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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Polymerized Micelle-Protected Platinum Clusters. Preparation and Application to Catalyst for Visible Light-Induced Hydrogen Generation

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To cite this Article Toshima, Naoki , Takahashi, Tadahito and Hirai, Hidefumi(1988) 'Polymerized Micelle-Protected Platinum Clusters. Preparation and Application to Catalyst for Visible Light-Induced Hydrogen Generation', Journal of Macromolecular Science, Part A, 25: 5, 669 – 686

To link to this Article: DOI: 10.1080/00222338808053392

URL: <http://dx.doi.org/10.1080/00222338808053392>

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POLYMERIZED MICELLE-PROTECTED PLATINUM CLUSTERS. PREPARATION AND APPLICATION TO CATALYST FOR VISIBLE LIGHT-INDUCED HYDROGEN GENERATION

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ABSTRACT

Platinum clusters protected by polymerized micelles were prepared by radical polymerization of unsaturated surfactants which were involved in micelle-protected platinum clusters. The micelle-protected platinum clusters were successfully prepared by photoreduction of hexachloroplatinic acid in water in the presence of unsaturated surfactants. The platinum clusters thus obtained were characterized by electron microscopy and IR and $^1\text{H-NMR}$ spectroscopies. The average diameter of the platinum particles was about 1 nm by electron microscopy, and the polymerization was confirmed by IR and $^1\text{H-NMR}$ spectra. The platinum clusters thus obtained proved to be highly active catalysts for visible light-induced hydrogen generation in the system of EDTA/ $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$. The polymerized micelle-protected platinum clusters showed higher catalytic activity than the linear polymer-protected one. The catalytic activity was affected by the electric charge of the surfactants in the polymerized micelle-protected platinum clusters. Nonionic polymers were superior to those having anionic and cationic hydrophilic groups from the viewpoint of catalytic activity. The non-

ionic polymerized micelle forms rigid hydrophobic cores which help charge separation and the formation of a sequential potential field.

INTRODUCTION

Effective utilization of solar energy is of great interest as one of the new energy resources alternatives to petroleum and coal [1]. A number of studies on photoexcited electron transfer systems, like tris(bipyridine)ruthenium(II) [$\text{Ru}(\text{bpy})_3^{2+}$] and methyl viologen (MV^{2+}), have been investigated not only from the viewpoint of new technology to convert solar energy into chemical energy, but also from their interest as models for the photosynthesis of plants [2]. In order to convert photoexcited energy to chemical energy, suitable catalysts are necessary. Platinum and hydrogenase are often used as reductive catalysts to get hydrogen gas, which is of much interest as a renewable energy resource without air pollution [3]. When the reductive catalysts are combined with an oxidative catalyst for oxygen generation, complete photodecomposition of water is possible just as in natural photosynthesis.

The present authors have already reported the preparation of colloidal catalysts for hydrogen generation by an alcohol reduction method [4]. In this method, hexachloroplatinic acid can be reduced with refluxing alcohol in the presence of a water-soluble polymer like poly(*N*-vinyl-2-pyrrolidone) to produce colloidal dispersions of platinum [5]. The particle size of platinum can be controlled by the reduction conditions. Investigations on the effect of the size of the platinum particles upon the catalytic activity have revealed that small colloidal particles, platinum clusters, show the highest activity for visible light-induced hydrogen generation in the system $\text{EDTA}/\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}/\text{Pt}$ [4, 6].

On the other hand, the organization of a reaction system with synthetic polymers or molecular assemblies has been investigated as a model of a natural thiracoid membrane [7]. Organized assemblies can increase the efficiency of charge separation or electron transfer in natural photosynthesis processes [8]. Micelles and vesicles are often used as synthetic organized assemblies [9].

With this background, we investigated the synthesis of micelle-protected platinum clusters to increase the efficiency of charge separation and subsequent smooth catalytic hydrogen generation over platinum clusters. In order to stabilize the micelle, polymerization of the micelle has been conducted in the present system by using unsaturated surfactants. The polymerized micelle-protected platinum clusters could give sequential potential fields where excited $\text{Ru}(\text{bpy})_3^{2+}$ with the highest potential could stay in an aqueous phase, methyl viologen, an electron mediator could locate near the surface of the micelle, and

a platinum cluster with the lowest potential could be confined near the center of the micelle by hydrophobic interactions.

