

Characterization and Catalytic Activity of Core–Shell Structured Gold/Palladium Bimetallic Nanoparticles Synthesized by the Sonochemical Method

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This is a report regarding the preparation of nanosized gold/palladium bimetallic particles utilizing a cavitation phenomenon induced by irradiation of high-intensity ultrasound in an aqueous solution of gold(III) and palladium(II) ions. The particles are found to be composed of gold-core and palladium-shell by a transmission electron microscopic and nanoarea energy-dispersive X-ray spectroscopic analyses. Sodium dodecyl sulfate added to the sample solution is found to be a stabilizer for the nanoparticles generated as well as an important source of reducing species for noble metal ions. The thickness of a palladium shell and the size of a gold core seem to depend on the ratio of the concentrations of noble metal ions. The morphological differences in the sonochemical and radiochemical products suggest that the formation of a core–shell structure can be affected by the physical effects of ultrasound, such as effective stirring, microjet stream, or shock wave during the collapse of a cavitation bubble. Bimetallic nanoparticles show higher activities for the hydrogenation of 4-pentenoic acid than for those of the mixtures of monometallic nanoparticles with a corresponding gold/palladium ratio. When the gold/palladium ratio is 1:4, the activity of the bimetallic particles is about three times higher than that of palladium monometallic nanoparticles prepared under the same conditions.

Introduction

Bimetallic nanoparticles are being investigated in many fields of science and industry. It is postulated that their interesting physicochemical properties result from the combination of two kinds of metals and their fine structures. The combination of gold and palladium is one of the most popular examples that is miscible at any ratio as can be seen in their phase diagram.¹ The morphologies of gold/palladium bimetallic particles have been studied since the early 1970s.² The preparation method of such bimetallic nanoparticles can be divided into two categories: successive and simultaneous. The simultaneous method is simple because the reaction system originally contains both metal sources. The simultaneous alcoholic reduction gave core–shell structured particles only when the gold/palladium ratio was 1:4.³ Other groups reported the formation of gold/palladium bimetallic particles having a palladium-rich shell by the simultaneous alcoholic reduction method.⁴ In contrast, successive alcoholic reductions did not give core–shell structured products but, instead, gave “cluster-in-cluster” structured products or the mixtures of monometallic particles.⁵ The ligand-stabilized core–shell clusters with larger diameters of 30–40 nm were prepared in successive chemical reductions using hydroxylamine hydrochloride.⁶ It was also reported that core–shell structured bimetallic nanoparticles are immobilized on the appropriate supports, silica.⁷ Generally, successive methods require complicated procedures including several steps and give particles with larger diameters than those obtained by simulta-

neous procedures. To our knowledge, no other studies have been reported for the simultaneous preparation of the gold/palladium bimetallic nanoparticles consisting of gold cores and palladium shells with arbitrary ratios of metals.

We have previously reported the sonochemical preparation of gold core/palladium shell structured bimetallic nanoparticles.⁸ In this paper, we report the structure and preparation method of gold/palladium bimetallic nanoparticles by sonochemical reduction of gold(III) and palladium(II) ions. The fine structures of the bimetallic particles were analyzed by high-resolution transmission electron microscopy (HRTEM) equipped with nanoarea energy-dispersive X-ray spectroscopy (EDX). The reduction mechanisms of the bimetallic nanoparticles and their catalytic activities for hydrogenation were also investigated. With a comparison of the radiochemically made particles, the characteristic properties of the reaction site induced by sonication were also discussed.

Experimental Section

Materials. Reagent-grade $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$, $\text{PdCl}_2 \cdot 2\text{NaCl} \cdot 3\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$, NaBr , palladium black, and sodium dodecyl sulfate (SDS) were purchased from Wako Pure Chemical and used without further purification. Argon (99.999% purity) was purchased from Osaka Sanso. Water was treated in a Millipore system (Milli-Q).

