Nanostructures

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Synthesis of Palladium Icosahedra with Twinned Structure by Blocking Oxidative Etching with Citric Acid or Citrate Ions**

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Palladium is well-known for its remarkable capacity for hydrogen absorption.[1] It is also widely used as the primary catalyst for low-temperature reduction of automobile pollutants, hydrogenation and dehydrogenation reactions, and carbon–carbon-bond-forming reactions such as Suzuki coupling.[2] Most of these applications are related to the adsorption of hydrogen on Pd nanoparticles. A recent simulation revealed that Pd icosahedra can absorb a larger quantity of hydrogen than their cubic analogues.[3] Another important property of Pd nanoparticles that remains largely unexplored is their surface plasmon resonance (SPR).[4] A potential application based on the SPR feature is surface-enhanced Raman scattering (SERS), whereby the enhancement factor is determined mainly by the strength of local electric field.[5] It has been reported that metal nanostructures with sharp corners or edges are especially active substrates for SERS, and the local value of $|E|^2$ could be more than 500 times that of the applied field.[6] For this reason, an icosahedron with 12 corners and 30 edges is anticipated to be a superior substrate for SERS detection. These opportunities inspired us to target the synthesis of Pd icosahedra.

Pd is a face-centered cubic (fcc) noble metal, and Pd nanoparticles may take three different shapes when fast nucleation and growth are involved: truncated cubes or octahedra, decahedra, and icosahedra.[7] The truncated cubes or octahedra are single crystals, whereas both decahedra and icosahedra are multiply twinned particles (MTPs). It has been shown by simulation that icosahedra are favored at small sizes, decahedra at intermediate sizes, and truncated cubes or octahedra at large sizes.[7] However, MTPs have never been the major product of typical solution-phase syntheses conducted in air. For example, the fast reduction of $Na_2[PdCl_4]$ by ethylene glycol produced only 10% decahedra; the major product (90%) was truncated cubes or octahedra.[8] This result can be attributed to the fact that both decahedra and icosahedra contain many twin boundary defects on the surface, which are the primary sites for oxygen absorption. As a result, MTPs are highly susceptible to an oxidative environment.[9] Our recent studies revealed that in the polyol synthesis, the MTPs were completely dissolved as a result of oxidative etching as the reaction was prolonged.[8] Therefore, it remains a grand challenge to synthesize Pd MTPs in relatively high yields. In comparison, the formation of Au and Ag MTPs is much easier to accomplish. A plausible explanation is that oxygen binds more strongly to the Pd surface than to Au or Ag,[10] which greatly accelerates the etching of Pd MTPs. For the same reason, it is impossible to completely block oxidative etching in a Pd synthesis by simply bubbling an inert gas through the reaction system.[8] Herein we demonstrate, for the first time, that the introduction of citric acid or citrate ions can block oxidative etching and promote the formation of MTPs, thanks to the strong binding of these species to the Pd surface. As a result, Pd icosahedra could be readily obtained in high yields in the presence of citric acid. We also demonstrate that the sizes of these MTPs can be controlled by adjusting the reaction time and temperature.

The synthesis was typically conducted in an aqueous solution that contained citric acid and poly(vinyl pyrrolidone) (PVP) at 90 °C for 26 h with $Na_2[PdCl_4]$ added as a precursor to Pd atoms. The PVP served as a stabilizer, and the citric acid acted as a reductant according to the mechanism of conventional citrate reduction.[11,12] Figure 1 a shows the SEM image of a typical product, which contained 80% icosahedra with edge lengths of approximately 25 nm and 20% slightly truncated octahedra (also see Figure S1 in the Supporting Information). The inset of Figure 1 a shows a high-magnification SEM image of an icosahedron, from which one can clearly resolve the exact shape. Each icosahedron is composed of 20 tetrahedra, and, as a result, has three types of rotational axes: twofold, threefold, and fivefold.[13] Figure 1 b shows a TEM image of the as-synthesized Pd icosahedra. The inset of Figure 1 b shows that most of the icosahedra have a projected hexagonal shape under TEM, which may correspond to the orientation with either a twofold or a threefold axis parallel to the electron beam. Orientation along the fivefold axis under TEM is rare because an icosahedron should preferentially lie on a flat surface against one of its faces rather than a corner. Figure 1 c and 1 d shows typical high-resolution TEM images of an icosahedron. It has a threefold axis oriented parallel to the electron beam, which is in

