Sonochemical Preparation of Ultrafine Palladium Particles

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Received June 26, 1995
Revised Manuscript Received November 30, 1995

Ultrafine particles of noble metals have attracted considerable attention in a wide variety of fields of chemistry because of their interesting physicochemical properties. Various methods for their preparation, e.g., controlled chemical reduction,[1−4] photochemical or radiation-chemical reduction,[5,6] photocatalytic reduction,[7,8] and metal vaporization techniques,[9,10] have been studied. The preparation of fine particles of noble metals by application of ultrasound is worthy of attention because of the many unique properties induced by acoustic cavitation, viz., the formation, growth, and collapse of bubbles in a liquid.[11−13] The inside of the collapsing cavitation bubbles has been characterized by high temperatures (several thousands of degrees) and high pressures (hundreds of atmospheres).[14] However, there have been only a few preliminary investigations on the reduction of noble-metal ions by a sonochemical method.[15−17]

A new application of ultrasound to the reduction of tetrachloropalladate ions in aqueous solutions was investigated, and it was found that stable fine particles of palladium are readily produced in the presence of a protective agent such as a surfactant or a water-soluble polymer and that the protective agents are a source of reducing radicals under sonication conditions. In this communication, the sonochemical reduction mechanism for Pd(II), the roles of the protective agents, and size control of the particles are examined.

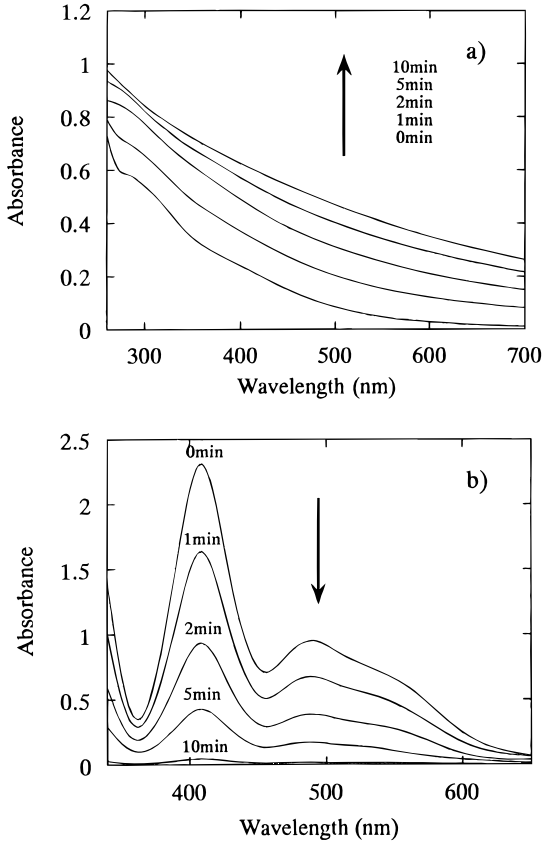

Figure 1. Absorption spectra of (a) irradiated $PdCl_2$ in SDS solution, (b) after addition of NaI solution to (a). $PdCl_2$, 0.5 mM; SDS, 8 mM; cell length, 0.5 cm.

Ultrasonic irradiation was carried out using a multiwave ultrasonic generator (200 kHz, 6.0 W/cm^2) and a barium titanate oscillator of 65 mm o.d. A cylindrical glass vessel (total volume 190 mL, diameter 55 mm o.d.) was used for ultrasonic irradiation, which had a silicon rubber septum for gas bubbling or sample extraction without exposing the sample to air. The bottom of the vessel was planar and 1 mm in thickness. The vessel was fixed at a constant position from the oscillator (λ/2; 3.75 mm). Argon-purged aqueous solutions of $PdCl_2 \cdot 2NaCl \cdot 3H_2O$ (0.1−1.0 mM, 60 mL) containing a protective agent, e.g., sodium dodecyl sulfate (SDS, 8 mM), poly(oxyethylene(20)sorbitan monolaurate) (Tween20, 5 g/L), poly(ethylene(40)glycol monostearate) (PEG40-MS, 0.4 mM), or poly(vinylpyrrolidone) (PVP, M_w 40 000, 1 g/L), were sonicated.

Figure 1a shows the change of absorption spectra of 0.5 mM of $PdCl_2$ in a SDS solution during ultrasonic irradiation under argon. Absorption peaks at about 300 and 400 nm characteristic of Pd(II) in aqueous solutions were observed before the irradiation, while these peaks decreased with the irradiation and broad absorption band from the UV to the visible region assigned to palladium particles[18] appeared. The color of the solu-

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0897-4756/96/2808-0315$12.00/0

tion changed from initial pale yellow to dark brown. At the same time, the scattering of the light from a He−Ne laser was observed, indicating the formation of colloidal palladium. The formation of metallic palladium was also confirmed by its X-ray diffraction pattern (Cu $K\alpha_1$): the data showed a diffraction peak centered at $2\theta = 39.3°$ (d spacing of 2.29 Å) corresponding to the (111) plane of elemental palladium.[19]