Ultrasound Irradiation. A multiwave ultrasonic generator (Kaijo 4210) and a barium titanate oscillator of 65 mm diameter were operated at 200 kHz with an input power of 200 W and used for sonication. A cylindrical glass vessel (50 mm inner diameter) with a total volume of 150 mL was used for ultrasonic irradiation. The vessel had an arm with a silicon rubber septum

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that permits sample extraction without exposing the sample to air. The bottom of the vessel was planar and made as thin as possible (1 mm). The vessel was mounted at a constant position (3.75 mm from an oscillator: $\lambda/2$ of ultrasound wave). A typical irradiation setup is described elsewhere.⁹ The sonication was carried out in a temperature-controlled bath (about 20 °C). The vessel was closed during the sonication.

Simultaneous Determination of Au(III) and Pd(II) Ions.

To investigate the kinetics of the particle formation, it is necessary to simultaneously determine gold and palladium concentrations, both ionic and zero-valent species in the irradiated sample solution, at each sonication time. An improved colorimetric method was employed for the simultaneous determination of both gold(III) and palladium(II) ion concentrations by dual-wavelength spectroscopy.¹⁰ A detailed method for the determination of noble metal ions was previously reported.⁸ The UV-vis spectra of noble metal ions and colloidal dispersions were measured by a spectrophotometer (Shimadzu UV-3100).

γ -Irradiation. For a comparative experiment involving a hydroxyl radical reaction, γ -irradiation was performed using ⁶⁰Co-source. An N₂O-saturated sample solution in a cylindrical glass vessel (35 mm inner diameter) was irradiated at a dose rate of 2.5 kGy h⁻¹, which was determined on the basis of the same formation rate of hydroxyl radicals as in the present sonolysis. The formation rates of hydroxyl radicals were measured by a colorimetric method using iron(II) ions.⁹

TEM Observations and EDX Measurements. Specimens for TEM observation and EDX measurement were prepared by drying droplets of colloidal dispersions on a carbon-supported copper mesh in a vacuum. The observations were carried out with JEOL-2010F and JEOL-2000EX electron microscopes operated at 200 keV. Both TEMs were equipped with a nanoarea energy-dispersive X-ray spectroscopic analyzer (EDX). The minimum size of the electron beam was ca. 0.7 nm. The sizes of more than 200 particles were measured on enlarged micrographs to obtain size distribution.

Hydrogenation of 4-Pentenoic Acid by the Bimetallic Nanoparticles. Hydrogenation of 4-pentenoic acid was performed for evaluation of the catalytic activity of the sonochemically prepared nanoparticles. The hydrogenation reaction was carried out in a conventional vacuum line equipped with a diaphragm manometer (total volume: 370 mL). The round glass vessel was used for the reaction, which had a silicon rubber septum for sample injection. An aqueous solution (30 mL) containing 0.319 mg of the particles (bimetal, monometal, or mixture of the monometal) or commercially available palladium black was pretreated under 760 Torr (1 Torr = 133 Pa) of hydrogen for 60 min at room temperature. After the sample solution was evacuated, 4-pentenoic acid (0.678 mmol) and hydrogen were introduced into the reaction system. Hydrogenation was carried out at 20 ± 1 °C under stirring at 760 Torr of hydrogen, and the rates of hydrogenation were evaluated by measuring the uptake amount of hydrogen.

Results and Discussion

Sonochemical Preparation of Gold/Palladium Bimetallic Nanoparticles. The color of the aqueous solution containing gold(III) and palladium(II) ions and SDS was found to turn from pale yellow, which originated from noble metal complexes, into reddish-violet at first, then into dark brown as the sonication progressed. We have previously concluded that the reduction of gold(III) and palladium(II) ions does not occur simultaneously but, rather, sequentially, first for gold and then for palladium, judging from the change in the UV-vis absorption spectra of