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

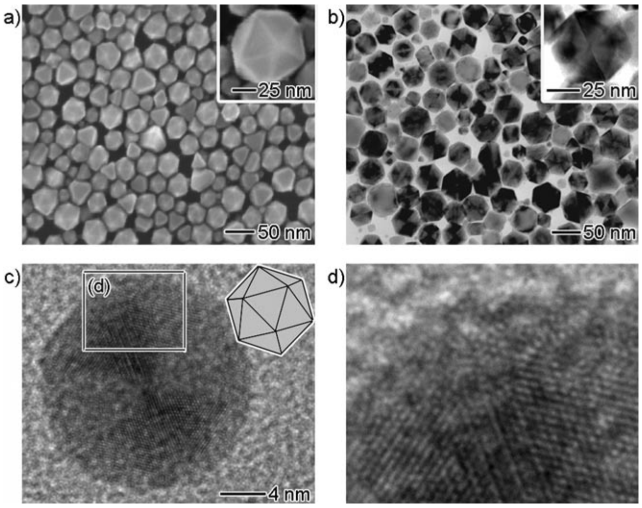

Figure 1. Electron microscopy characterization of Pd icosahedra synthesized at 90 °C in the presence of 0.13 M citric acid with a molar ratio of the repeating unit of PVP to the Pd precursor of 5:1. a) SEM image; b) TEM image; and c, d) high-resolution TEM images. The insets of (a) and (b) show the magnified SEM and TEM images, respectively, of a single icosahedron. The inset of (c) shows a schematic illustration of the icosahedron. The reaction time was 26 h.

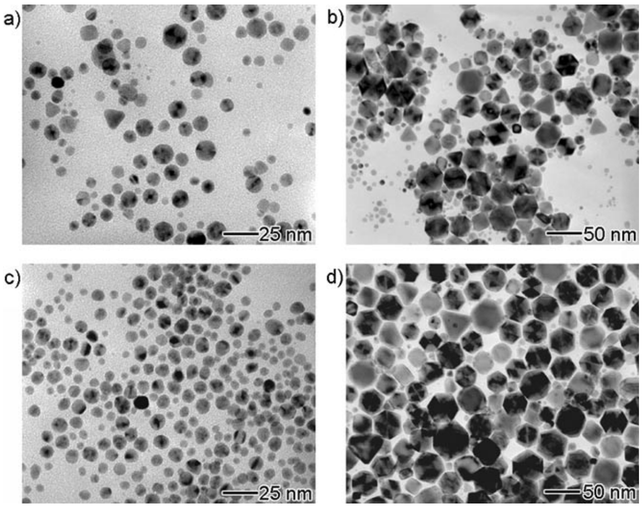

Figure 2. a, b) TEM images of samples prepared under the same conditions as those in Figure 1 except that the reaction time was shortened to 5 h and 21 h, respectively. c) TEM image of the product synthesized under the same conditions as those in Figure 1 except that sodium citrate was used instead of citric acid. d) TEM image of the product synthesized under the same conditions as those in Figure 1 except that the hydroxy end group of PVP had been removed by oxidation with $AgNO_3$.

accordance with both experimental observation and simulation of Au icosahedron.[13] The inset of Figure 1 c gives a geometrical model that corresponds to the icosahedron shown in the same figure. The phase purity and high crystallinity of the Pd icosahedra is also supported by powder X-ray diffraction (XRD). All of the peaks in a typical XRD pattern of an as-synthesized sample (see Figure S2 in the Supporting Information) can be assigned to fcc Pd (JCPDS card 05-0681). The ratio between the intensities of the (111) and (200) peaks is higher than the value reported for a conventional powder sample (2.66 versus 2.38), which indicates that the diffraction from {111} planes was enhanced for the icosahedra owing to texturing effects. This result can be understood by noting that icosahedra preferentially lie on a flat substrate against their flat {111} faces and thus increase the diffraction intensity from these planes.

To elucidate the growth mechanism of the Pd icosahedra, we monitored the evolution of their shape with TEM by taking samples at various reaction times. Figure 2 a and b shows TEM images of Pd nanoparticles sampled at 5 hours and 21 hours, respectively. At $t = 5$ h, the sample contained mainly icosahedra with an average size of 8 nm, which suggests that the icosahedra could be formed in a stage as early as nucleation, rather than through the evolution of single-crystal cubes or octahedra in the growth process. If the reaction was allowed to proceed, the size uniformity of the icosahedra gradually improved: nanoparticles below a certain size slowly disappeared while relatively large icosahedra became bigger. This observation can be attributed to the involvement of Ostwald ripening in the growth process, by which big particles grow at the expense of smaller ones.

