

Preparation and Characterization of Pd Nanoparticles by Sonochemical Reduction of $[\text{Pd}(\text{NH}_3)_4]^{2+}$ in the Presence of 1-Propanol

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Ultrafine Pd nanoparticles with an extremely narrow distribution were prepared by sonochemical reduction of $[\text{Pd}(\text{NH}_3)_4]^{2+}$ in the presence of 1-propanol. The average diameter of the particles was approximately 5 nm. These nanoparticles were extremely stable in the colloidal state, even in the absence of stabilizers. After vacuum drying, the primary particles connected to each other and formed radially arranged nanostructures of about 30–50 nm.

To prepare metal nanoclusters or colloids with monodispersity is an ongoing endeavor incited by the theoretical importance of the task and the potential applications for nanostructured materials.¹ In 1857, Faraday reported the first preparation method of metal nanoparticles in an aqueous medium.² Since then, various methods of preparing them have been developed.

The preparation of nanoparticles by a sonochemical method is worthy of attention because of the unique properties induced by acoustic cavitation. The chemical effects of ultrasound derive primarily from the acoustic cavitation. Bubble collapse in liquids results in an enormous concentration of energy from the conversion of the kinetic energy of the liquid motion into heating of the bubble contents. The high local temperatures and pressures, combined with extraordinarily rapid cooling, provide a unique means for driving chemical reactions under extreme conditions.

The research on the sonication of the ammine complex as a source of metal is insufficient, although ultrasonic cavitation has been used in the preparation of Pd nanoparticles.^{3–5} We report here the preparation and characterization of Pd nanoparticles by sonochemical reduction of $[\text{Pd}(\text{NH}_3)_4]^{2+}$ in the presence of 1-propanol.

Ultrasonic irradiation was carried out using a multiwave ultrasonic generator (Kaijo 4021) with a barium titanate oscillator 65 mm in diameter, which was operated at 200 kHz with an input power of 200 W. A cylindrical glass vessel with a total volume of 180 cm³ was used for the ultrasonic irradiation. This reaction vessel had a silicon rubber septum for gas bubbling or sample extraction without exposing the sample to air. The bottom of the vessel was planar, 1 mm in thickness, and 55 mm in diameter. The vessel and the oscillator were placed in a temperature-controlled water bath at 20 °C. The bottom of the vessel was fixed at 1 mm from the oscillator. Prior to the experiment, the intensity of the ultrasound was determined by the sonication of 60 cm³ of 0.1 mol dm⁻³ KI solution,⁶ and the rate of I³⁻ formation under Ar atmosphere was estimated to be about 2 μmol dm⁻³ min⁻¹.

Reagent-grade $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 \cdot 1.18\text{H}_2\text{O}$ powder was purchased from N. E. Chemcat Corporation. Sixty cubic centimeters of 0.2 mmol dm⁻³ $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ solution was prepared and added to the vessel. To remove air, this solution was bubbled with Ar for 30 min, and then 0.5 cm³ of 1-propanol (Wako Pure

Chemical Ind. Ltd.) was injected into the solution using a microsyringe through a septum. Subsequently, the solution was sonicated for 120 min.

The UV–visible absorption spectra of the irradiated solutions were measured by a JASCO Ubest-550 spectrometer. The size distribution of Pd nanoparticles in the solutions was obtained by the dynamic light scattering method performed with a Microtrac UPA 150 ultrafine particle analyzer. Transmission electron microscopy (TEM) images of Pd nanoparticles were taken with a JEOL JEM-2010F microscope, operated at an acceleration voltage of 200 kV. Specimens for the TEM analysis were prepared by placing a small drop of the sonicated solutions onto a microgrid covered with carbon thin film supported on a Cu grid, and then drying them under vacuum at room temperature for 1 day. The TEM images were recorded on the imaging plates at magnifications of 100,000 and 500,000 times.

The aqueous solution of 0.2 mmol dm⁻³ $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ was transparent, and its colorlessness hardly changed during ultrasonic irradiation, even in Ar atmosphere. In the presence of 1-propanol, on the other hand, the color of the solution gradually changed to dark brown after ultrasonic irradiation.

Figure 1 demonstrates the change in the absorption spectra of the solution in the presence of 1-propanol during ultrasonic irradiation. A broad absorption band from the visible to the ultraviolet region was clearly obtained after irradiation and rapidly increased with increasing irradiation time. As Figure 1 shows, a surface plasmon peak ascribed to ultrafine particles of Pd metal ($\lambda = 225 \text{ nm}$)⁷ was also observed.

Figure 2 shows the size distribution histogram of Pd nanoparticles in the solution sonicated for 120 min. The average diameter of the particles was approximately 5 nm with a relatively narrow distribution. Although no stabilizer existed in the solution, the Pd nanoparticles were extremely stable in the colloidal state.

