

Synthesis of Monodisperse Palladium Nanoparticles

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ABSTRACT

We have synthesized monodisperse Pd nanoparticles with particle sizes of 3.5, 5, and 7 nm from the thermal decomposition of a Pd-surfactant complex. The particle size of Pd nanoparticles was controlled by varying the concentration of stabilizing surfactant.

The development of uniform nanometer sized particles has been intensively pursued because of the many technological and fundamental scientific interests associated with these nanoparticles.¹ These nanoparticulate materials often exhibit very interesting electronic, optical, magnetic, and chemical properties, which are unachievable for their bulk counterparts.² They have a characteristic high surface-to-volume ratio, and consequently a large fraction of the metal atoms are at the surface, and hence are available for catalysis. Many colloidal nanoparticles of transition metals have been synthesized and applied as catalysts for organic reactions.³ Recently, the synthesis of uniform sized (or monodisperse) nanoparticles became a very important research area.⁴ Klabunde and co-workers synthesized highly monodisperse gold nanoparticles from the digestive ripening, which employed aging of polydisperse nanoparticles in the presence of excess surfactant.⁵ Even though there are many reports on the synthesis of Pd nanoparticles, there is virtually no report on monodisperse Pd nanoparticles.⁶ Here, we report on the synthesis of monodisperse Pd nanoparticles from the thermal decomposition of Pd-surfactant complexes.

The current synthetic procedure is a modified version of the method developed by our group for the synthesis of monodisperse nanocrystals of metal oxides, and which employs the formation of a metal-surfactant complex followed by aging at high temperature.⁷ In the synthesis, Pd-surfactant complex, which was prepared at room temperature, was slowly heated to a high temperature, followed by aging at that temperature. The following describes the detailed synthetic procedure for monodisperse 3.5 nm Pd nanoparticles.

At first, Pd-TOP complex was prepared by reacting 0.1 g of Pd(acac)₂ (0.33 mmol) and 1 mL of trioctylphosphine (TOP) in an argon atmosphere. The color of the solution changed from yellow to orange after complete dissolution of the precursor, demonstrating the formation of the Pd-TOP complex. The FT-IR spectrum of the complex shows a C=C stretching peak at 1630 cm⁻¹, which demonstrates the release of acetylacetonate from the palladium center of the precursor (see Figure S1 in the Supporting Information). The resulting metal complex solution was injected into 9 mL of trioctylphosphine (TOP) at room temperature. The resulting solution was slowly heated to 300 °C, and was further aged at that temperature for 30 min, generating a black colloidal nanoparticle solution. CO molecules generated in situ from the thermal decomposition of acetylacetonate seem to act as reductants. A black precipitate was obtained by adding 50 mL of EtOH into the colloidal solution. The precipitate could be easily redispersed in nonpolar organic solvents such as hexane or THF to yield a clear homogeneous solution.

The transmission electron microscopic (TEM) image (Figure 1) shows that 3.5 nm sized nanoparticles are well arranged in a 2-dimensional hexagonal closed packed array, demonstrating the monodisperse particle size distribution. These monodisperse nanoparticles were obtained without any size selection process, which is important for the large-scale production, and is the first report for Pd nanoparticles. The electron diffraction pattern, shown in the inset of Figure 1, exhibited three diffused rings, which could be assigned to (111), (220), and (311) reflections of face centered cubic Pd. The X-ray powder diffraction pattern confirmed the face centered cubic structure of the metallic Pd. The particle size calculated from the line broadening of (111) reflection using

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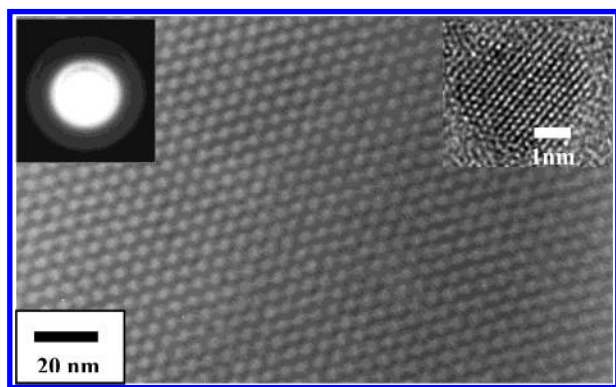


Figure 1. TEM of 3.5 nm sized monodisperse Pd nanoparticles. HRTEM image of a single nanoparticle (right inset). Electron diffraction pattern of nanoparticles (left inset).

