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Icosahedral Nanoparticles

Controllable Polyol Synthesis of Uniform Palladium Icosahedra: Effect of Twinned Structure on Deformation of Crystalline Lattices**

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Palladium plays a key role in technologies used for hydrogen storage, hydrogen purification, water treatment, and fuel cells.[1] Palladium is also widely used as the primary catalyst for low-temperature reduction of automobile pollutants, organic reactions, hydrogenation, and petroleum cracking.[2,3] These numerous applications result in palladium drawing considerable interest. Most applications of palladium are related to its remarkable hydrogen-adsorption capacity. A recent study indicated that icosahedral palladium nanoparticles (Pd NPs) can absorb a larger quantity of hydrogen than their cuboctahedral analogues.[4] Moreover, the catalytic activity of a metal NP is commonly enhanced by surface atoms located on the corners and edges.[5] Accordingly, icosahedral Pd NPs, with a high density of twins and corners on their surfaces, are expected to be the most active catalysts, and this has led to an explosion of interest in their synthesis.

Much effort has been devoted to synthesizing various metal NPs with specific shapes in aqueous or nonhydrolytic media.[6–10] Among these strategies, the polyol process[11] is a convenient, versatile, and low-cost route for the synthesis of metal NPs. In recent years, this technique has been further modified through the introduction of polymers, foreign ions, and seeds, as well as careful regulation of reaction temperature, to yield metal NPs with well-defined sizes and geometric shapes.[6,8,12,13] Initial nucleation is known to be one of the determining factors for the shape of final products. The metal nuclei can adopt single-crystal, singly twinned, or multiply twinned structures.[14] Compared with gold, multiply twinned Pd nuclei are highly susceptible to oxidation under the reaction conditions.[15] Multiply twinned Pd NPs are depleted in favor of stable single-crystalline NPs during the growth process. Consequently, the shape of the final Pd products of a solution-phase synthesis is restricted to spherical NPs, single-crystalline plates, bars, rods, cubes, and cuboctahedra owing to highly oxidative etching, poorer protection of the twinned structures, and fast reduction and growth rate.[15,16] In comparison, under slow reaction conditions, nucleation of metal atoms and growth of nuclei can be kinetically controlled through polymers or foreign ions.[13] The icosahedral structure is favored over both decahedral and cuboctahedral structures for Pd at small sizes (number of Pd atoms $N < 309$).[14b] Therefore, it is possible to selectively synthesize high-quality Pd icosahedra by carefully manipulating the growth process of icosahedral seeds generated by slow reactions. Thus, Pd icosahedra were synthesized in 80% yield by a water-based synthetic strategy.[17] To the best of our knowledge, it remains a challenge to control the synthesis of uniform Pd icosahedra in high yield.

Here we present a facile and effective polyol route for controllable synthesis of icosahedral Pd NPs with uniform size in ethylene glycol (EG) solution. A high yield of icosahedral Pd NPs was obtained in a one-pot reaction. Furthermore, the dimensions of the icosahedral NPs can be readily tailored from 15 to 42 nm by tuning the experimental parameters. A unique powder X-ray diffraction (PXRD) pattern of Pd owing to the multiply twinned structure was observed for the first time for Pd icosahedra. The as-synthesized Pd icosahedra are stable in air for months. Compared with spherical Pd NPs, Pd icosahedra can maintain their high catalytic activity even after several cycles.

For a typical synthesis of Pd icosahedra, an EG solution containing a given amount of sodium chloride (NaCl), polyvinylpyrrolidone (PVP, $M_w = 360\,000$), and sodium tetrachloropalladate (Na_2PdCl_4) was vigorously stirred and heated in air at an appropriate temperature (see the Supporting Information). Transmission electron microscopy (TEM) images demonstrate that the Pd NPs synthesized in an EG solution containing 5 mM Na_2PdCl_4, 10 mM NaCl, and 200 mM PVP have a hexagonal projection with a size of 31 ± 2 nm (Figure 1a and b). Energy-dispersive X-ray spectroscopy (EDS, Figure S1, Supporting Information) and field-emission scanning electron microscopy (FESEM, Figure 1c) analyses showed that these Pd NPs consist of only Pd and have an icosahedral shape. Figure 1d shows a high-resolution TEM

