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Photoreduction of Rhodium(Ⅲ) Ions in Water with Ultraviolet Light Aiming to Prepare the Dispersions of Ultrafine Particles

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Rhodium (Ⅲ) ions in an aqueous solution were successfully photoreduced by ultraviolet light irradiation. In the presence of a soluble polymer or a surfactant as a protective agent, the stable dispersions of ultrafine metal particles of rhodium were prepared. Besides, the photoreduction proceeded on irradiation with visible light in the presence of ethanol or 2-propanol.

Noble metal ions such as platinum and palladium in water are easily reduced to the corresponding elemental metals on irradiation with visible light. In the presence of soluble polymers or surfactants, the photoreduction results in the formation of stable dispersions of ultrafine noble metal particles.1,2) Ultrafine metal particles protected by micelles or vesicles are regarded as to have characteristic potential fields owing to highly ordered assemblies of amphiphilic molecules.3,4) We have already reported that micelle-protected ultrafine platinum particles exhibit specific photochemical activities and catalyses.2,4,5) However, extremely mild reduction conditions such as light irradiation are required to prepare these micelle-protected ultrafine particles without destruction of the molecular assemblies. Although the photoreductions of noble metal ions have also been reported on gold6) and silver,7) there are scarcely any reports on the photoreduction of Rh(Ⅲ) ions.

In the present study, we have achieved the photoreduction of Rh(Ⅲ) ions by irradiation of an aqueous solution of rhodium(Ⅲ) chloride with ultraviolet light in a quartz cell instead of a Pyrex one. The photoreduction successfully resulted in formation of the stable dispersions of ultrafine rhodium particles in the presence of a surfactant or a soluble polymer as a protective agent. The reduction was accelerated by addition of primary or secondary alcohols. Moreover, the photoreduction became possible even on irradiation with visible light by addition of ethanol or 2-propanol.

Dodecyltrimethylammonium chloride (DTAC) and poly(N-vinyl-2-pyrrolidone) (PVP) were used as protective agents. Rhodium(Ⅲ) chloride and the protective agent were dissolved in water at the concentrations of $[RhCl_3]$ = 1.0×10^{-3} mol dm^{-3} and [DTAC] = 2.0×10^{-2} mol dm^{-3} or [PVP] = 2.0 g dm^{-3}. The solution in a quartz cell was degassed twice by freezepump-thaw-cycles and then irradiated by the light of λ > 200 nm with a 500 W xenon lamp. A UV-31 cut filter, which has similar transmission property to Pyrex glass, was put at the light path in front of the cell when the irradiation with visible light was required. UV-Vis absorption spectra of the dispersions were recorded with a Hitachi 340 recording spectrophotometer and with an Otsuka Electric MCPD-110A rapid scan multi-channel photodiode array spectrophotometer.

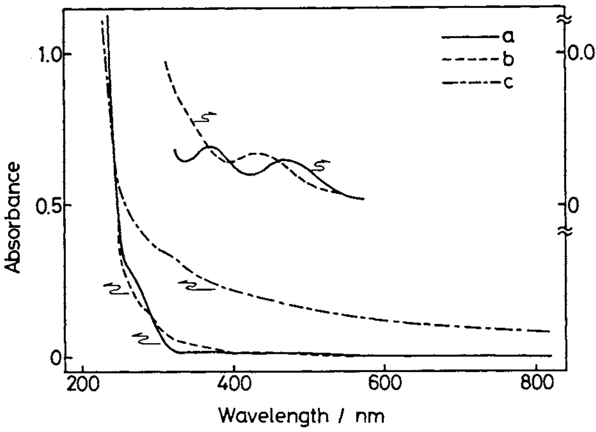

Fig. 1. Changes of absorption spectra in the course of the photoreduction of Rh(Ⅲ) in H_2O in the presence of DTAC. **a**, Before irradiation; **b**, after irradiation through a UV-31 filter for 72 h; c, after subsequent irradiation of **b** without the filter for 20 h. Partial spectra of **a** and **b** are magnified with the right ordinate scale. Cell length, 2 mm.

