

A Water-Based Synthesis of Octahedral, Decahedral, and Icosahedral Pd Nanocrystals**

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Noble-metal nanocrystals have attracted increasing attention owing to their potential use in catalysis, electronics, and biology.^[1] The physicochemical properties of these nanocrystals are highly sensitive to their shape and size. For example, the number, location, and intensity of surface plasmon resonance (SPR) bands of Au and Ag nanocrystals display a strong correlation with the shape of the particle.^[2] Furthermore, the reactivity and selectivity of metal nanocatalysts depend strongly on the crystallographic planes exposed on the surface of the particles and can therefore be tuned by controlling the morphology of these particles.^[3] An exquisite shape control of noble metal nanocrystals is therefore highly desirable for tailoring their properties and is also required for high performance in many applications.

Palladium nanocrystals are widely used as primary catalysts for the low-temperature reduction of automobile pollutants, hydrogenation reactions, and organic reactions such as Suzuki, Heck, and Stille coupling.^[4] Pd is also well-known for its remarkable capacity in hydrogen absorption.^[5] Most of these applications are related to the adsorption of hydrogen onto the surface of Pd nanocrystals. Recent studies have revealed that the hydrogen-absorption capacity and surface-enhanced Raman scattering (SERS) activity of Pd nanocrystals are dependent on their shape.^[6,7] A wide variety of Pd nanocrystals, including cuboctahedra, cubes, rods, and bars, have been prepared to date, mostly by the polyol method, in which ethylene glycol (EG) serves as both a reductant and a solvent.^[8] However, the major products of a polyol synthesis are often restricted to shapes such as truncated cubes or cuboctahedra, owing to the fast reduction and growth rate associated with the polyol process.

An alternative water-based system could provide a more convenient and environmentally benign route to the synthesis of noble-metal nanocrystals, because it does not involve toxic organic solvents or reagents. Recently, our group reported the syntheses of Pd thin plates and icosahedra in aqueous solution using poly(vinyl pyrrolidone) (PVP) and citric acid as the reducing agent, respectively.^[9,10] It is worth pointing out that

an octahedron and a decahedron are two particle shapes that face-centered cubic (fcc) noble metals can potentially take, although high-yield syntheses of these two types of nanostructures are yet to be realized for Pd.^[11]

The formation of a particular shape in the synthesis of metal nanocrystals is often explained in terms of the presence of surfactants or capping agents,^[8,10] which can change the order of free energies of different facets through their interactions with the metal surface in a solution-phase synthesis.^[12] This alteration may significantly affect the relative growth rates of different facets and thus lead to different morphologies for the final products. To achieve shape control of a nanocrystal, however, not only the thermodynamics or physical restrictions imposed by the surface stabilizing agent must be considered, but also nucleation and kinetics. Herein, we report on a water-based system for the facile synthesis of Pd nanocrystals with various shapes by reducing a Pd precursor with citric acid. Citric acid or citrate ion can also serve as a capping agent in this system thanks to their strong binding to the {111} facets of Pd.^[10,13] More specifically, we demonstrate that citric acid favors the formation of a structure such as an octahedron, icosahedron, or decahedron whose surface is covered by {111} planes. We also demonstrate that the shape of the Pd nanocrystals can be controlled by varying the concentrations of the Pd precursor and citric acid. We have been able to selectively produce Pd octahedra, icosahedra, and decahedra in high yields using this simple approach.

The synthesis was conducted in an aqueous solution containing Na₂PdCl₄, PVP, and citric acid at 90 °C for 26 h. Na₂PdCl₄ and PVP are used as a Pd precursor and a stabilizer, respectively. Citric acid serves as a mild reductant and a capping agent in a manner similar to the mechanism of a conventional citrate-based synthesis of gold or other noble-metal nanoparticles.^[14] Several hours into the reaction, the color of the solution changed from light yellow to deep brown, thereby indicating the formation of Pd nanocrystals. We explored a range of concentrations for both Na₂PdCl₄ (5.8–17.4 mM) and citric acid (0.13–0.39 M) to determine the optimal conditions for the preparation of Pd nanocrystals with different shapes.