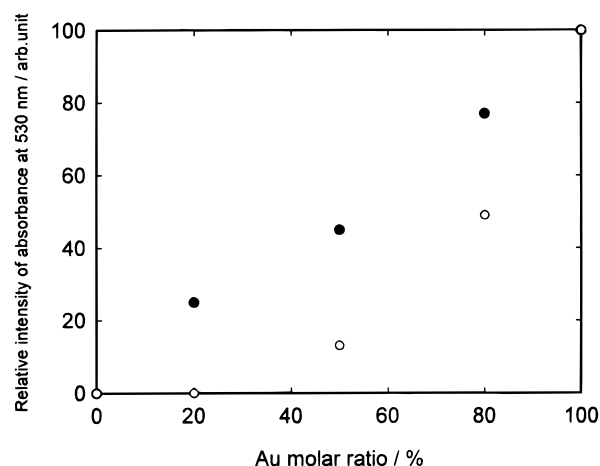


Figure 1. Relationship between the relative intensity of absorption at 530 nm and the molar ratio of noble metal. (○), gold/palladium bimetallic nanoparticles prepared by the sonochemical method, and (●), the mixtures of gold and palladium monometallic nanoparticles by the sonochemical method.

the sample solution,¹¹ and the time profile of the concentrations of gold(III) and palladium(II) ions is measured by the improved colorimetric method throughout the duration of the sonication.⁸ The blue shift of the surface plasmon absorption band of gold nanoparticles was observed. It was reported that an increase of electron density in a metal particle causes a blue shift of the plasmon resonance.¹² Comparing absorption spectra of sonochemically prepared bimetallic particles with those of the mixtures of separately prepared monometallic nanoparticles, it was suggested that gold and palladium interact with each other in the case of the bimetallic particles, judging from the intensity and the wavelength of the surface plasmon absorption band of gold nanoparticles. Figure 1 shows the relationship between the relative intensity of the surface plasmon absorption of gold nanoparticles at 525 nm and the molar ratio of gold. The gold/palladium bimetallic nanoparticles have a much weaker intensity of the absorption than the mixtures of the gold and palladium particles with the same metal ratios. The plasmon bands of gold nanoparticles disappeared when the palladium ratio exceeded 80% (mole/mole). These facts support the observation that the colloidal dispersions obtained by the sonochemical reduction of aqueous solutions containing gold(III) ions, palladium(II) ions, and SDS are not composed of simple mixtures of pure gold and palladium particles. Some interaction seems to exist between gold and palladium in the system of bimetallic nanoparticles. The intensity of the surface plasmon absorption of gold nanoparticles can be regarded as a promising indicator providing the morphological information of the products.

Characterization of Sonochemically Prepared Gold/Palladium Bimetallic Nanoparticles. Figure 2 shows TEM images of sonochemically synthesized bimetallic nanoparticles ((a) gold/palladium = 1:1 and (b) gold/palladium = 1:4). The shapes of the bimetallic nanoparticles were more spherical and well dispersed than those of the monometallic particles.⁸ The bimetallic particles had much narrower size distributions. In each case of bimetallic particles, gold/palladium = 1:1 or 1:4, the average diameter was about 8 nm and the surfaces of the particles were smooth. The diameter of the particles seems to depend on the total concentration of both noble metal ions. In the central part of bimetallic particles, a moiré pattern is observed and the contrast at the edge of a bimetallic particle is different from that at the center. This feature in the contrast is more outstanding when gold/palladium = 1:4 (Figure 2(b)). These observations suggest that the particles consist of core and

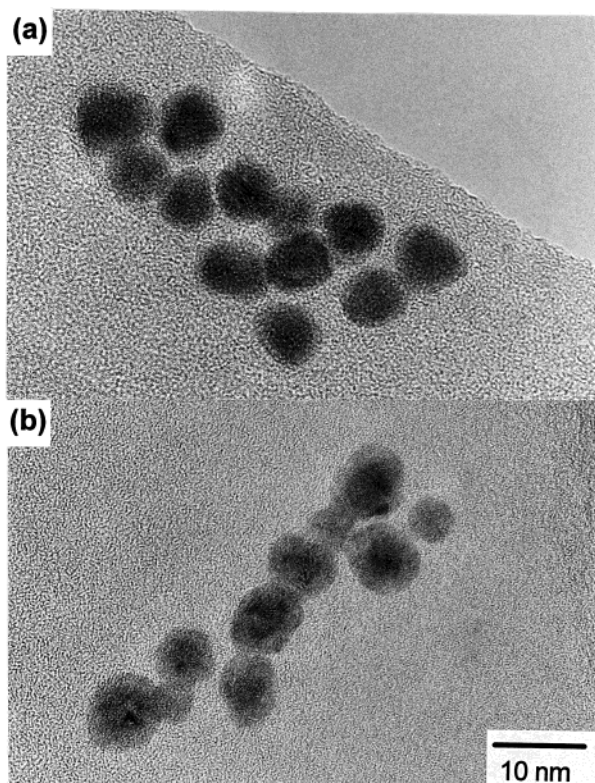


Figure 2. TEM images of sonochemically prepared gold/palladium (a) (1:1) and (b) (1:4) bimetallic nanoparticles.

