedrons for hydrogenation of 2-methyl-3-butyn-2-ol (MBY) toward 2-methyl-3-buten-2-ol (MBE) and 2-methyl-3-butan-2-ol (MBA).[32] In this study, there were two types of active sites (i.e., surface atoms on the planes and at the edges) with different activity and selectivity due to their different coordination numbers. Specially, semihydrogenation of MBY to MBE occurred preferentially at the plane sites with an activity 3.5-fold higher than that at the edge sites regardless of their crystallographic orientation, whereas overhydrogenation from MBE to MBA occurred mainly at the edge sites. Selectivity toward MBE increased monotonically with particle size in the order of cubes > octahedrons > cuboctahedrons at full conversion. A two-site Langmuir−Hinshelwood mechanism was proposed to model the reaction
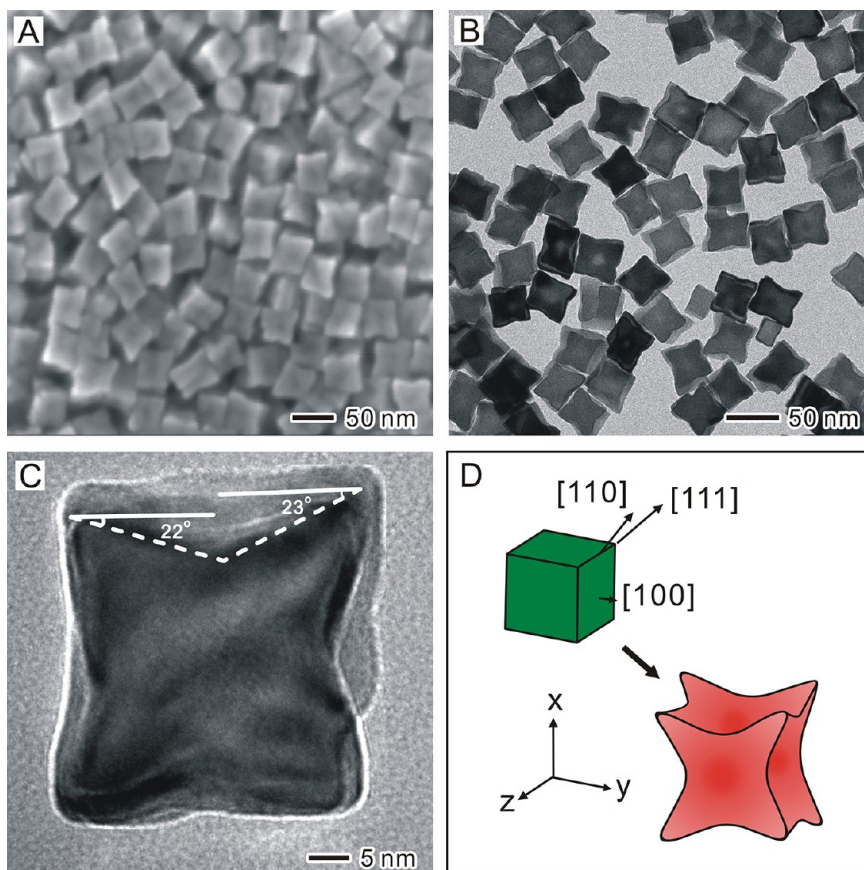
FIGURE 6. (A) SEM and (B, C) TEM images of Pd concave nanocubes that were prepared by manipulating the concentrations of reagents, including Na_2PdCl_4, KBr, and ascorbic acid. (D) Schematic showing the formation of a Pd concave nanocube from a cubic seed via preferential overgrowth at the corners and edges.[21]

kinetics with one single set of kinetic and adsorption constants specific to the reaction path, showing good match between experimental and simulation results. By considering both activity and selectivity toward MBE as the optimization criteria, a promising catalyst was predicted to be cubes of roughly 3−5 nm in size. This study provides new insight into the structure sensitivity for alkynol hydrogenation, offering a powerful tool for rational catalyst design under industrial conditions.

Oxygen Reduction Reaction. Oxygen reduction reaction (ORR) is the rate-determining step in a proton-exchange membrane fuel cell (PEMFC). The sluggish kinetics of ORR at the cathode of a PEMFC and thus the need for a significant amount of the catalyst has become one of the main obstacles for the commercialization of this technology. Although Pt is by far the most effective catalyst for ORR, it is an extremely expensive and scarce material. Much effort has been devoted to the development of new catalysts based on other noble metals. Among various metals around Pt in the period table, Pd is probably the best alternative because it is much less

expensive than Pt, together with providing high stability against the acidic environment of a PEMFC. Significantly, the catalytic properties of Pd for ORR can be tuned by controlling the shape with an optimal value comparable to that of Pt. We recently examined the ORR activity of Pd cubes and octahedrons enclosed by {100} and {111} facets, respectively.[33] These two types of Pd nanocrystals with an average size of 6−8 nm were synthesized by selectively passivating a specific facet with the use of bromide ions for cubes and citric acid for octahedrons. The Pd nanocrystals were then deposited on carbon powders (denoted as Pd/C cubes and octahedrons, respectively) and then tested as electrocatalysts for the ORR, with Pd/C (BASF) and Pt/C (TKK) serving as the benchmarks.