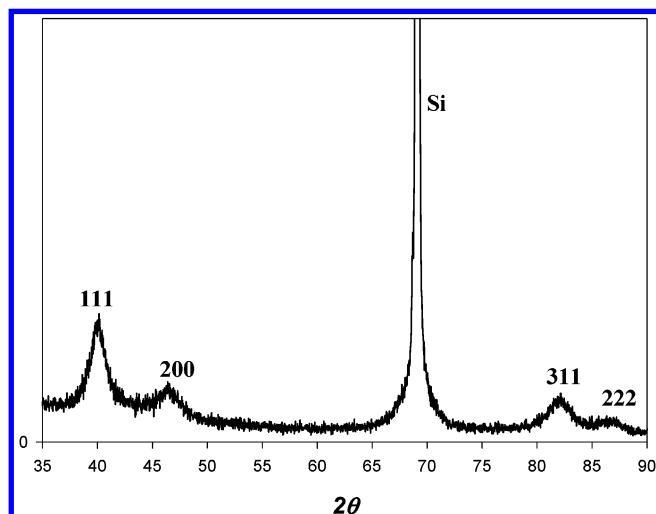


Figure 2. Powder X-ray diffraction (XRD) pattern of 3.5 nm sized Pd nanoparticles.

the Scherrer formula was 4 nm, which matched very well with TEM data (Figure 2). A high-resolution TEM (HRTEM) image of a single particle, shown in the inset of Figure 1, revealed atomic lattice fringe, demonstrating the crystalline nature of the nanoparticle. HRTEM image covering several nanoparticles, however, revealed that most nanoparticles were severely twinned and deformed (see Figure S2 in the Supporting Information).

To investigate the mechanism of monodisperse nanoparticle formation, TEM images were taken for the samples retrieved during the various reaction periods. TEM studies revealed that polydisperse and smaller nanoparticles with irregular nonspherical shape were generated right after the decomposition of Pd–surfactant complex and that particle size increased and particle size distribution became narrower as high-temperature aging was conducted (see Figure S3 in the Supporting Information). This result demonstrates that the digestive ripening mechanism, which was proposed by Klabunde and co-workers for the synthesis of monodisperse gold nanoparticles, seems to work for our current synthetic process.⁵

When a mixture of TOP and oleylamine was used as surfactants and solvent, Pd nanoparticles with particle sizes

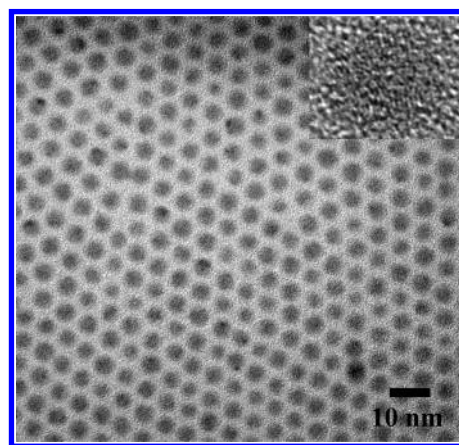


Figure 3. TEM of 5 nm sized monodisperse Pd nanoparticles. Inset is a high-resolution TEM image of a single nanoparticle.

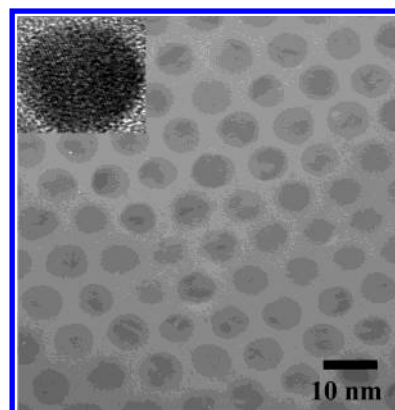


Figure 4. TEM of 7 nm sized monodisperse Pd nanoparticles. Inset is a high-resolution TEM image of a single nanoparticle.

of 5 and 7 nm were obtained. In this case, 0.1 g of Pd(acac)₂ was added into 1 mL of TOP to form orange Pd–metal complexes. The metal complex solution was added to 10 mL of oleylamine, and the resulting solution was slowly heated to 250 °C and was aged at that temperature for 30 min. During this process, the initial orange color of the solution was gradually changed to dark brown. The resulting solution was cooled to room temperature and ethanol was added to yield a black precipitate, which was then separated by centrifuging.

The TEM image of the nanoparticles showed fairly uniform sized 5 nm nanoparticles. After one-cycle of a size selective process, which employs the addition of an appropriate amount of ethanol into the hexane solution of nanoparticles, we obtained monodisperse Pd nanoparticles with a particle size of 5 nm. The uniformity of these nanoparticles is demonstrated in the TEM image shown in Figure 3. The similar procedure was applied to obtain 7 nm nanoparticles, except by using 1 equivalent of TOP surfactant (Figure 4). When oleylamine was used both as a surfactant and a solvent, polydisperse and bigger particles with particle sizes larger than 10 nm were produced.

In conclusion, we have synthesized monodisperse Pd nanoparticles with particle sizes of 3.5, 5, and 7 nm from the thermal decomposition of Pd–surfactant complexes.

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Supporting Information Available: Infrared spectra of Pd(acac)₂ precursor, Pd-TOP complex and Pd nanoparticles. TEM images of 5 and 7 nm sized Pd nanoparticles before the size selection process. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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