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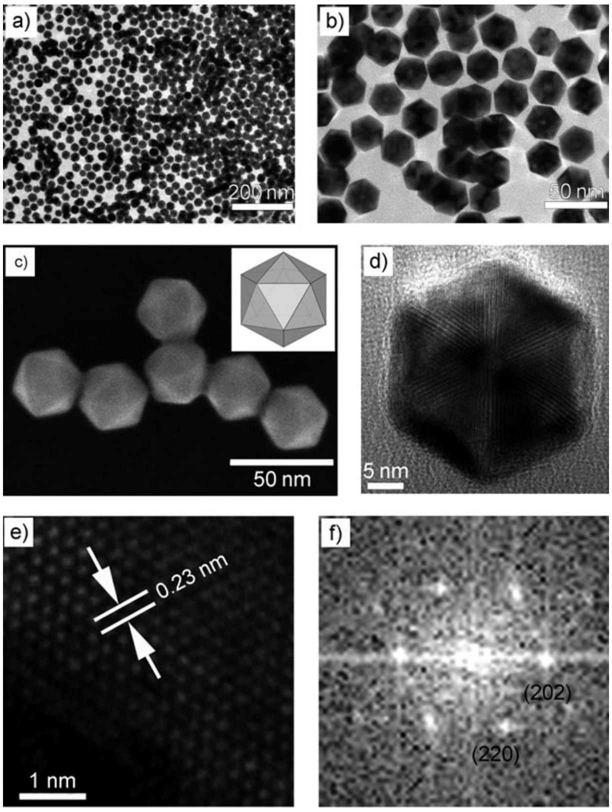

Figure 1. a) Low- and b) high-magnification TEM images, and c) FESEM image of the as-synthesized icosahedral Pd NPs. The inset shows a schematic illustration of the icosahedral structure. d) HRTEM image of a single Pd icosahedron. e) HRTEM image of one of the surfaces of a Pd icosahedron and f) the corresponding FFT pattern.

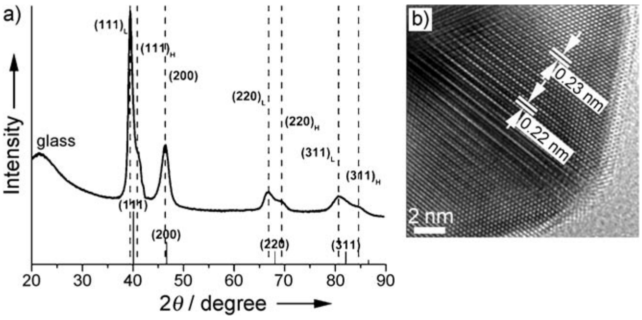

Figure 2. a) X-ray diffraction pattern and b) HRTEM image recorded on the twin boundary of a Pd icosahedron.

(HRTEM) image of a single Pd NP. Multiply twinned structures were observed on the surfaces of the NP. This image shows a threefold axis oriented parallel to the electron beam, which is in accordance with both experimental observations and simulations of noble metal icosahedra.[18] The lattice spacing of one of the faces of the icosahedron is 2.30 Å, which is larger than the standard value of 2.246 Å, and it was indexed as the {111} plane of Pd. The spots of the corresponding fast Fourier transform (FFT) with hexagonal symmetry were indexed to {220} reflections, which further revealed that the {111} lattice planes were the basal surfaces of the Pd icosahedron.

Figure 2a shows the corresponding PXRD pattern of the Pd icosahedra, which identifies the NPs as face-centered cubic (fcc) Pd. The intensity ratio of the (200) to the (111) diffraction peak in the XRD pattern of 0.30 is lower than that of 0.42 for a conventional powder sample (JCPDS 00-005-0681). This also suggests that the Pd icosahedra are rich in {111} planes. No diffraction peak of palladium oxide ($2\theta_{(100)} = 29.555°$, JCPDS 01-085-0713) was detected. However, this PXRD pattern is obviously distinct from those of Pd particles recorded in JCPDS, in that several X-ray diffraction peaks are clearly split. The *d* values calculated from the PXRD pattern deviate from the standard values (see Figure S2, Supporting Information), that is, the lattice spacings are altered in the icosahedral Pd NPs. Moreover, two different *d* values for each lattice plane except for (200) were obtained, that is, the lattice spacings vary with position even for the same planes. Previous studies revealed that the presence of twins has a significant effect on the PXRD pattern, in which the degree of pattern alteration is a function of the density of twins.[19] The geometric structure of an icosahedron is generally considered as an assembly of 20 fcc-structured single-crystalline apex-sharing tetrahedra.[14a] However, the assembly does not fully fill space, so inhomogeneous strain or distortion of the bond lengths is required to produce a space-filling structure, which leads to formation of 30 twin boundaries in an icosahedron. The distortions at the twin boundaries in our Pd icosahedra were clearly observed by HRTEM, as shown in Figures 2b and S2b (Supporting Information). Consequently, the strain is induced by distortions at the twin boundaries, and this in turn greatly alters the lattice spacing of planes. By carefully examining the lattice spacings of {111} planes at different positions, we found that, compared with the standard value, the interatomic distances at the twin boundaries are compressed, while those at the center of a face are expanded. Therefore, we believe that the deviation of the measured PXRD pattern originates from the high density of twin boundaries, which induces great strain that alters the lattice spacing. To the best of our knowledge, this is the first direct observation of the effect of the twinned structure of metal icosahedra on their PXRD pattern. The mean size of our Pd icosahedra calculated from PXRD pattern according to the Scherrer equation is only 4.3 nm from the (111) peak. The marked discrepancy between crystal sizes obtained from electron microscopy and from PXRD analysis is attributed to the presence of a numerous twin boundaries.