Irradiation with the light of λ > 200 nm resulted in successful reduction of Rh(Ⅲ) ions and in formation of stable dispersions of ultrafine rhodium particles in the presence of DTAC or PVP. Changes of the absorption spectra of the solution are shown in Fig. 1. By the irradiation, the initial pale rose color of the solution changed to pale yellow and finally into dark brown with complete disappearance of the absorption peaks around 350—500 nm due to d-d transition of Rh(Ⅲ) ions. The dispersions obtained exhibit intense and broad absorption throughout UV-Vis region with characteristic increase in absorbance at the longer wavelength of visible region. Transmission electron micrograph of the dispersion revealed fine rhodium particles of average diameter of ca. 20 Å with narrow size distribution, as shown in Fig. 2. On the other hand, the irradiation through a UV-31 cut filter resulted in only the color change of the solution to pale yellow without any increase in absorbance at the longer wavelength even after 3 days, and no distinct images could be observed with a

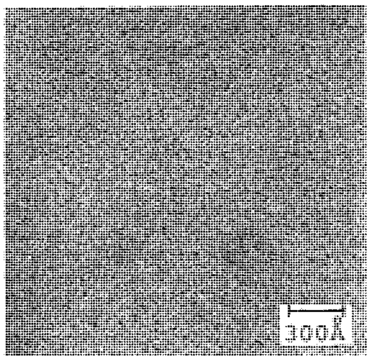

Fig. 2. Transmission electron micrograph of ultrafine rhodium particles protected by DTAC obtained by the photoreduction in H_2O.

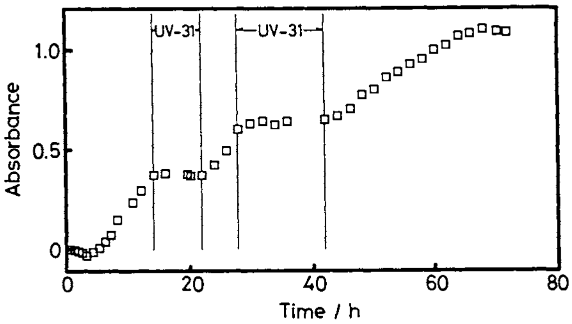

Fig. 3. The time course of absorbance at 550 nm through the photoreduction of Rh(Ⅲ) by irradiation with UV/Vis light switched by a UV-31 cut filter in the presence of DTAC in H_2O.

transmission electron microscope. The color change of the solution to pale yellow can be ascribed to aquation of Rh(III) ions, since the Cl^- ligands of Pt and Rh complexes are known to be easily exchanged by H_2O on irradiation with visible light.[8)]

Removal of the UV-31 cut filter from the light path initiated subsequent photoreduction with increase in absorbance at the longer wavelength, and finally the dark brown dispersion was obtained. Increase in absorbance at the longer wavelength, which ascribed to progress of the photoreduction, can be stopped and resumed by insertion and removal of the UV-31 filter, respectively. The time course of absorbance at 550 nm when the irradiation was switched by the UV-31 filter is depicted in Fig. 3. These results obviously indicate that ultraviolet light in the range from 200 nm up to 300 nm is efficient for the present photoreduction of Rh(III) ions in water. Additionally, the present photoreduction was accelerated by addition of ethanol. In this case, acetaldehyde was detected in the obtained dispersion by the Tetrazolium Blue test.[9)]

Moreover, it was revealed that even with the light of λ > 300 nm, Rh(III) ions could be photoreduced in the presence of ethanol. Addition of organic solvents to an aqueous system tends to destroy micelles. In fact, preparation of micelle-protected ultrafine particles was unsuccessful in 50 vol% aqueous ethanol resulting in black precipitates of metallic rhodium. In 10 vol% aqueous ethanol, however, photoreduction by irradiation through the UV-31 filter successfully resulted in formation of the stable dispersion of ultrafine rhodium particles protected by micelles of DTAC. Photoreductions of Rh(III) ions in the presence of various alcohols were carried out by irradiation with the light of λ > 300 nm using a UV-31 filter. The results are summarized in Table 1. The progress of the reduction, evaluated by increase in absorbance at 550 nm, was most prominent in the presence of 2-propanol although almost no reduction proceeded with 2-methyl-2-propanol. These results are consistent with the order of the tendency of α-hydrogen subtraction as follows: 2-propanol > ethanol > water $\gg$ 2-methyl-2-propanol.[7)]