Figure 1 shows scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of Pd octahedra synthesized in the presence of 7.3 mM Na₂PdCl₄ and 0.13 M citric acid with a molar ratio of the repeating unit of PVP to the Pd precursor of 5:1. The sample contains approximately 90% octahedra with edge lengths of approximately 20 nm and around 10% other shapes, including triangular plates and decahedra (see also Figure S1 in the Supporting Information). Although an octahedral shape has

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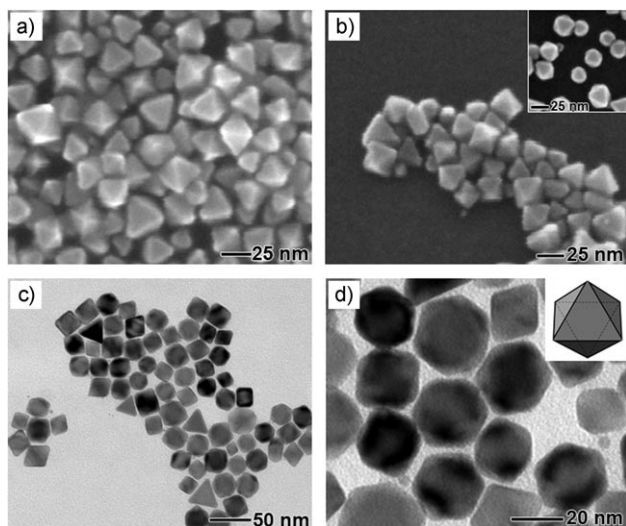


Figure 1. a, b) SEM and c, d) TEM images of Pd octahedra synthesized at 90°C for 26 h in the presence of 7.3 mM Na_2PdCl_4 and 0.13 M citric acid. The molar ratio of the repeating unit of PVP to the Pd precursor is 5:1. The SEM image in (b) was taken by tilting the substrate by 30°. The inset in (b) shows an SEM image of Pd octahedra whose C_3 axes are oriented perpendicular to the substrate. The inset in (d) shows a schematic illustration of the octahedron.

been previously reported for Au, Ag, and Pt nanoparticles,^[15] this is the first synthesis of Pd octahedra as a majority product. The SEM images (Figure 1 a,b) clearly show the octahedral shape bound by {111} planes. The Pd octahedra exhibit sharp edges and corners as well as smooth surfaces. Figure 1 c,d shows typical TEM images of the Pd octahedra. These octahedra exhibit two differently projected shapes, namely a rhombus and a hexagon, depending on their orientation relative to the electron beam. An octahedral particle lying on a flat surface against one of its faces rather than a corner or edge has a projected hexagonal shape, as shown in Figure 1 d. Both SEM and TEM images show the absence of octahedra with truncated corners.

We monitored the evolution of the particle shape by removing samples at various reaction times and then viewing them by TEM. Figure 2 a–c shows TEM images of Pd nanoparticles sampled at 1, 3, and 20 h, respectively. At $t = 1$ h, the sample mainly contains small particles with a nearly spherical profile, which could be either cuboctahedral or twinned seeds. At $t = 3$ h, particles with an octahedral shape and sizes of less than 10 nm are observed. These results indicate that the octahedra probably evolve from cuboctahedral seeds. After $t = 20$ h all the small nanocrystals below a certain size have disappeared while the larger octahedra have become bigger, thereby suggesting the involvement of Ostwald ripening in the growth process. We also found that the shape of the Pd nanocrystals is highly sensitive to the concentration of the Pd precursor. For instance, reducing the concentration of Na_2PdCl_4 by 20% and maintaining the concentration of citric acid and the molar ratio of PVP to Pd precursor at 0.13 M and 5:1, respectively, gives icosahedra as the major (>80%) species in the product (Figure 2 d), whereas increasing the concentration of Na_2PdCl_4 by 20%

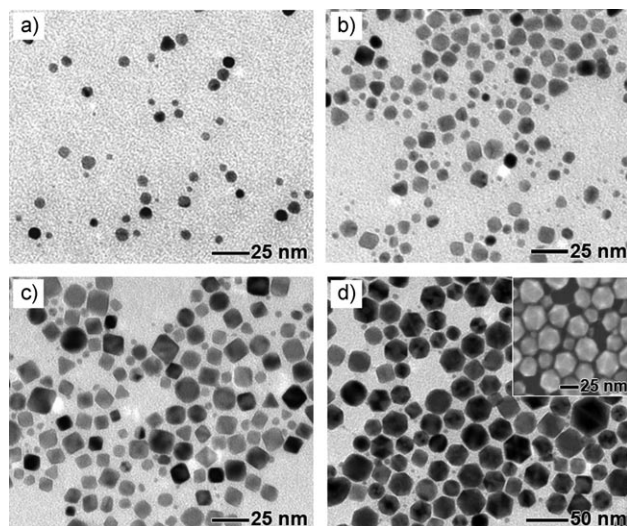


Figure 2. a–c) TEM images of three samples prepared under the same conditions as those in Figure 1 except that the reaction time was shortened to 1, 3, and 20 h, respectively. d) TEM image of Pd icosahedra synthesized under the same conditions as in Figure 1 except that the concentration of Na_2PdCl_4 was reduced to 5.8 mM. The inset in (d) shows an SEM image of the Pd icosahedra.

gives octahedra (see Figure S2 in the Supporting Information). These results indicate that formation of single-crystal Pd octahedra is more favorable than that of icosahedra at a relatively high initial concentration of Pd precursor.