TABLE 1: Results of EDX Analyses of Gold/Palladium Bimetallic Nanoparticles

	(a) Au/Pd = 1:1			(b) Au/Pd = 1:4		
	whole	center	edge	whole	center	edge
Au (atom %)	49.6	76.0	3.6	24.9	55.8	0.7
Pd (atom %)	50.4	24.0	96.4	75.1	44.2	99.3

shell, and this can be confirmed by EDX measurements. The EDX measurements were carried out by illuminating electron beams on a whole particle, the middle, and the edge of the particle. When an electron beam was sharpened and aimed at the edge of the bimetallic particles, where the contrast of the image was weaker than that at the center, the edge was found to consist of palladium (more than 95% (mole/mole)). When the whole part of the particle was analyzed by the broadened electron beam, the obtained gold/palladium ratios were approximately consistent with the ratio of gold (III)/palladium (II). The results of the EDX measurements are summarized in Table 1. HRTEM observations together with EDX results clearly show that sonochemically prepared gold/palladium bimetallic nanoparticles are composed of gold core and palladium shell. Cross-section models of core-shell structured gold/palladium bimetallic particles are shown in Figure 3. The calculated sizes of core and thickness of shell can be easily obtained taking into account the density, molar weight, and initial molar ratio of gold and palladium. In addition, their diameters were measured from TEM images. The diameter of the gold core and the thickness of the palladium shell, which were measured from HRTEM images, coincide with the calculated values (Table 2). In the sonochemical formation of gold/palladium bimetallic nanoparticles, the sizes of gold core and palladium shell could be controlled by changing the concentrations of gold(III) to palladium(II) ions. The average diameter of gold monometallic nanoparticles, prepared from an aqueous solution containing 0.5 mM NaAuCl₄ and 8 mM SDS, was 8.3 nm and larger than the

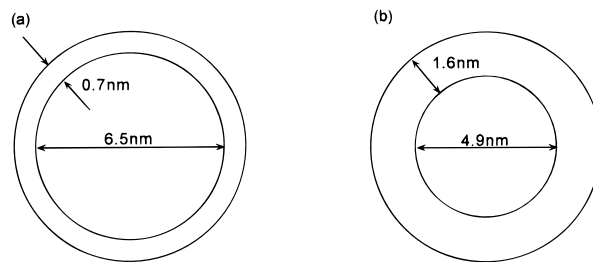


Figure 3. Cross-section models for (a) gold/palladium (1:1) and (b) gold/palladium (1:4) bimetallic nanoparticles prepared by the sonochemical method.

TABLE 2: Sizes of Gold Core and Palladium Shell of Bimetallic Nanoparticles

molar ratio ^a	diameter ^b	measured ^b		calculated	
		Au-core	Pd-shell	Au-core	Pd-shell
Au/Pd = 1:1	8.0 nm	6.0 nm	1.0 nm	6.4 nm	0.8 nm
Au/Pd = 1:4	8.0	5.0	1.5	4.8	1.6

^a Total concentration is 1.0 mM. ^b Measured from TEM image.