Because the icosahedra were formed in the very early stage, the exceptional stability and high yield of MTPs in the current system is worth investigating. As demonstrated in our recent studies, formation of MTPs requires the elimination of oxidative etching from a reaction system.[8,9b] In the present case, there are two possible factors responsible for the absence of etching: the reducing power and the binding ability of citric acid. To decipher the mechanism, ascorbic acid (with a reducing power close to that of citric acid) was used as the reducing agent. In this case, the product consisted mainly of single-crystal nanocubes (see Figure S3 in the Supporting Information). In contrast, the use of sodium citrate as a reducing agent also produced MTPs (Figure 2 c). As shown by structural analysis and computational studies, both citric acid and citrate ion bind to the Pd surface more strongly than ascorbic acid.[14] We believe that this strong binding is responsible for the absence of etching when citric acid or citrate ion is present. The strong binding of citric acid or citrate ion can block oxidative etching through two different mechanisms: 1) These species can compete with oxygen adsorption on the surface of Pd icosahedra, and thus reduce the amount of adsorbed oxygen. 2) After binding to the particle surface, it is easier for these species to react with and completely exhaust the adsorbed oxygen atoms. We used Raman spectroscopy to identify the species (i.e., citric acid or citrate ion) adsorbed on the surface of Pd icosahedra. However, as the number of adsorbed species on the Pd icosahedra is quite small and the electrical field enhancement by Pd is limited, the Raman signals from aggregated films of Pd icosahedra were not strong enough for resolving the peaks. To solve this problem, we deposited the Pd icosahedra on to an aggregated film of Ag nanocubes and then recorded the SERS spectrum (see Figure S4 in the Supporting Information). The signals obtained from samples prepared in this way were significantly enhanced, from which it could be concluded that a mixture of citric acid and citrate species were present on the surface of the Pd icosahedra.

Besides its role as a stabilizer, PVP can also serve as a reducing agent in the synthesis. Most recently, we demonstrated that the ends of commercially available PVP are terminated in hydroxy groups, which can serve as a reductant for the synthesis of metal nanoparticles.[15] To clarify this point, we performed a synthesis by using PVP whose hydroxy end groups had been removed in advance by oxidization with $AgNO_3$. Figure 2 d shows a typical TEM image of the sample prepared in the presence of PVP that lacks the hydroxy end group. No major morphological difference could be found when compared with sample prepared by the normal synthesis. However, synthesis in the absence of PVP produced some MTPs with irregular shapes (see Figure S5 in the Supporting Information). These results suggest that PVP served mainly as a steric stabilizer to eliminate random agglomeration and direct the particles to grow into the well-defined icosahedral shape during the synthesis.

The range of temperature was also critical to the formation of Pd icosahedra. For example, we found that both the shape and the size of the product depended on temperature in two different ways (see Figure S6 in the Supporting Information). Firstly, low temperatures resulted in the incomplete reduction of $Na_2[PdCl_4]$ by citric acid together with slow growth rates for the Pd nanoparticles. As a result, icosahedra synthesized at 80 °C were relatively small. This dependence provides a practical way to tune the size of icosahedra. Secondly, with the increase of temperature, the oxidative etching was greatly enhanced and the binding of citric acid or citrate ion to the Pd surface became weaker, thus making it much easier to etch the MTPs. The yield of MTPs was substantially decreased when the temperature was increased from 90 to 100 °C.

The blocking of oxidative etching with citric acid or citrate ion seems to be a generic method for improving the yield of MTPs. In a recent work, a typical polyol synthesis produced 90 % single-crystalline, truncated cubes or octahedra and 10 % MTPs after 5 minutes.[8] When the reaction time was prolonged to 3 hours, all the MTPs dissolved owing to oxidative etching. By introducing citric acid into the polyol synthesis, the MTPs could be preserved and thus accumulated throughout the reaction. Figure 3 shows the dependence of the yield of MTPs on the concentration of citric acid. The reaction time was set at 3 hours, a period long enough to ensure the complete dissolution of MTPs in the absence of citric acid. The yield of MTPs increased slightly to 20 % when citric acid was added to the reaction at a final concentration of 0.13 mM. The MTPs were stable over a period of more than one week. The effect of citric acid on blocking the oxidative etching was also found to be applicable to the aqueous synthesis of Ag and Au MTPs (see Figure S7 in the Supporting Information). Notably, sodium citrate has also been used as a stabilizer in the preparation of twinned seeds that were used for the growth of Ag and Au nanorods.[16] However, it has been ignored by the research community that the citrate anion may actually play an important role in preserving MTPs by completely blocking the oxidative etching process.