EXPERIMENTS

Sodium 10-Undecenoate ($C'_{10}COO^-$) and Sodium Undecanoate ($C_{10}COO^-$)

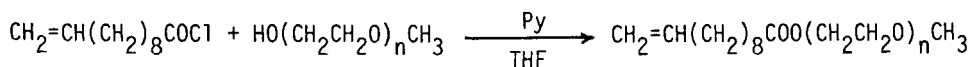
10-Undecenoic acid (Tokyo Kasei) was purified by distillation under reduced pressure (117°C/1 torr), and dissolved in ethanol. Sodium 10-undecenoate ($C'_{10}COO^-$) was obtained as a white precipitate by neutralization of the above alcoholic solution of 10-undecenoic acid with sodium hydroxide or sodium ethoxide. Sodium undecanoate ($C_{10}COO^-$) was synthesized in the same way. The solid obtained was filtered and washed several times with ethanol.

Nonionic Unsaturated Surfactant ($C'_{11}EO$)

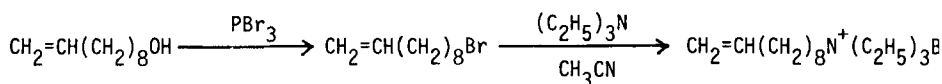
Poly(ethylene glycol) monomethyl ether 10-undecenoate was synthesized by esterification of 10-undecenoic acid according to Scheme 1 [10]. Poly(ethylene glycol) monomethyl ether (Aldrich, MW 550) was dissolved in anhydrous tetrahydrofuran (THF), and the solution was vigorously stirred on an ice bath for 3 h with dropwise addition of 10-undecenoyl chloride (Tokyo Kasei, purified by distillation under reduced pressure, 90°C/2 torr) in the presence of pyridine, and finally stirred at room temperature overnight. The crude product was obtained as a viscous liquid by evaporating the solvent after the reaction. The liquid obtained was redissolved in chloroform and purified by passing it through a column of activated alumina.

Cationic Unsaturated Surfactant ($C'_{11}N^+$)

10-Undecenyltriethylammonium bromide ($C'_{11}N^+$) was synthesized according to Scheme 2. 11-Bromoundec-1-ene was obtained by adding phosphorus tribromide to an anhydrous THF solution of 10-undecen-1-ol (Aldrich, used as received) in the presence of triethylamine. The solvent was distilled off,



SCHEME 1.



SCHEME 2.

and the resulting liquid was purified by distillation under reduced pressure. The 11-bromoundec-1-ene and triethylamine obtained were dissolved in acetonitrile, and the mixture was refluxed for 24 h. The resulting precipitate was filtered and washed several times with acetonitrile.

Other Chemicals

Dodecyltrimethylammonium chloride ($\text{C}'_{12}\text{N}^+$) was commercially obtained from Tokyo Kasei and purified by recrystallization from methanol-ether.

Poly(*N*-vinyl-2-pyrrolidone) (PVP, K30, Tokyo Kasei), poly(acrylic acid) (PAA, Aldrich), EDTA·2Na (Koso Chemicals), hexachloroplatinic acid (Kojima Chemicals), and methyl viologen hydrate (Aldrich) were used as received without further purification. Solvents were purified by conventional methods.

Reduction of Hexachloroplatinic Acid with Visible Light Irradiation

A photoreduction method was used to prepare platinum clusters protected by micelles [11] because, in an alcohol-reduction method, micelles are easily destroyed by the presence of alcohol and only the platinum precipitates are obtained, even in the presence of surfactants. Hexachloroplatinic acid (0.2 mM) and appropriate amounts of surfactants or polymers were dissolved in pure water and degassed three times by freeze-thaw-pump cycles. The deaerated solution was irradiated by visible light using a 500-W super-high-pressure mercury lamp (Ushio) in a Pyrex tube until the solution turned brownish. The average diameter of the cluster particles obtained was determined by transmission electron micrographs (TEM, Hitachi HU-12A).