To estimate the rate of sonochemical reduction of Pd(II), the concentration of Pd(II) ions in the irradiated solutions was determined by an improved colorimetric method. The addition of KI solution to the sample solution (standard method[20]) resulted in the formation of Pd(II)−iodide complex with large absorbance (ϵ = 9600 M^{-1} cm^{-1}) at λ = 408 nm, probably due to the reaction of $Pd(II) + 4I^- \rightarrow [PdI_4]^{2-}$. The aggregation of colloidal Pd occurred, and this could be removed by filtration. At the same time, however, the surfactants aggregated and the solution became turbid, disturbing the determination of Pd(II). When NaI was used instead of the KI, the same ligand exchange reaction and the aggregation of colloidal Pd successfully proceeded without aggregation of the surfactants, so that the concentration of Pd(II) in the reaction mixtures was spectrophotometrically determined without interference from the surfactants and colloidal Pd.

Figure 1b shows the absorption spectra of a Pd(II)−iodide complex obtained from the irradiated Pd(II) in SDS solution by using the NaI colorimetric method. The absorption peak at 408 nm of the Pd(II)−iodide complex decreased with the irradiation time. Similar absorption spectra was obtained in a PEG40-MS solution. In a PVP solution and a Tween20 solution, the absorption peak appreciably shifted and the magnitude of absorbance was considerably enhanced (ϵ = 21 000 M^{-1} cm^{-1} at λ = 342 nm), but a good linear line dependence of absorbance vs concentration of Pd(II) was obtained as in the SDS and PEG40-MS solutions. From the plots, we estimated the rate of reduction of Pd(II) (equals the rate of formation of Pd particles) to be 110 μM/min at an initial concentration of 0.5 mM of Pd(II).

The rates of formation of palladium particles were different among the various protective agents. The rates (μM/min) were of the following orders: none, 6.9; PVP, 87; SDS, 130; PEG-MS, 230; Tween20, 400, respectively, at an initial concentration of 1 mM of Pd(II). The rates were found to be accelerated at least 10-fold by the addition of protective agents.

It has been reported that there are three different regions in the aqueous sonochemical process: (1) The inside of the collapsing cavitation bubbles where the high temperatures (several thousands of degrees) and high pressures (hundreds of atmospheres) are produced. Here water vapor is pyrolyzed into H atoms and OH radicals. (2) The interfacial region between cavitation bubbles and the bulk solution where the temperature is lower than the inside of the cavitation bubbles but still high enough for thermal decomposition of solutes to occur. In addition, the concentrations of local OH radicals were reported to be very high in this region.[21] (3) The bulk solution at ambient temperature where the reactions of solute molecules with OH radicals or H atoms, which escaped from the interfacial region, take place.

The ultrasonic power injected into the reactions under our experimental conditions was measured in terms of the sonochemically generated OH radicals and H atoms from water. The rates of formation of these radicals determined from the yields of H_2O_2 and H_2 were equally estimated to be 20 μM/min.[22] The rate of formation of Pd particles in pure water (6.9 μM/min) indicates that about 70% of H atoms contributed to the reaction, assuming the reduction of Pd(II) to Pd requires two H atoms. While in the presence of protective agents the rates were 87−400 μM/min, which are 13−58 times faster than in pure water. Consequently we assumed that the protective agents act as the reductive agents toward Pd(II) in the sonochemical process as well as serving as the stabilizers of the palladium particles.

According to our previous report[17] on the reduction of Ag(I) by ultrasonic irradiation, OH radicals (H atoms) react with the protective agents and secondary reducing radicals, R$^\bullet$, were formed by analogy with the reaction of propan-2-ol with OH radicals (H atoms) to form the reducing radical, $(CH_3)_2\dot{C}OH$:

$$RH + {}^\bullet OH(H^\bullet) \rightarrow R^\bullet + H_2O(H_2)$$

(RH denotes a surfactant)

$$R^\bullet + Ag^+ \rightarrow R' + Ag + H^+$$

However the rate of reduction of Pd(II) was much higher than the sum of the rates of formation of OH radicals and H atoms, and therefore the increase in the rate could not be explained only by the yields of H atoms or secondary radicals attributed to the reaction of OH radicals and H atoms with RH.