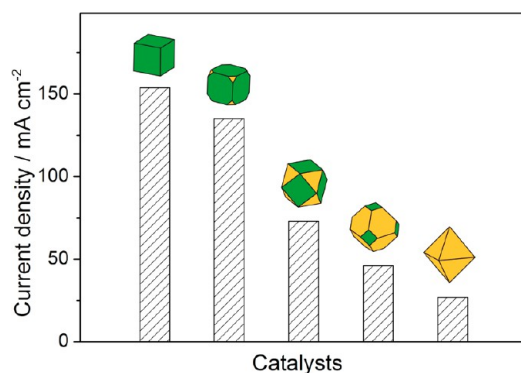To minimize the particle size effect, the commercial Pd/C and Pt/C were treated at 500 °C in Ar for 3 h to achieve a size in the range of 6−8 nm (denoted as Pd/C-HT and Pt/C-HT, respectively). The electrocatalytic properties of these catalysts are compared in Figure 7. The oxygen polarization curve of Pd/C cubes shifted to much more positive potentials in comparison with those of Pd/C octahedrons and Pd/C-HT,
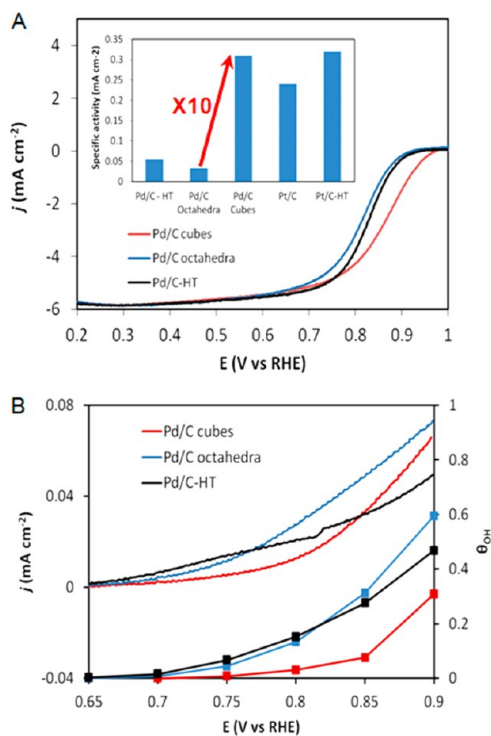
FIGURE 7. (A) ORR polarization curves for Pd/C cubes, Pd/C octahedrons, and Pd/C-HT recorded in 0.1 M $HClO_4$ at room temperature. (B) ORR polarization curves after subtracting the double layer current density and coverage of OH for Pd/C cubes, Pd/C octahedrons, and Pd/C-HT. The inset shows a comparison of specific activities for these catalysts at 0.9 V vs a reversible hydrogen electrode.[33]

FIGURE 8. Maximum current densities of formic acid oxidation over Pd cubes, truncated cubes, cuboctahedrons, truncated octahedrons, and octahedrons enclosed by {111} and {100} facets in different proportions.[26]

indicating that the Pd/C cubes were much more active for ORR. Calculated from the corresponding polarization curves, the Pd/C cubes had a specific activity of 0.31 mA/cm^2 for ORR at 0.9 V vs a reversible hydrogen electrode, which was 10 and 6 times those of Pd/C octahedrons and Pd/C-HT, respectively. In addition, the Pd/C cubes were even more active than the commercial Pt/C and comparable to Pt/C-HT. The high ORR activity of the Pd/C cubes was attributed to the high onset potentials and low coverage of chemisorbed OH (OH_{ad}). These data indicate that facet engineering can drastically enhance the activity of Pd nanocrystals and thus lead to the development of Pd-based catalysts for ORR.

Formic Acid Oxidation. Formic acid oxidation has attracted considerable attention because of its importance in direct formic acid fuel cells, and Pd is a primary catalyst for this reaction with substantially higher performance. The availability of Pd nanocrystals with controlled shapes and different proportions of {100} to {111} on the surface[26] provides an ideal system to systematically evaluate and optimize their catalytic properties. Figure 8 compares the catalytic properties of five different Pd-based catalysts toward formic acid oxidation. The maximum current density

increased in the order of octahedrons < truncated octahedrons < cuboctahedrons < truncated cubes < cubes, indicating that the oxidation of formic acid on Pd(100) was faster than that on Pd(111). Meanwhile, their anodic potentials increased in a similar trend with increasing the proportion of {100} to {111}. With consideration of both current density and anodic potential, Pd nanocubes with slight truncation at the corners are the best catalyst for formic acid oxidation.

Concluding Remarks

We have discussed a number of synthetic strategies based on oxidative etching, surface capping, and kinetic control for the synthesis of Pd nanocrystals with a variety of shapes. We have strived to elucidate the key factors that control the twinned structures of seeds and growth rates of different crystallographic planes and eventually determine the final shape of a nanocrystal. The mechanistic understanding also offers guidance for the design and synthesis of nanocrystals with other compositions. The ability to maneuver the shape of metal nanocrystals, together with an understanding of the shape-dependent catalytic properties, offers a great opportunity to rationally design new catalysts with substantially enhanced performance. In addition, manipulating the defect structures presented on the surface of a nanocrystal may also provide another parameter to tailor the catalytic properties of nanocrystals.[34] Future efforts should be devoted to the synthesis of bimetallic nanocrystals and nanocrystals with high-index facets. We also need to pay attention to the scale up of synthesis with losing control over size, shape, and composition.

BIOGRAPHICAL INFORMATION

Hui Zhang is an Associate Professor in Zhejiang University. He received his B.S. in Materials Science and Engineering (1995) and Ph.D. in Materials Physics and Chemistry (2005) from Zhejiang University. He spent 2 years in the Xia group as a visiting scholar from 2009 to 2011. His research interests include synthesis and utilization of nanomaterials.

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FOOTNOTES

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