A fivefold twinned decahedron, which can be described as an ensemble of five tetrahedral single crystals with twin-related adjoining faces, is one of the shapes that are enclosed by {111} facets.^[16] To achieve further shape control of Pd nanocrystals, we searched for reaction conditions that lead to decahedral nanoparticles and found that increasing the concentrations of the Pd precursor and citric acid above those that lead to octahedra and icosahedra allowed us to obtain Pd decahedra in high yields. Figure 3 shows SEM and TEM images of Pd decahedra synthesized in the presence of 17.4 mM Na_2PdCl_4 and 0.39 M citric acid. Both types of images reveal that decahedral nanoparticles (>80%) with a regular pentagonal symmetry and sizes of 25–40 nm are produced in addition to a small amount of triangular plates. The presence of fivefold twinning from the center of the decahedral particle can be seen in the magnified TEM image (Figure 3 d).

To elucidate the formation mechanism of Pd decahedra, we conducted the reactions at different concentrations of citric acid whilst maintaining the concentration of Na_2PdCl_4 at 17.4 mM. Figure 4 shows TEM images of four samples that illustrate the strong dependence of the yield of Pd decahedra on the concentration of citric acid. At a relatively low concentration of citric acid (0.13 M), the sample contains mainly Pd octahedra (Figure 4 a). However, the yield of decahedra increases drastically up to 90% as the concentration of citric acid is increased from 0.20 M to 0.39 M (Figures 4 b–d). This result indicates that the capping effect of citric acid favors the formation of decahedra.

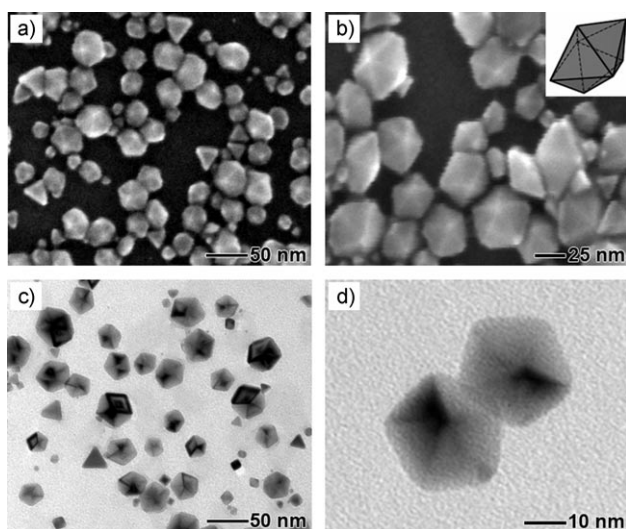


Figure 3. a, b) SEM and c, d) TEM images of Pd decahedra synthesized in the presence of 17.4 mM Na_2PdCl_4 and 0.39 M citric acid. The molar ratio of the repeating unit of PVP to the Pd precursor is 5:1. The inset of (b) shows a schematic illustration of the decahedron.

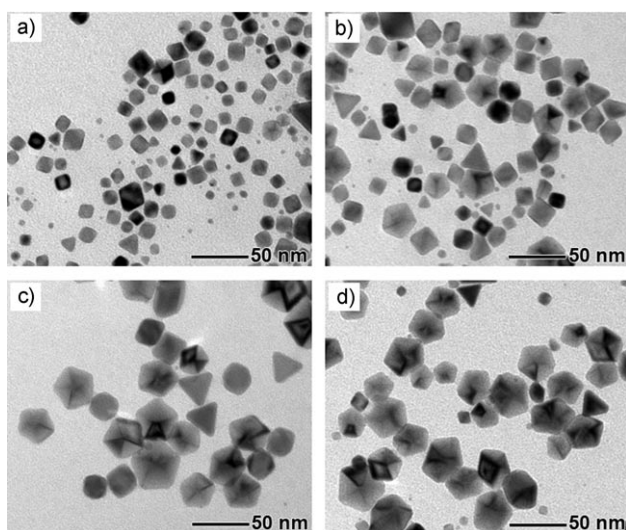


Figure 4. TEM images of samples prepared under the same conditions as those in Figure 3 except that the citric acid was added to the reaction mixture at different concentrations: a) 0.13, b) 0.20, c) 0.26, and d) 0.39 M. The decahedra in (d) are similar to those shown in Figure 3.