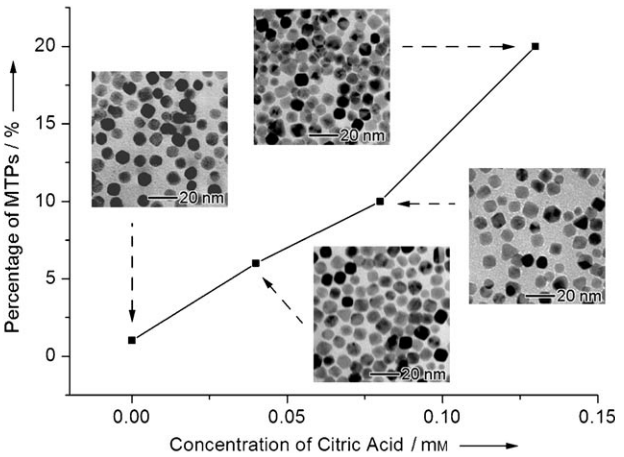

Figure 3. Correlation between the percentage of MTPs and the concentration of citric acid. The number of MTPs was counted for both icosahedra and decahedra. All syntheses were performed with ethylene glycol as the solvent and reductant at 110 °C for 3 h in the presence of citric acid at various concentrations. The molar ratio of the repeating unit of PVP (MW = 55 000) to the Pd precursor was 1.5:1. The insets show TEM images of samples synthesized under the corresponding conditions.

The icosahedra are presumed to exhibit SPR features different from those of truncated cubes. Figure 4 a shows the UV/Vis extinction spectrum taken from an aqueous suspension of Pd icosahedra 25 nm in edge length. The SPR band is red-shifted relative to that of Pd truncated cubes of similar

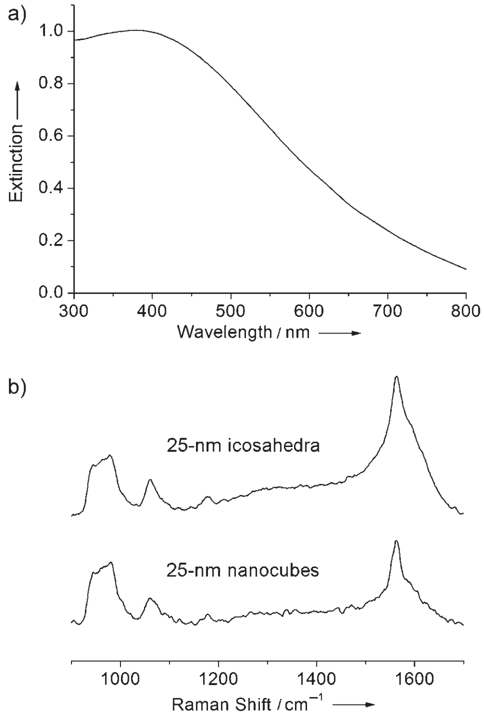

Figure 4. a) UV/Vis extinction spectrum of the as-prepared Pd icosahedra shown in Figure 1. b) Raman spectra of 1,4-BDT molecules adsorbed onto 25-nm edge length icosahedra (top, see Figure 1) and nanocubes[4b] (bottom) of Pd. The spectra were normalized against the signals of silicon (at 977.63 cm^{-1}).

size (390 nm versus 330 nm).[4b] The SPR peaks of Pd nanostructures are relatively broad, mainly because the dielectric function of Pd has a large imaginary part.[17] The exceptionally wide range of wavelengths across which Pd icosahedra strongly absorb light could potentially make them useful as nanoscale photothermal heating elements.[18]

The Pd icosahedra with well-defined surfaces provide an ideal substrate for SERS to study the compositional dependence of chemical adsorption and reactions on Pd nanocatalysts.[19] As an initial study of the SERS activities of these nanoparticles, we measured the SERS spectra of 1,4-benzendithiol (1,4-BDT) molecules immobilized on Pd icosahedra as well as on 25-nm edge length truncated cubes of Pd. Well-resolved SERS spectra (Figure 4b) could be readily obtained for the Pd icosahedra. The magnitude of signals in the spectrum of the icosahedra was 2.4 times that of the truncated cubes. We recently estimated the surface enhancement factor of the 25-nm edge length Pd cubes to be approximately 2.2×10^3,[5e] which means that the icosahedra would have a surface enhancement factor on the order of about 5.3×10^3. This improvement is most likely related to their sharp corners and edges, as well as their more red-shifted SPR band. These results indicate that Pd icosahedra are attractive substrates for SERS detection of molecular species. We expect that well-defined Pd icosahedra will advance the use of Pd in various SERS-related applications.