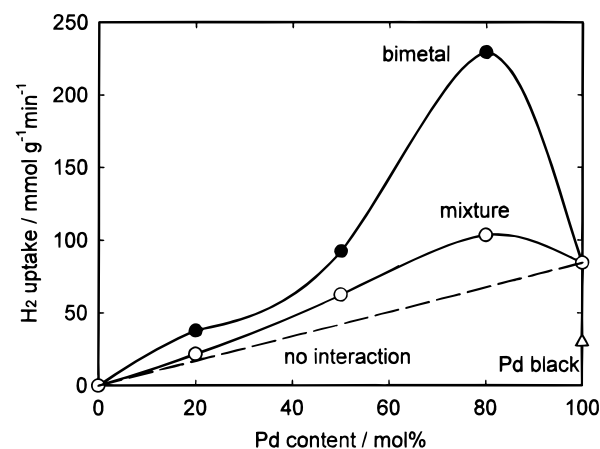


Figure 4. Initial rates of catalytic hydrogenation of 4-pentenoic acid over the bimetallic gold/palladium nanoparticles (●), palladium black stabilized by SDS (Δ), and the mixtures of gold and palladium monometallic nanoparticles (○). The rates estimated for the mixtures of gold and palladium nanoparticles without mutual interaction are also shown (dashed line).

gold-core size of the gold/palladium (1:1) bimetallics. If the nucleation of gold core was independent of the coexisting palladium, the core size should be nearly the same as the diameters of gold monometallic nanoparticles. In the formation process of gold/palladium bimetallic particles, coexisting palladium ions may participate in the nucleation of gold, although the reduction seems to proceed stepwise.

Hydrogenation of 4-Pentenoic Acid Catalyzed by the Gold/Palladium Bimetallic Nanoparticles. Figure 4 shows the catalytic activities of sonochemically prepared gold/palladium bimetallic nanoparticles with various gold/palladium ratios. The activities of the sonochemically prepared gold and palladium monometallic nanoparticles, their mixtures at various gold/palladium ratios, and commercially available palladium black are also shown. Gold monometallic particles have almost no activity. The core-shell structured gold/palladium bimetallic particles, especially when gold/palladium = 1:4, have higher activities than does the mixture with same gold/palladium ratio. It is reported that the catalytic activities of gold/palladium bimetallic particles for hydrogenation of cis-hex-2-ene become higher when the particles have a thinner palladium shell.¹³ Taking the electron negativity of gold and palladium into

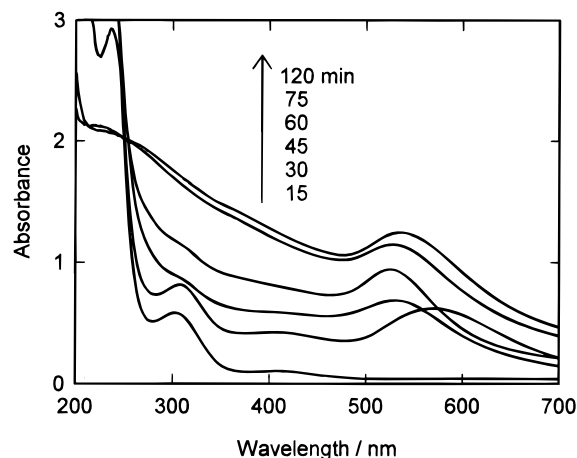


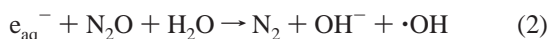
Figure 5. Change in the absorption spectra of a solution containing 0.5 mM NaAuCl₄, 0.5 mM PdCl₂, and 8 mM SDS with the duration of γ -irradiation.

account, palladium shell deposited on a gold core has more positive charge than pure palladium. The 4-pentenol acid, whose double bond has an excess of electrons, can more readily approach the surface of the heterogeneous catalyst if its surface has a deficiency of electrons. It seems that the efficiency for the hydrogenation significantly depends on the nanostructure of the gold/palladium particles. The difference in surface area is not responsible for the catalytic activities of the particles because the average diameters and the surface area of palladium are much alike in both cases, gold/palladium = 1:1 and 1:4 particles. The mixture of both gold and palladium monometallic dispersions did not give such high activities as the bimetallic particles; however, they still have higher activities than the values estimated from the sum of the activities of gold and palladium monometallic particles without mutual interaction. Gold particles coexisting in the same system with palladium particles would affect only slightly the activity of palladium particles even in their mixed system.