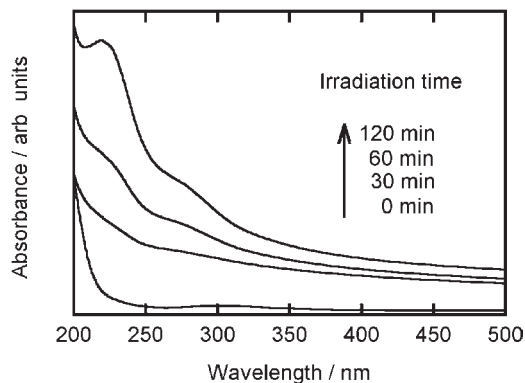


Figure 1. Changes in the absorption spectra of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ solution in the presence of 1-propanol during ultrasonic irradiation.

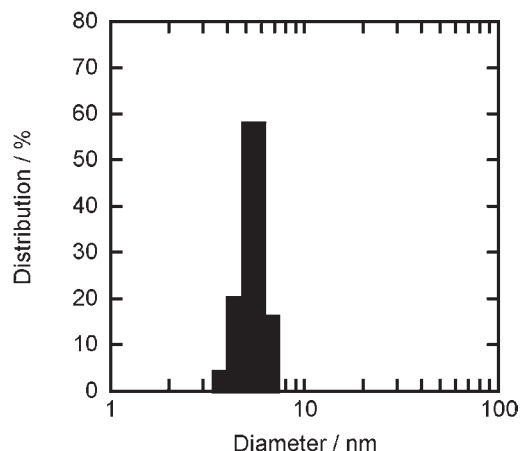
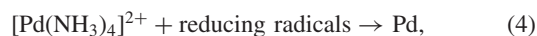


Figure 2. Size distribution histogram of the number of Pd nanoparticles in the sonicated solution. The data were obtained by the dynamic light scattering method.

Figure 3 displays TEM images of the Pd nanoparticles formed by ultrasonic irradiation of 120 min. Most primary particles had ellipsoid shapes. The average diameter of the primary particles was about 5 nm, which is consistent with that obtained by the dynamic light scattering method. As Figure 3 shows, these primary particles connected to each other and formed radially arranged nanostructures of about 30–50 nm. These nanoclusters are nonexistent in the solution because the particles of about 30–50 nm were undetected by the dynamic light scattering method, as Figure 2 presents. This unique agglomeration would occur when the TEM specimens were dried under vacuum at room temperature.

The formation mechanism of the primary particles can be represented by the following equations:



where the symbol))) indicates the action of ultrasonic irradiation and RHOH denotes 1-propanol. In our experiments, the Pd nanoparticles did not generate in the absence of 1-propanol. On the other hand, the rate of $[\text{PdCl}_4]^{2-}$ reduction was reported to accelerate with increasing of the molecular size of alcohol.⁴ These findings suggest that R·OH radicals are one of the most important radicals for reducing the $[\text{Pd}(\text{NH}_3)_4]^{2+}$ ions.

In the sonochemical preparation, the sizes of particles are dependent on several irradiation parameters, e.g., the intensity of ultrasound, the initial concentration of solution, and the temperature. Kinds of metal source and organic additive are also important. In the case of sonochemical reduction of $[\text{PdCl}_4]^{2-}$, relatively larger particles were generated, and these particles precipitated if a protective agent was not added.³ On the other hand, when the ammine complex was used as the source of metal, the nanoparticles were extremely stable in the colloidal state, even in the absence of a protective agent. Presumably, the coordinating ability of the N atom in the ammine complex would give a stable state of the colloid and also affect the

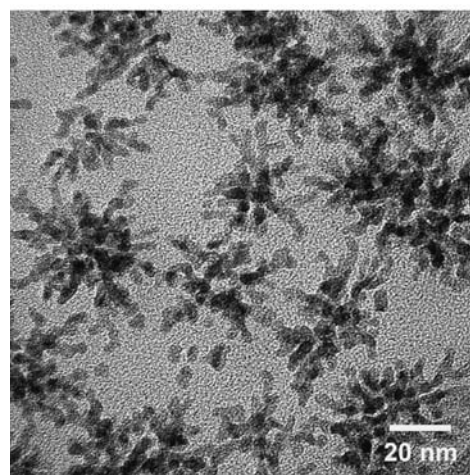
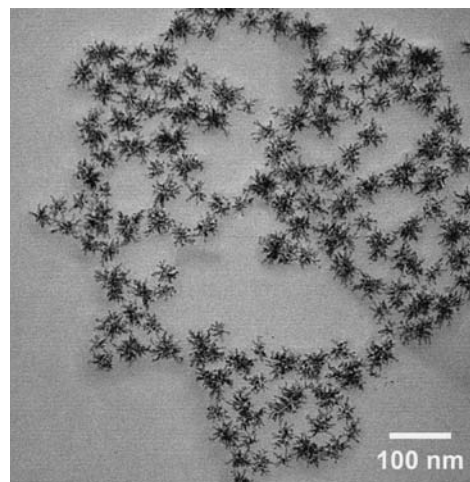


Figure 3. TEM images of the Pd nanoparticles generated by ultrasonic irradiation for 120 min.

agglomeration of the nanoparticles. Future research on sonochemical reductions of several ammine complexes will provide more information about this process.

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