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COLLOIDAL PLATINUM PROTECTED BY POLYMERIZED MICELLE. PREPARATION AND APPLICATION TO CATALYSIS FOR PHOTOCHEMICAL HYDROGEN GENERATION FROM WATER

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Colloidal platinum protected by polymerized micelle was prepared by photoreduction of chloroplatinic acid in the presence of unsaturated surfactants and the subsequent UV-polymerization of the surfactants. This colloidal platinum acts as an active catalyst for photochemical hydrogen generation from water in the system of EDTA/$Ru(bpy)_3^{2+}$/MV^{2+}.

A number of studies on artificial photosynthesis have been in progress and photochemical hydrogen generation from water is receiving a great interest because it has a possibility to convert solar energy into renewable chemical energy.1-4) Colloidal platinum is generally used for redox catalyst for hydrogen generation in the artificial photosynthesis system like tris(bipyridine)ruthenium(II) [$Ru(bpy)_3^{2+}$] and methyl viologen(MV^{2+}), and there have been quite a few reports about preparation of colloidal platinum.5-8) On the other hand, a micellar system is often reported to be effective for photochemical reactions in respect of charge separation and electron transfer.9-11) In the present paper a new method to prepare a stable and active colloidal catalyst using a micellar system is proposed. We have already reported that colloidal platinum protected by surfactants is successfully prepared.12) However, it is too unstable to be used for the catalyst for hydrogen generation under the conditions of such high ionic strength. So we have examined polymerizing the micelle to make it stable enough to be used.

Sodium undecenoate was chosen for an unsaturated surfactant.13,14) 10-Undecenoic acid was purified by distillation under reduced pressure (1.0 mmHg, 117 °C), and neutralized by equimolar amount of sodium ethoxide in an ethanol solution. An aqueous solution of sodium undecenoate (1×10^{-1} mol dm^{-3}) and chloroplatinic acid (2×10^{-4} mol dm^{-3}) was put into a Pyrex tube, and irradiated with a high pressure Hg lamp for more than two hours producing colloidal platinum protected by monomeric micelle, as reported in the previous paper.12) Polymerization of sodium undecenoate was performed in the following procedure. Colloidal platinum protected by monomeric micelle was put into a quartz ample and added a small amount of sodium persulfate as an initiator. The mixed solution was irradiated with 30 W low pressure Hg lamp for 24 hours. After that the resulting solution was concentrated to about 10 cm^3 by evaporation under reduced pressure, and poured into large excess of ethanol for reprecipitation. The precipitate was

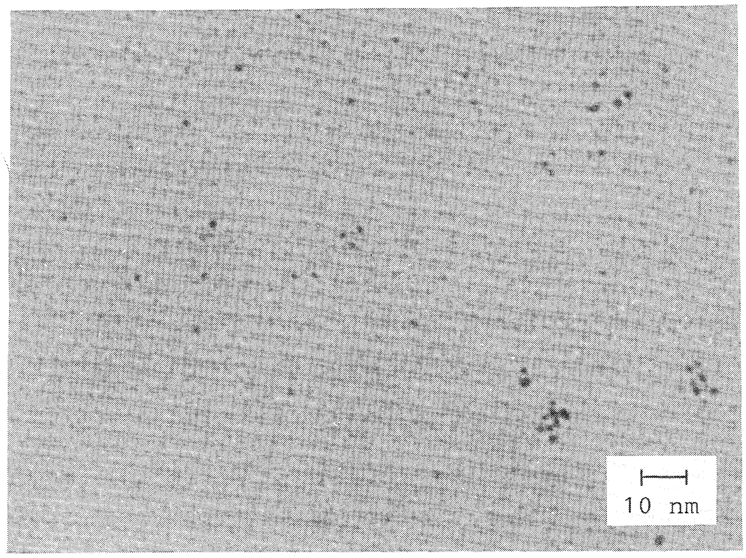

Fig. 1. Electron micrograph of colloidal particles protected by polymerized micelle.

filtered and dried in vacuo. Colloidal platinum protected by polymerized micelle was obtained in the form of brownish powder. The conversion was about 15% and the concentration of platinum in the brownish powder was about 0.28wt% from atomic absorption. When the obtained powder was dissolved in water again, the homogeneous colloidal dispersion was obtained.