Radiochemical Preparation of Gold/Palladium Bimetallic Nanoparticles and Their Characterization. Figure 5 shows the time profile of the UV-vis absorption spectra of an N₂O-purged aqueous solution containing gold(III) and palladium(II) ions and SDS during the γ -irradiation. A water molecule was radiolytically decomposed to form various chemical species, such as hydrogen atoms, hydroxyl radicals, hydrated electrons, and so on.



Since the generation of hydrated electrons in the sonolysis of water molecules was confirmed to deny,¹⁴ the hydrated electrons formed in the γ -radiolysis should be scavenged by N₂O and converted to hydroxyl radicals.



The spectrum of the solution γ -irradiated for 60 min is similar to that of the mixture of gold and palladium monometallic nanoparticles prepared separately by sonication. It should be noted that the shapes of the surface plasmon absorption of gold nanoparticles are not damped at the latter part of the irradiation. However, the same sequence of the reduction as in the sonochemical method of using first gold then palladium was confirmed by the colorimetric determinations of gold(III) and palladium(II) ions. HRTEM observation together with EDX

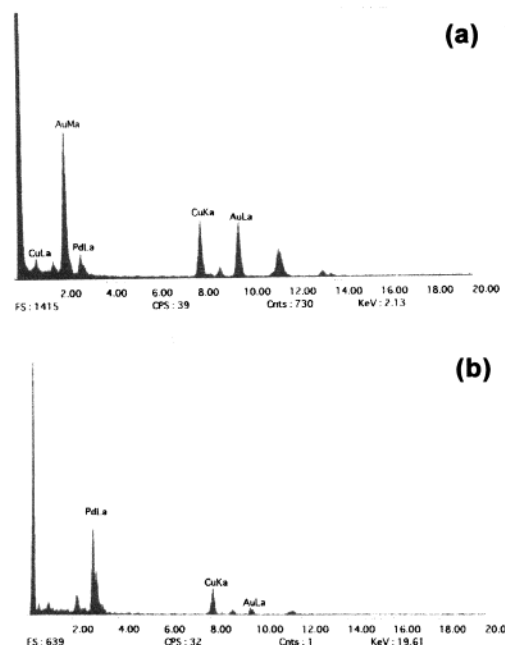
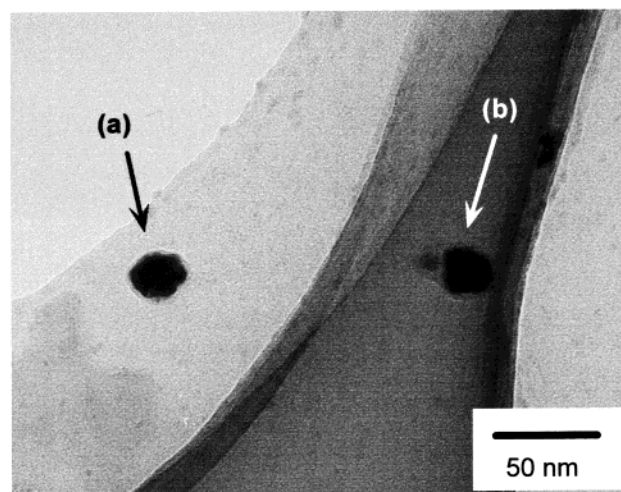


Figure 6. TEM image and EDX spectra of radiochemically reduced products from an aqueous solution containing gold (III) ions, palladium (II) ions, and SDS.

analyses support this suggestion. Figure 6 shows FRTEM images and EDX spectra of a radiolytical product from an N₂O-purged aqueous solution containing gold(III) ions, palladium(II) ions, and SDS. The sizes of the products are larger than those produced by the sonochemical method, and EDX data reveal that they are individually monometallic and not bimetallic.

In both the sonochemical and radiolytic methods, an improved colorimetric determination of noble metal ions verified that the nucleation of gold core preceded the reduction of palladium ions.¹⁵ The morphological difference of the products seemed to originate from the physical effect of the ultrasound. For example, vigorous microstirring, microjet stream obtained by sonication, and shock wave generated during the collapse of the cavity might promote the interaction between preformed gold core and post-reduced palladium. Similar considerations have been made in the preparation of platinum-monometallic particles by the sonochemical and radiochemical methods.¹⁶

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References and Notes

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