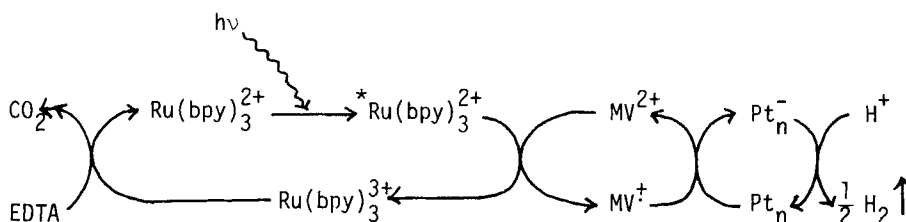
Polymerization of the Micelles

Polymerization of the unsaturated surfactant micelle was performed by UV light irradiation with a 30-W low-pressure mercury lamp (Eikosha) for 24 h in the presence of a water-soluble radical initiator (sodium persulfate) or by γ -ray irradiation with a ^{60}Co γ -ray source (Research Center for Nuclear Science & Technology of the University of Tokyo). The polymerization of

micelles was successful even when the micelles contained platinum clusters. In the case of anionic poly(sodium undecenoate), the polymerized micelle obtained was purified by reprecipitation from ethanol. The platinum content of the polymerized micelle-protected clusters was determined by atomic absorption measurement (Shimadzu AA-646). Polymerization was confirmed by IR (Jasco A-3) or $^1\text{H-NMR}$ (JEOL FX 90Q) spectra. In other dispersions of polymerized micelle-protected clusters, the dispersions obtained by γ -ray irradiation for 24 h at room temperature (0.14 Mrd/h) [12] were used without further treatment. Polymerization was confirmed by GPC measurement of the concentrated solution in chloroform.

Photochemical Hydrogen Generation Study

Photochemical hydrogen generation studies were performed on a system of EDTA/Ru(bpy) $_3^{2+}$ /MV $^{2+}$ /Pt in water, which works as shown in Scheme 3. An aqueous solution of [EDTA·2Na] = 50 mmol/L, [Ru(bpy) $_3^{2+}$] = 50 $\mu\text{mol/L}$, [MV $^{2+}$] = 5 mmol/L, and [Pt] = 50 $\mu\text{mol/L}$ was irradiated by visible light ($\lambda > 390$ nm with a cut-off filter Toshiba UV-39) using a 500-W super-high-pressure mercury lamp under argon atmosphere at 25°C. The hydrogen gas evolved was quantitatively analyzed by gas chromatography (Ohkura Model-701) using a column of 13X Molecular Sieves with argon gas as the carrier. The accumulation of methyl viologen cation radicals was traced by the absorption at 605 nm (Hitachi 340), which is characteristic of the methyl viologen cation radical, by using a deoxygenated mixed solution containing polymers but no platinum catalysts.



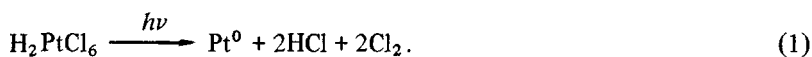
SCHEME 3.

RESULTS AND DISCUSSION

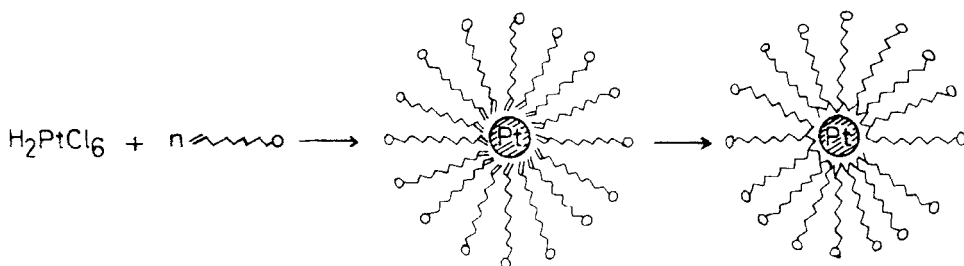
Preparation of Polymerized Micelle-Protected Platinum Clusters

Preparation of polymerized micelle-protected platinum clusters was achieved by reduction of hexachloroplatinic acid in the presence of unsaturated surfactants followed by polymerization of the unsaturated surfactants, as illustrated in Scheme 4.