The roles of the reagents and conditions (NaCl, PVP, reaction temperature, etc.) were investigated to determine how they influence formation of the Pd icosahedra. First, we found that the addition of Na_2PdCl_4 to an EG solution containing PVP surfactant at room temperature, which results in the formation of a PVP–$[PdCl_4]^{2-}$ complex, is important for the synthesis of Pd icosahedra. To prove this, acetone was added to an EG solution containing PVP and $[PdCl_4]^{2-}$ ions (Figure S3, Supporting Information). Because PVP is insoluble in acetone, orange floccules of PVP–$[PdCl_4]^{2-}$ complex formed. The solution became colorless after centrifugation, that is, no $[PdCl_4]^{2-}$ ions remained in solution. When the experiment was repeated without PVP, no orange floccules were observed; the color of the solution only became fainter. The rate of reduction of $[PdCl_4]^{2-}$ ions in the polyol synthesis of icosahedra is obviously decreased by formation of the PVP–$[PdCl_4]^{2-}$ complex. For instance, when $[PdCl_4]^{2-}$ ions were introduced directly into a EG solution containing PVP at 120 °C, the solution immediately turned the deep brown color of Pd NPs. Transmission electron microscopy showed that the final product after heating for 48 h is mainly composed of 5–8 nm NPs with random shapes rather than icosahedra (Figures S4a and S4b, Supporting Information). In addition, $[PdCl_4]^{2-}$ ions were reduced quickly to Pd metal at 120 °C in a solution of Na_2PdCl_4 in EG prepared without PVP at room temperature. Large Pd agglomerates were formed in a few minutes due to the lack of protection (Figures S4c and S4d, Supporting Information), which suggests that the surfactant PVP is doubly significant for the synthesis of Pd icosahedra.

A series of experiments in which only the concentration of PVP was changed was performed to study the effect of PVP concentration. At a PVP concentration of 50 mм, the product was predominately made up of icosahedral NPs (Figure S5a, Supporting Information). Uniform Pd icosahedra were produced in high yield when the PVP concentration was in the range of 100–300 mм (Figures S5b and S5c, Supporting Information). The size of the icosahedra decreased slightly from 32 to 28 nm as the PVP concentration was increased from 100 to 300 mм. At PVP concentrations greater than 500 mм, the major products were 5 nm Pd NPs (Figure S5d, Supporting Information). In this case, the high coverage of PVP on the surface of the NPs inhibits their growth and leads to a smaller product. Experiments with lower molecular weight PVP were also conducted, at a PVP concentration of 200 mм. The surfactant PVP with a molecular weight $M_w = 40\,000$ still favors the formation of icosahedral Pd NPs which are 17 nm in diameter. In this case, the as-synthesized products tended to form aggregates of Pd icosahedra (Figure S6a and S6b, Supporting Information). When PVP with $M_w = 10\,000$ was used instead, the reduction rate of the $[PdCl_4]^{2-}$ ions was accelerated, which resulted in the final products being dominated by Pd NPs with random shapes (Figure S6c and S6d, Supporting Information). This shows that high molecular weight PVP is crucial for the formation of stable Pd icosahedra.