As we and others have demonstrated for the silver system, the crystallinity of a seed plays a key role in determining the shape of a particle.^[2c,17] The Pd nanocrystallite or seed can take a single-crystal, single-twinned, or multiple-twinned structure (including both decahedral and icosahedral structures) in the solution phase. As we have shown in a previous study, the use of a mild reducing agent such as citric acid (rather than EG) can promote the formation of twinned seeds.^[10] It has also been shown by simulation that icosahedral seeds are favored for Pd at small sizes (with the number of

atoms N less than 309), while decahedral and cuboctahedral seeds predominate at larger sizes ($N > 309$).^[18] When the concentration of Pd precursor is low the icosahedral seeds remain small for a long period of time due to the slow addition of Pd atoms, which means that icosahedra are formed in high yields in a slow reduction process (Figure 5). When the

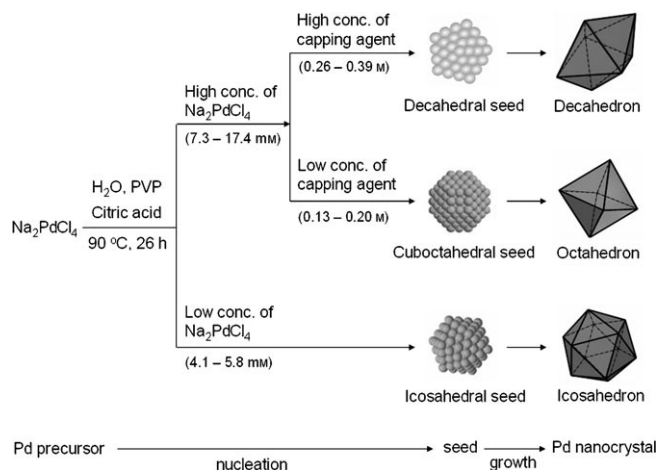


Figure 5. Reaction pathways that lead to Pd nanocrystals with different shapes.

concentration of Pd precursor is increased, however, the generation of Pd atoms becomes faster, and most seeds will take a decahedral or cuboctahedral shape because of their increased size. The formation of decahedra with sizes larger than 20 nm is not favorable because of the internal strain in the lattice caused by twin defects.^[19,20] Moreover, these defects make decahedral seeds much more susceptible to oxidative etching by the O_2/Cl^- pair than single-crystal seeds, which results in their dissolution.^[20,21] This means that single-crystal octahedra are more likely to remain in the final product, as can be seen in Figure 1. The yield of decahedra can be improved by increasing the concentration of the capping agent (citric acid or citrate ion in this case), as demonstrated in Figure 4. Citric acid or citrate ion can reduce the surface energies of the {111} facets of a decahedron by binding strongly to them and thus compensate for the extra strain energy caused by twinning. In addition, these species can block the oxidative etching by competing with oxygen adsorption on the surface of the Pd decahedra or exhausting the adsorbed oxygen atoms. Accordingly, the decahedra are preserved and thus accumulate throughout the reaction. We expect that the methodology established for this Pd system might be extendible to other fcc noble metals such as Au, Ag, and Pt, although some modifications to the experimental conditions might be required.

In summary, Pd nanocrystals with controllable shapes have been synthesized by reducing a Pd salt with citric acid in aqueous solution. The distribution of single-crystal and multiple-twinned seeds can be altered at the nucleation stage by adjusting the amounts of Na_2PdCl_4 and citric acid added to the reaction mixture. A number of polyhedra covered by {111} facets (octahedron, icosahedron, and

decahedron) have been rationally and reproducibly prepared in high yields according to this approach. These Pd nanostructures with well-controlled shapes might find uses in catalysis, hydrogen storage, photothermal cancer treatment, and optical imaging contrast enhancement.

Experimental Section

In a typical synthesis of Pd nanocrystals, poly(vinyl pyrrolidone) (PVP; MW = 55 000, Aldrich) and citric acid (Fisher) were dissolved in water (8.0 mL) in a 25-mL, three-necked flask equipped with a reflux condenser and a teflon-coated magnetic stir bar and heated to 90 °C in air with stirring. Sodium tetrachloropalladate(II) (Aldrich) was dissolved in water (3.0 mL) at room temperature, and this aqueous solution of Na₂PdCl₄ was then rapidly added to the flask with a pipette. The molar ratio of Na₂PdCl₄ to the repeating unit of PVP was kept at 1:5 in all experiments. The reaction mixture was heated at 90 °C in air for 26 h and then the product was collected by centrifugation, washed once with acetone, and finally washed twice with ethanol to remove excess PVP.

TEM images were recorded with a Phillips 420 transmission electron microscope operating at 120 kV. SEM images were recorded with an FEI field-emission scanning electron microscope (Sirion XL) operating at an accelerating voltage of 10 kV. Samples for TEM and SEM studies were prepared according to a reported method.^[10] The yield of each type of nanocrystal was calculated from 200–300 nanoparticles.

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