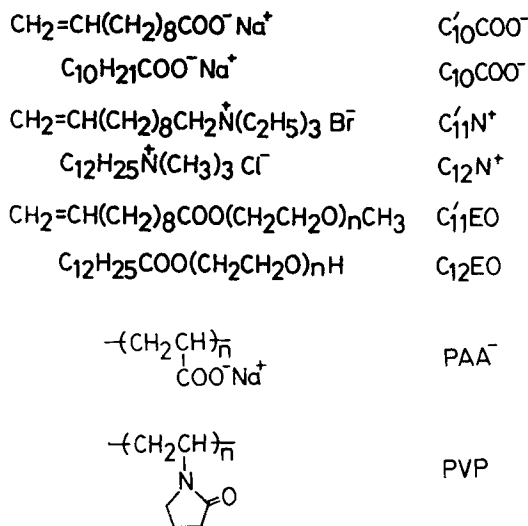
Generally speaking, the micelle-protected platinum clusters could be prepared by the addition of surfactants to aqueous dispersions of platinum clusters which had been prepared in advance [6]. According to the experience obtained in investigations of the preparation of noble metal clusters by an alcohol-reduction method [4, 5, 13], however, it was expected that the platinum clusters had to be prepared by the reduction of platinum ion in the presence of surfactants. Therefore, the reduction of platinum(IV) ion in the presence of surfactants by several methods was examined. Thus, photoreduction was found to be the best among the methods examined [11]. Hexachloroplatinic acid can be reduced by visible light according to



Aqueous dispersions of platinum clusters can be obtained by visible light irradiation of an aqueous solution of hexachloroplatinic acid in the presence of sodium undecanoate ($\text{C}_{10}\text{COO}^-$), sodium undecenoate ($\text{C}'_{10}\text{COO}^-$), dodecyltrimethylammonium chloride (C_{12}N^+), 10-undecenyltriethylammonium bromide ($\text{C}'_{11}\text{N}^+$), poly(ethylene glycol) monolaurate (C_{12}EO), poly(ethylene glycol) monomethylether 10-undecenoate ($\text{C}'_{11}\text{EO}$), poly(sodium acrylate)



SCHEME 4.



SCHEME 5.

(PAA⁻), and poly(*N*-vinyl-2-pyrrolidone) (PVP). The structures of these surfactants and polymers are shown in Scheme 5. In every case the aqueous dispersions obtained are stable enough to be kept at room temperature and then treated in the next step if the concentration of the surfactant is above its critical micelle concentration (CMC). The platinum particles were between 10 and 30 Å in diameter in every case, according to electron micrograph measurements.

The second step of Scheme 4 is polymerization of unsaturated surfactants which form micelles and protect platinum clusters. The polymerization occurred by irradiation with ultraviolet light in the presence of an initiator or irradiation with γ -ray.

A water-soluble initiator, sodium persulfate, initiated the polymerization to produce polymerized micelles, while a water-insoluble initiator like azobisisobutyronitrile (AIBN) did not give any polymer. Both UV irradiation with an initiator and γ -ray irradiation gave the same products.

The polymerization of the unsaturated surfactants was confirmed by IR and ¹H-NMR spectra. In the case of sodium undecenoate (C'₁₀COO⁻), the polymerized products were separated from the monomers by precipitation from ethanol. The brownish powder of the polymerized products was used for the spectral measurements. The spectra are shown in Fig. 1, together with