Further experiments revealed that the presence of oxygen is necessary for the synthesis of icosahedral Pd NPs. If the solution of Na_2PdCl_4 in EG was heated under nitrogen (oxygen in the solution was removed by freezing–pumping–thawing), the final product was dominated by uniform Pd NPs with random shapes and a smaller size of 5 nm (Figure S7a, Supporting Information). This suggests that oxidative etching by O_2/Cl^- pairs plays a positive role in the synthesis of icosahedral Pd NPs. However, oxidative etching is commonly believed to remove the twinned seeds and provide single-crystalline NPs in high yield.[6,15] As far as we know, this claim is made when the synthesis is conducted under conditions of highly oxidative etching and less protection of the twinned structures. This prevalent viewpoint on the role of oxidative etching conflicts with our experiments and previous reports.[17] Furthermore, we found that enhancing oxidative etching by using NaCl favors formation of uniform Pd icosahedra. In the absence of NaCl, the product is dominated by Pd icosahedra with a broad size distribution (Figure S7b, Supporting Information). In this case, smaller Pd icosahedra are not eliminated by Ostwald ripening with the aid of oxidative etching, that is, large and small icosahedra alike are very stable in this polyol system. Uniform Pd icosahedra were not harvested even after a reaction time of 10 d (Figure S7c, Supporting Information). In the present polyol synthesis, Pd atoms are obtained by reducing PVP–$[PdCl_4]^{2-}$ complexes in an EG solution. When the concentration of Pd atoms reaches supersaturation, they will start to nucleate and grow into Pd NPs. It is important to separate the nucleation and growth stages, that is, inhibit new nucleation events in the growth process, for the synthesis of uniform NPs.[20] On the basis of our experimental results, we infer that new nucleation events are effectively inhibited by enhancing oxidative etching with NaCl. The oxidative etching capability of O_2/Cl^- pairs can be greatly enhanced in the presence of H^+ ions.[15b] Our hypothesis was further proved by introducing HCl instead of NaCl into the initial solution of Na_2PdCl_4 in EG. In this case, uniform Pd NPs were synthesized as expected (Figure S7d, Supporting Information). However, in contrast to NaCl, the major product consists of single-crystalline Pd NPs with a cuboctahedral shape, that is, in our polyol system, the excessively oxidative etching conditions favor formation of single-crystalline Pd NPs rather than those with multiply twinned structures. This is consistent with previous reports on the polyol synthesis of Pd nanostructures.[15,16]

Generally, in polyol synthesis, the reaction temperature greatly affects the reduction rate of metal precursors, which alters the degree of supersaturation of metal atoms and hence the final size of the NPs. Experimental results with different reaction temperatures showed that the Pd icosahedra are produced predominantly at low temperatures. The color of the solution of Na_2PdCl_4 in EG changed quickly from orange to deep brown when the temperature was increased to 150 °C, and 2–6 nm NPs were formed (Figure 3 a). When the reaction temperature was lower than 140 °C, icosahedra were pro-

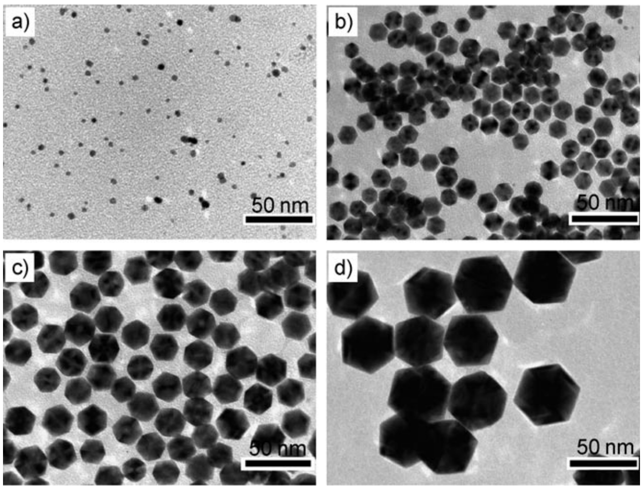

Figure 3. TEM images of samples synthesized at different temperatures: a) 150, b) 140, c) 130, and d) 100 °C (for 120 °C, see Figure 1).

duced exclusively. Moreover, the diameter of the Pd icosahedra increased from 15 to 42 nm as the reaction temperature decreased from 140 to 100 °C (Figure 3b–d). These results demonstrate that the Pd icosahedra can be obtained in high selectivity over a wide range of temperatures and that the size of NPs can be manipulated by varying the reaction temperature. Consequently, the PVP-mediated polyol process presented here is a reliable and effective means of synthesizing icosahedral Pd NPs.