In summary, citric acid and the citrate ion have been utilized to prevent oxidative etching from a reaction system by taking advantage of their strong binding to the Pd surface. As a result, Pd icosahedra could be synthesized in aqueous solutions in high yields in the presence of citric acid. The introduction of citric acid into polyol syntheses also helped improve the yield of MTPs. We expect that this method can be extended to other reaction systems, although some modifications to the experimental conditions might be required. As a potential application, these Pd icosahedra could serve as active substrates for SERS detection. The exceptional chemical sensitivity of Pd towards hydrogen should make these Pd icosahedra especially useful for hydrogen storage and SPR-based sensing of hydrogen species.[1,20] Moreover, these Pd icosahedra might also find use as catalysts, photothermal heating elements, absorption contrast agents, and chemically specific optical sensors.

Experimental Section

In a typical synthesis of Pd icosahedra, poly(vinyl pyrrolidone) (PVP, 0.0356 g, MW = 55000, Aldrich) and citric acid (0.060 g, 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 stirring bar) and heated to 90 °C in air with stirring. Meanwhile, sodium tetrachloropalladate(II) (0.0188 g Aldrich) was dissolved at room temperature in water (3.0 mL). The aqueous solution of $Na_2[PdCl_4]$ was then rapidly injected into the flask by pipette. The molar ratio of $Na_2[PdCl_4]$ to the repeating unit of PVP was kept at 1:5. The reaction mixture was heated at 90 °C in air for 26 h, and then the product was collected by centrifugation, washed with acetone once, and finally with ethanol three times to remove excess PVP. The samples were characterized by transmission electron microscopy (TEM), high-resolution TEM, electron diffraction (ED), scanning electron microscopy (SEM), and UV/Vis spectroscopy.

TEM images were captured on a Phillips 420 transmission electron microscope operated at 120 kV. HRTEM images and ED patterns were taken on a JEOL 2010 LaB_6 high-resolution transmission electron microscope operated at 200 kV. SEM images were taken on a FEI field-emission scanning electron microscope (Sirion XL) operated at an accelerating voltage of 10 kV. Samples for TEM and SEM studies were prepared by drying a drop of the aqueous suspension of particles on a piece of carbon-coated copper grid (Ted Pella, Redding, CA) or silicon wafer under ambient conditions. The TEM grid or silicon wafer was then transferred to a gravity-fed flow cell and washed for 1 h with deionized water to remove excess PVP. Finally, the sample was dried and stored in vacuum for TEM and SEM characterization. All the percentages of particles herein were calculated from 200–300 nanoparticles. Powder XRD patterns were recorded on a Philips 1820 diffractometer equipped with a $Cu_{K\alpha}$ radiation source ($\lambda = 1.54180$ Å). UV/Vis spectra were measured on a Hewlett–Packard 8452A diode-array spectrophotometer.

The substrates for SERS studies were prepared by drop-casting the aqueous sol (0.5 µL) onto a Si wafer and allowing it to dry completely under vacuum. Once dried, the films were incubated in a 1 mM solution of 1,4-benzendithiol (1,4-BDT) in ethanol for 1 h. The samples were then taken out, rinsed with copious amounts of ethanol to remove any unadsorbed 1,4-BDT molecules, and dried in a stream of air. Raman spectra were taken with a Renishaw inVia Raman spectrometer attached to a Leica DMLM optical microscope using a 50 × objective (numerical aperture = 0.63) and laser excitation at 514 nm (4 mW at the sample). The Raman scattering signals were collected on a thermoelectrically cooled (−60 °C) CCD detector.

For the SERS detection of species adsorbed on Pd icosahedra, the as-synthesized Pd particles were washed with ethanol and water three times to remove any free citric acid or citrate ion. After complete washing, the samples were dispersed in water and then drop-cast onto a Si wafer that was initially covered by an aggregated film of 100-nm edge length Ag nanocubes. Once dried, the samples were characterized on the same day by using the Raman system.

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