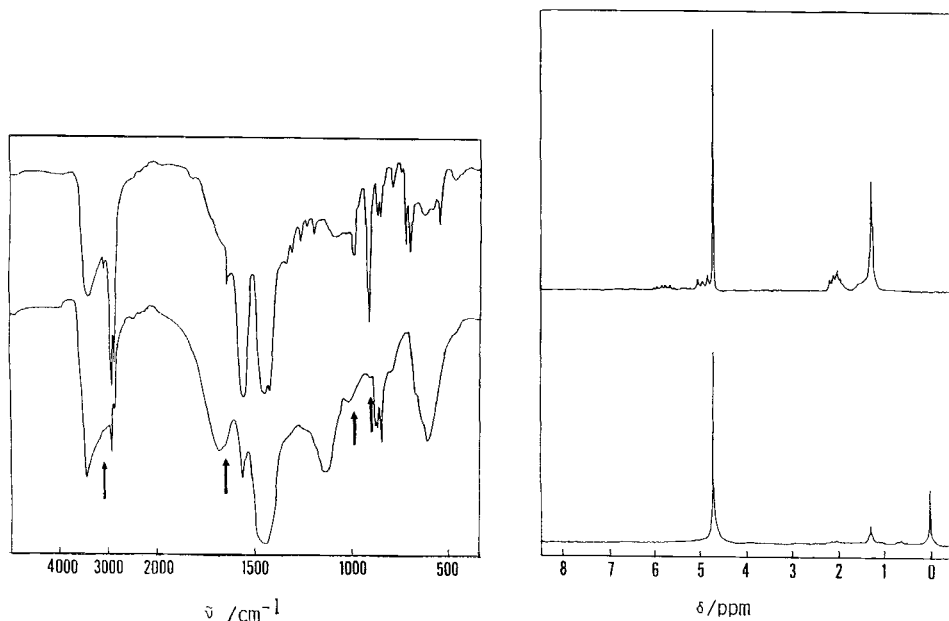


FIG. 1. IR and $^1\text{H-NMR}$ spectra of (upper) sodium undecenoate ($\text{C}'_{10}\text{COO}^-$) and (lower) polymerized sodium undecenoate.

those of sodium undecenoate. All the peaks characteristic for a carbon-carbon double bond of the starting materials disappeared in the IR and NMR spectra of the polymerized products. Thus, in the NMR spectra the peaks from 5 to 7 ppm disappeared and the rest of the peaks were broadened, and in the IR spectra the peaks at 3100, 1640, 990, and 910 cm^{-1} disappeared.

The brownish powder of the polymerized micelle-protected platinum clusters prepared from sodium undecenoate ($\text{C}'_{10}\text{COO}^-$) was determined to contain about 0.28 wt% platinum by atomic absorption. When the powder obtained was dissolved in pure water again, homogeneous dispersions of polymerized micelle-protected platinum clusters were obtained. The particle size of the platinum cluster thus obtained was determined to be nearly equal to that of micelle-protected platinum clusters before polymerization. An example of the electron micrographs of platinum clusters is shown in Fig. 2 for polymerized micelle-protected ones when $\text{C}'_{10}\text{COO}^-$ or $\text{C}'_{11}\text{EO}$ was used as the unsaturated surfactant. The histograms from Fig. 2, shown in Fig. 3, clearly in-

dicates that the platinum particles is 11 Å in average diameter and nearly monodispersed (standard deviation = 5.6 Å).

For 10-undecenyltriethylammonium bromide ($C'_{11}N^+$) and poly(ethylene glycol) monomethyl ether 10-undecenoate ($C'_{11}EO$), isolation of the polymerized products from the reaction mixtures was difficult. Therefore, polymerization was confirmed by gel permeation chromatography (GPC). The chromatogram shown in Fig. 4 indicates that the mixtures still involve rather small amounts of unsaturated monomeric surfactants but that the polymers are produced in about 75% yield and are about 3000 in average molecular weight (using polystyrene as the standard). Therefore, the platinum clusters thus obtained were protected by mixtures of polymerized and monomeric micelles. The electron micrograph of Pt-PC'₁₁EO is shown in Fig. 2(b), which indicates that the average diameter is 19 Å and the standard deviation is 17.9 Å.

Visible Light-Induced Hydrogen Generation

All the polymerized micelle-protected platinum clusters obtained were subjected to photochemical hydrogen generation experiments together with monomeric micelle-protected ones for comparison. The hydrogen generation experiments were performed by visible light irradiation of the mixed aqueous solution of EDTA·2Na, Ru(bpy)₃²⁺, MV²⁺, and platinum clusters, which are examples of a sacrificial reagent, a visible light sensitizer, an electron mediator, and a hydrogen generation catalyst, respectively, and together work as a system, as shown in Scheme 3.