It has been reported[23] that the surfactants (e.g., SDS, dodecyltrimethylammonium chloride, etc.) in water are subjected to pyrolysis by ultrasonic irradiation to give some radicals such as ${}^\bullet CH_3$, ${}^\bullet CH_2R$, etc. Since these surfactants are nonvolatile and the reaction of these surfactants in the cavitation bubbles may be excluded, this event mainly occurred at the interfacial region where the surfactants are accumulated at sufficiently high concentrations.[23] Such radicals would be formed under our experimental conditions because the rate of reduction of Pd(II) increased with increasing concentrations of SDS (30 μM/min at 0.1 mM of SDS, 100 μM/min at 1 mM of SDS). The acceleration of the reduction was also observed upon addition of *tert*-butyl alcohol or *n*-pentanoic acid which would behave similarly to surfactants at the interface.[24] The rates were 250 μM/min in a 10 mM *tert*-butyl alcohol solution[25] and 300 μM/min in a 10 mM *n*-pentanoic acid solution. These values

(19) In contrast, a diffraction peak corresponding to the (101) plane of PdO at $2\theta = 33.9°$ was not detected. The observed peak at $2\theta = 39.3°$ was broad and its half-width was 0.035 radian. Other definitive diffraction peaks were not observed. X-ray diffraction studies were performed for a sample obtained by using the following specific preparation conditions: initial concentration of tetrachloropalladate ions is 10 mM, isopropyl alcohol 100 mM, irradiation time 60 min.

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(25) When the concentration of *t*-BuOH is 1 mM, OH radicals produced by the sonolysis of water are perfectly scavenged in our experiment.

Table 1. Stability of Palladium Particles Prepared by Sonication under Argon

sample (1 mM)	protective agent	state of reduced metal
$PdCl_2$	SDS	colloid[a]
	Tween20	colloid
	PEG-MS40	colloid
	PVP	colloid−ppt[b]
	none	Ppt[c]

[a] Colloid: stable more than a few months. [b] Colloid-ppt: precipitation after a week. [c] Ppt: precipitation after several hours.

were about 3 times faster than in PVP solutions and about 40 times faster than in pure water. On the other hand, the rate of radiolytic reduction of Pd(II) in SDS solution under N_2O, in which the rate of formation of OH radicals is equal to that of sonolysis of water, was 34 μM/min. From these results, we suggest that *tert*-butyl alcohol, pentanoic acid, surfactants, or water-soluble polymers are subjected to pyrolysis at the interfacial region and eventually some reducing radicals are produced, and these radicals contribute to the increase in the rate of reduction of Pd(II):

$$RH \rightarrow \text{reducing radicals} + {}^{\bullet}CH_3 \text{ etc.}$$

$${}^{\bullet}CH_3 \text{ etc.} + RH \rightarrow CH_4 \text{ etc.} + \text{reducing radicals}$$

$$Pd(II) + \text{reducing radicals} \longrightarrow Pd(0)$$

Table 1 shows the stability of palladium particles prepared under various conditions at 1 mM of initial concentration of Pd(II). The particles prepared in pure water were unstable and gave aggregates within several hours under both air and argon, but most of the particles prepared in protective agents solutions were stabilized and have persisted over several months of the colloidal state.

Figure 2 shows the size distribution of palladium particles from a solution of 0.5 mM of Pd(II) measured by a dynamic light-scattering photometer (Ohtsuka DLS-700). The average size of the particles was 9.5 nm. The palladium particles obtained in all protective agents were very fine and their size had narrow distribution in the range of several nanometers. Table 2 shows the dependence of the initial concentrations of Pd(II) on the size under various conditions. The size of the particles became smaller with decreasing initial concentration of

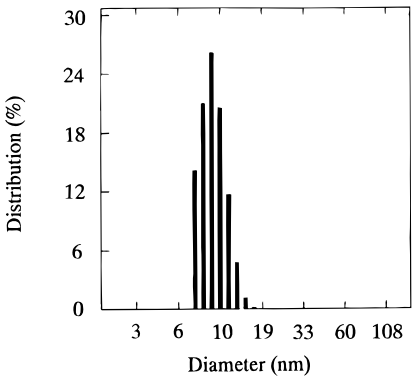

Figure 2. Size distribution of palladium particles prepared under argon. $PdCl_2$, 0.5 mM; SDS, 8 mM; irradiation time, 10 min.

Table 2. Average Particle Size of Palladium Prepared under Ar

initial concn of Pd(II) (mM)	protective agent	size (nm)
0.1	SDS	8.4
0.5	SDS	9.5
0.75	SDS	10
1.0	SDS	88
0.1	PVP	6.1
0.5	PVP	7.5
0.75	PVP	7.5
1.0	PVP	110
1.0	Tween20	5.3
1.0	PEG40-MS	14

Pd(II) and was dependent on the kind of protective agents. The average sizes of the particles were 6 and 110 nm at concentration of 0.1 and 1.0 mM of Pd(II) in PVP solutions, respectively. Since it appears that the sizes of the Pd particles are dependent on the experimental conditions (such as initial concentration of Pd(II) and/or the protective agent, the kinds of protective agents, and the rates of reduction of Pd(II)), it is suggested that the preparation of the particles with various sizes in the range of several nanometers to hundreds of nanometers is possible. This method of sonochemical reduction of noble-metal ions appears to be a promising one for the preparation of noble-metal colloids in aqueous solutions. And in addition, preliminary results suggest that these colloidal dispersions of palladium prepared by the sonochemical method exhibit interesting catalytic activity.

CM950285S