The colloidal platinum thus obtained was characterized by electron micrography, IR and ^{1}H NMR spectroscopies. Figure 1 shows the electron micrograph of obtained colloidal particles. The average particle size was about 1.1 nm, a little larger than that prepared in a monomeric micelle (0.9 nm for sodium undecanoate). The irradiation with UV light and the presence of radical initiators little influenced upon the growth of the colloidal particles. Figure 2 shows the ^{1}H NMR spectra of sodium undecenoate before (a), and after (b) UV-irradiation. The polymerization of undecenoate was confirmed by the disappearance of the peaks from 5 ppm to 7 ppm, ascribed to the olefinic protons, as well as by the brodening of the rest of the peaks. In IR spectra, the peaks at 3100, 1640, 990, and 910 cm^{-1} were all disappeared, indicating the formation of polymerized micelle again. Polymers were not obtained in the absence of the water-soluble initiator.

Photochemical hydrogen generation was examined in the aqueous solution of $Ru(bpy)_3^{2+}$ (5×10^{-5}mol dm^{-3}), MV^{2+} (5×10^{-3}mol dm^{-3}), and EDTA (5×10^{-2}mol dm^{-3}), in the presence of 5×10^{-5}mol dm^{-3} of Pt. Platinum dispersions having various types of protective colloid were used for comparison. The protective colloids used were poly(sodium undecenoate) (Pt-PUE•Na, polymerized micelle), sodium undecanoate (Pt-UA•Na, monomeric micelle), poly(sodium acrylate) (Pt-PAA•Na, anionic linear polymer), and poly(N-vinyl-2-pyrrolidone) (Pt-PVP, nonionic linear polymer). All colloidal dispersions were prepared by a photoreduction method in the same conditions in the presence of the same amounts of the various protective colloid. The catalytic activities were compared by the

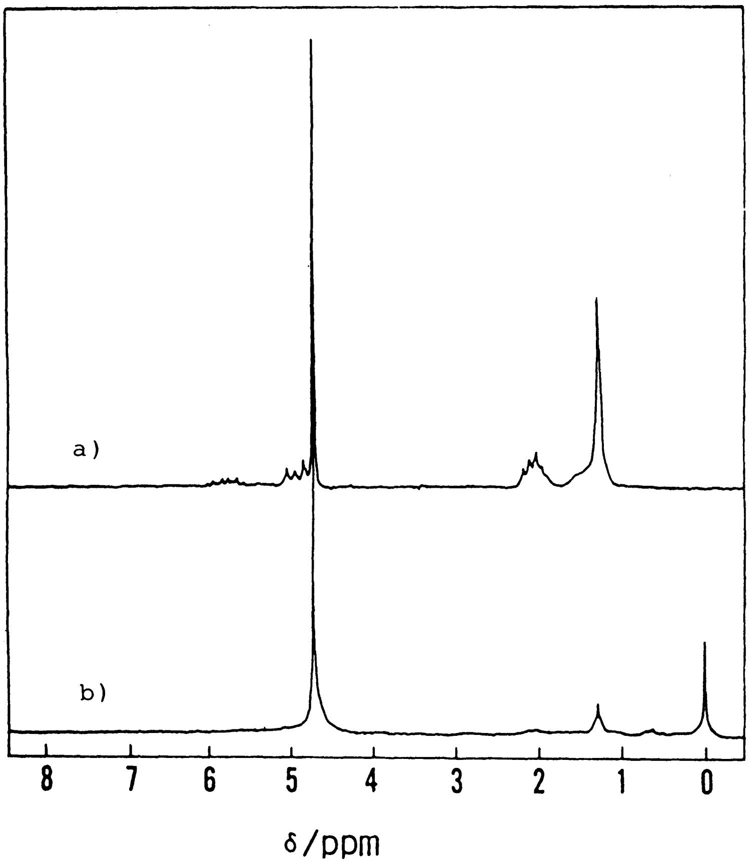

Fig. 2. ^{1}H-NMR spectra of sodium undecenoate in micelles in D_2O before (a), and after (b) UV irradiation.