From the results obtained, the following mechanism could be proposed. The aquated rhodium ion excited by ultraviolet light is regarded as to subtract a hydrogen atom from

Table 1. Formation of ultrafine rhodium particles by photoreduction of $RhCl_3$ in $H_2O^{a)}$

Wavelength	Additive (10 vol%)	$A_{550}{}^{b)}$
>300nm$^{c)}$	None	0.07
>300nm	Ethanol	0.15
>300nm	2-Propanol	0.23
>300nm	2-Methyl-2-propanol	0.02
>200nm$^{c)}$	None	0.76
>200nm	Ethanol	1.89

a) Irradiation for 24 h unless otherwise mentioned. b) Absorbance at 550 nm; cell length, 10 mm. c) Irradiation for 72 h.

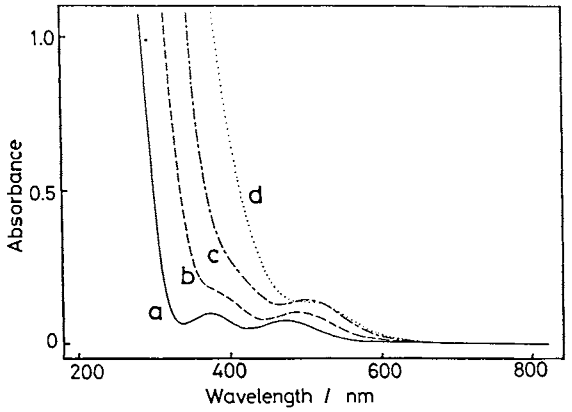

Fig. 4. Absorption spectra of $RhCl_3$ solutions. Cell length, 10 mm. Solvent: a, H_2O; b, ethanol; c, 2-propanol; d, 2-methyl-2-propanol.

$$(M^{n+}, H_2O) \xrightarrow{h\nu} M^{(n-1)+} + H^+ + \dot{O}H \tag{1}$$

$$RCH_2OH + \dot{O}H \longrightarrow R\dot{C}HOH + H_2O \tag{2}$$

$$R\dot{C}HOH + M^{n+} \longrightarrow M^{(n-1)+} + H^+ + RCHO \tag{3}$$

$$(M^{n+}, RCH_2OH) \xrightarrow{h\nu'} M^{(n-1)+} + H^+ + R\dot{C}HOH \tag{4}$$

the coordinated water molecule, and consequently, the lower valence metal ion can be formed as well as proton and hydroxy radical, as shown in Eq. 1. Hydroxy radical is more easily scavenged by ethanol than by water so that the coexisting ethanol is considered to scavenge the hydroxy radical producing $CH_3\dot{C}HOH$ radical, which performs further reduction of rhodium ions resulting in formation of acetaldehyde as shown in Eqs. 2 and 3. In the presence of alcohols the α-hydrogen of the alcohols which coordinate to the rhodium ion is directly subtracted by the excited rhodium ion resulting in the reduction of the rhodium ion as shown in Eq. 4. A similar mechanism has been proposed for photoreduction of silver perchlorate.$^{7)}$ It was also found that the CT absorption edge of $RhCl_3$ around 300 nm in an aqueous solution shifted to longer wavelength in alcoholic solutions as exhibited in Fig. 4. Thus, it is supposed that in the presence of alcohols the Rh(III) ions solvated by the coexisting alcohols become to be excited by the light of λ > 300 nm.

In conclusion, reduction of Rh(III) ions in water was achieved by irradiation with ultraviolet light in the range of 200 nm < λ < 300 nm resulting in formation of the dispersions of ultrafine rhodium particles protected by DTAC micelles or PVP. The achievement of the present photoreduction is attributed to hydrogen subtraction from the coordinated molecules of Rh(III) ions by excitation with photoirradiation.

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