We further investigated the formation process of the Pd icosahedra in a one-pot reaction; TEM images of Pd NPs sampled after 10 min, 3 h, 15 h, 40 h, and 48 h are presented in Figure S8 (Supporting Information). After heating for 10 min, ultrafine Pd NPs with sizes of less than 1 nm were formed (Figure S8a, Supporting Information). However, it is difficult to determine the morphologies of these ultrafine Pd NPs due to electron beam induced shape variations.[18] After a reaction time of 3 h, some of the ultrafine NPs had developed into icosahedral NPs of about 10 nm in size (Figure S8b, Supporting Information) together with spherical NPs with sizes smaller than 2 nm. After 15 h, the sample was mainly composed of icosahedral NPs, and their size had increased to 18 nm. At the same time, 4–7 nm spherical Pd NPs were also observed in the sample (Figure S8c, Supporting Information). As the heating time increased, the amount of spherical NPs decreased. Correspondingly, the icosahedral NPs grew larger, and this suggests Ostwald ripening occurred in the growth process: icosahedral Pd NPs grow by exhausting the spherical Pd NPs. At 40 h, the product was dominated by 28 nm icosahedra (Figure S8d, Supporting Information). The product was completely transformed into icosahedral Pd NPs after heating the sample for 48 h (Figure S8e, Supporting Information). It is well known that the morphology of initial nucleation plays a key role in determining the shape of a final NP. On the basis of our experimental results, we infer that the nuclei of Pd in the present polyol synthesis have preferentially spherical and icosahedral shapes due to their minimum-energy configurations.[14a] When bare surfaces are considered, small icosahedral Pd NPs are stable, while large Pd icosahedra become less favorable owing to their high surface free energy.[14] Polyvinylpyrrolidone molecules are strongly adsorbed on the surface of Pd icosahedra, as was verified by the FTIR spectrum (Figure S9, Supporting Information). Adsorption of chemical species on the surface of metal NPs can greatly decrease their surface energy.[7a,8a,16b] Thus, the surface free energy of Pd icosahedra is decreased by adsorption of PVP, which ensures production of large Pd icosahedra. Moreover, strong adsorption of polymers or foreign ions on the surfaces of Pd NPs can effectively block oxidative etching by O_2/Cl^- pairs.[17] Our experimental results show that icosahedral Pd NPs surrounded by {111} planes are stable compared with the spherical Pd NPs with several planes. We thus believe that PVP molecules are adsorbed onto the {111} planes more strongly than onto others, as illustrated in Figure S8f (Supporting Information), and effectively block oxidative etching of Pd icosahedra. Interestingly, in contrast to large single crystalline cubic Pd NPs with the {200} lattice plane as basal surface,[16a] the icosahedral Pd NPs presented here, which are bounded by {111} lattice planes, are very stable in air. No Pd oxide shells were observed for these NPs when stored for 100 d in ethanol solution or on a TEM grid exposed to air (Figure S10, Supporting Information). This suggests that Pd icosahedra synthesized by our method indeed reach an intrinsic equilibrium configuration.

The optical absorption properties of the Pd icosahedra were studied (Figure S11, Supporting Information). No extinction peak was detected for icosahedra with sizes smaller than 22 nm. The larger icosahedra display a single extinction peak, which is assigned to a surface plasmon resonance (SPR).[17a] The SPR peaks for Pd icosahedra with sizes of 31 and 42 nm were located at 248 and 252 nm, respectively, that is, the SPR peak position of the icosahedra shifts to the red as the NP size increases. The broad SPR peak of the NPs is due to the large imaginary component of the dielectric function of Pd.[21]

We carried out the Suzuki coupling reaction of iodobenzene and benzeneboronic acid as a model reaction to examine the catalytic activity of Pd icosahedra. According to GC-MS results, iodobenzene is quantitatively converted to biphenyl (Figure S12, Supporting Information), that is, Pd icosahedra are highly active for this reaction. Moreover, compared with spherical Pd NPs, the catalytic activity of which was lost after one cycle due to precipitation of Pd metal,[3] our Pd icosahedra can maintain their high catalytic activity even after several cycles, which is very important in the light of industrial applications. Observations by TEM demonstrate that the size of Pd icosahedra was slightly decreased after the Suzuki coupling reaction, and the shape of Pd icosahedra had changed from perfect icosahedra to icosahedra with rounded corners. The multiply twinned structure of the Pd icosahedra was retained (Figure S13, Supporting Information).

In summary, we have presented a facile and effective polyol route for the controllable synthesis of uniform Pd icosahedra with high selectivity. Palladium icosahedra with various sizes were selectively synthesized in the presence of PVP surfactant by manipulating the experimental parameters. The effect of twin boundaries on the interatomic distances of Pd was observed for the first time in the PXRD pattern. The high density of twins and sharp edges on the surface of the icosahedral NPs should result in high catalytic activity, and promises applications in low-temperature reduction of automobile pollutants, hydrogenation reactions, hydrogen storage, organic reactions, and surface-enhanced spectroscopy. Moreover, the Pd icosahedra can maintain their high catalytic activity even after several cycles. The excellent stability of the icosahedral NPs when stored in air shows that the Pd icosahedra synthesized by our method indeed reach an intrinsic equilibrium configuration.

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