Table 1. Catalytic activities of colloidal platinum catalysts prepared by photoreduction method for photochemical hydrogen generation in a system of $Ru(bpy)_3^{2+}/MV^{2+}/EDTA$[a)]

Platinum catalyst	Protective colloid	Relative activity[b)]
Pt-PUE·Na	anionic polymerized micelle	100
Pt-UA·Na	anionic monomeric micelle	8
Pt-PAA·Na	anionic linear polymer	57
Pt-PVP	nonionic linear polymer	95

a) [EDTA·2Na] = 5 x 10^{-2} mol dm^{-3}, $[Ru(bpy)_3^{2+}]$ = 5 x 10^{-5} mol dm^{-3}, $[MV^{2+}]$ = 5 x 10^{-3} mol dm^{-3}, [Pt] = 5 x 10^{-5} mol dm^{-3}.

b) Relative rate of hydrogen generation on irradiation of the mixed solution at 25 °C (λ>390 nm).

total amount of hydrogen gas generated in the period of 24 hours. Table 1 shows the relative catalytic activity of the colloidal platinum catalysts. At first, on comparison of catalytic activities of platinum dispersions protected by protective colloids having the same functional group, i.e. an anionic carboxylic group, the colloidal platinum protected by the polymerized micelle shows higher catalytic activity than that protected by the corresponding monomeric micelle or linear polymer. In the case of monomeric micelle, the precipitates came out at the preparation of the irradiation sample. The colloidal platinum protected by polymerized micelle, however, was stably dispersed even under such a condition of high ionic strength. The catalytic activities in these three samples can be explained in terms of stability of each colloidal dispersion. The monomeric micelle and linear polymer are anticipated to protect the colloidal particles reversibly, resulting in being less stable than that of polymerized micelle. On the other hand, when compared with the functional group, Pt-PVP shows almost the same activity as Pt-PUE Na in spite of the structural disadvantage. This fact suggests that nonionic environment is superior to ionic environment in this type of reaction. In anionic condition, methyl viologen cation radicals (MV^{+}) are supposed to interact strongly with carboxylic groups, and to be accumulated near the protective colloids, resulting in formation of the dimer, which stabilizes the light-induced electrons.

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References

1) K. Kalyanasundaram, J. Kiwi, and M. Grätzel, Helv. Chim. Acta, 61, 2720 (1978).
2) M. Kirch, J.-M. Lehn, and J.-P. Sauvage, Helv. Chim. Acta, 62, 1345 (1979).
3) M. Grätzel, Ber. Bunsenges. Phys. Chem., 84, 981 (1980).
4) A. Launikonis, J. W. Loder, A. W.-H. Mau, W. H. F. Sasse, and D. Wells, Isr. J. Chem., 22, 158 (1982).
5) N. Toshima, M. Kuriyama, Y. Yamada, and H. Hirai, Chem. Lett., 1981, 793.
6) B. Kraeutler and A. J. Bard, J. Am. Chem. Soc., 100, 4317 (1978).
7) J. Kiwi and M. Grätzel, J. Am. Chem. Soc., 101, 7214 (1979).
8) P.-A. Brugger, P. Cuendet, and M. Grätzel, J. Am. Chem. Soc., 103, 2923 (1981).
9) P. P. Infelta and P.-A. Brugger, Chem. Phys. Lett., 82, 462 (1981).
10) T. Nagamura, T. Kurihara, T. Matsuo, M. Sumitani, and K. Yoshihara, J. Phys. Chem., 86, 4368 (1982).
11) K. Kurihara, P. Tundo, and J. H. Fendler, J. Phys. Chem., 87, 3777 (1983).
12) N. Toshima, T. Takahashi, and H. Hirai, Chem. Lett., 1985, 1245.
13) C. E. Larabee, Jr., and E. D. Sprague, J. Polym. Sci., Polym. Lett. Ed., 17, 749 (1979).
14) R. Thundathil, J. O. Stoffer, and S. E. Friberg, J. Polym. Sci., Polym. Chem. Ed., 18, 2629 (1980).

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