All the platinum clusters obtained showed catalytic activity, but the degree of activity depended upon the kind of protective materials. The time course of hydrogen generation is shown in Fig. 5 as examples for the cases of platinum clusters protected by micelles of sodium undecanoate (Pt-MC₁₀COO⁻) and those protected by polymerized micelles of sodium undecenoate (Pt-PC'₁₀COO⁻). This figure clearly demonstrates that the polymerized micelle-protected platinum clusters (Pt-PC'₁₀COO⁻) have much higher catalytic activity in the present system than those protected by monomeric micelles (Pt-MC₁₀COO⁻).

When nonionic surfactants were used, hydrogen was generated as shown in Fig. 6, where the monomeric micelle-protected platinum cluster (Pt-MC₁₂EO) and the polymerized micelle-protected one (Pt-PC'₁₁EO) showed nearly the same catalytic activity according to the slopes in Fig. 6. This result is quite different from that for the anionic surfactants. Furthermore, in the case of the nonionic polymerized micelle (Pt-PC'₁₁EO), hydrogen is not generated at the beginning of photoirradiation and has an induction period of about 1 h, probably because the nonionic polymerized micelles contain about 25% unre-

a)



500 Å

FIG. 2. Electron micrographs of (a) anionic (Pt-PC'₁₀COO⁻), and (b) non-ionic (Pt-PC'₁₁EO) polymerized micelle-protected platinum clusters.

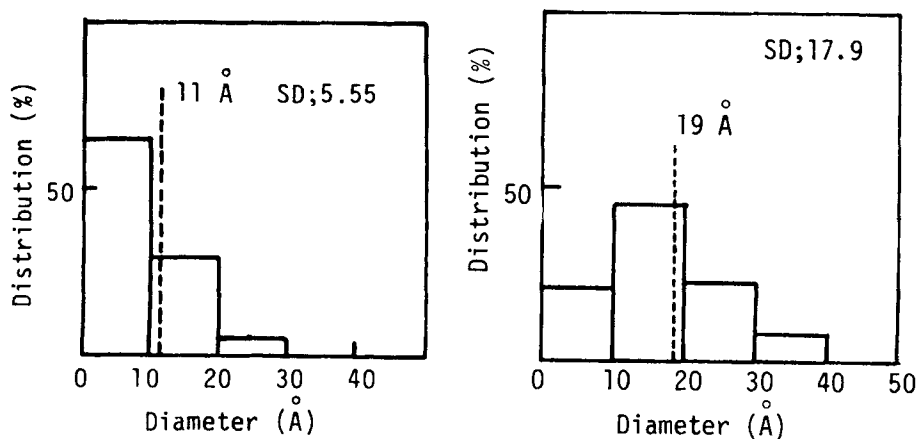


FIG. 3. Particle size distribution of (left) anionic (Pt-PC'₁₀COO⁻), and (right) nonionic (Pt-PC'₁₁EO) polymerized micelle-protected platinum clusters. Broken lines indicate average diameters.

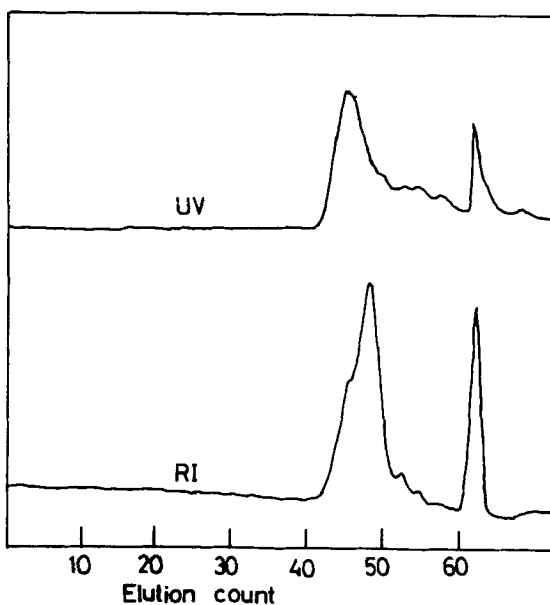


FIG. 4. GPC traces of the γ -ray irradiation products of the micelles of poly-(ethylene glycol) monomethyl ether undecenoate (C'₁₁EO) by using UV and RI detectors.

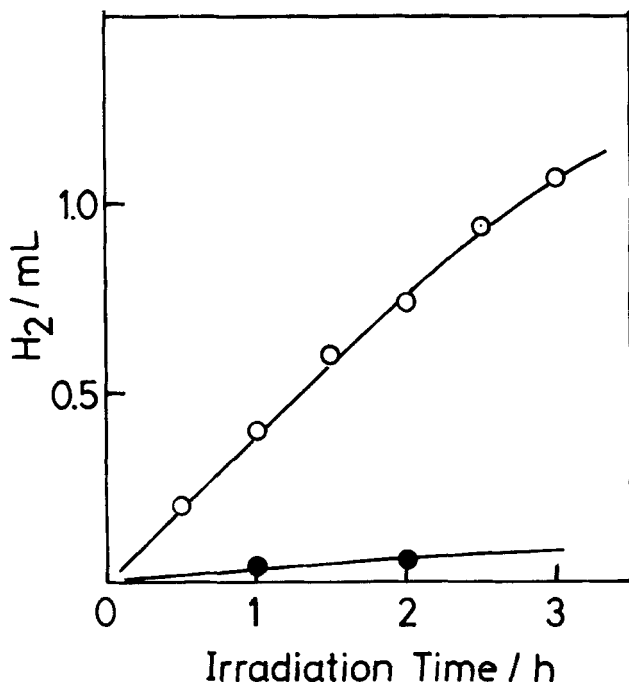


FIG. 5. Visible light-induced hydrogen generation catalyzed by anionic polymerized micelle-protected platinum clusters ($\text{Pt-PC}'_{10}\text{COO}^-$, \circ) and monomeric micelle-protected platinum clusters ($\text{Pt-MC}_{10}\text{COO}^-$, \bullet).

acted unsaturated surfactant molecules which are hydrogenated over platinum catalysts by the hydrogen generated in the initial stage of photoirradiation. The range of the induction period corresponds to the time necessary for the system to generate enough hydrogen for hydrogenation of the unsaturated surfactant molecules contaminated in the system.

The catalytic activities of the various platinum clusters prepared by the photoreduction method are shown in Table 1, where the relative activity is calculated by comparison to the initial rate of hydrogen generation for platinum clusters protected by poly(*N*-vinyl-2-pyrrolidone) (PVP) as the standard (100).

Effect of Polymerized Micelle

In a previous paper [4] the present authors showed that the activity of platinum catalysts for photochemical hydrogen generation depends upon the

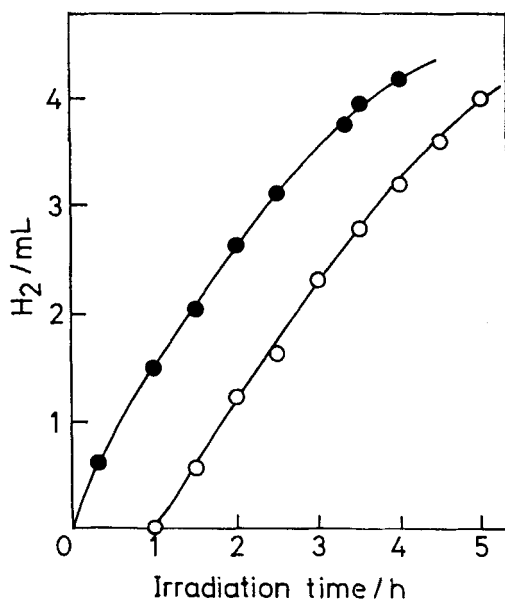


FIG. 6. Visible light-induced hydrogen generation catalyzed by nonionic polymerized micelle-protected platinum clusters (Pt-PC'₁₁EO, ○) and monomeric micelle-protected platinum clusters (Pt-MC₁₂EO, ●).

average particle size of the platinum. In the present investigations the average particle sizes are nearly equal because common reduction conditions were applied. Table 1 clearly demonstrates that the catalytic activities of platinum clusters depend upon the structure and electric charge of the protective materials.

The polymerized micelle-protected platinum clusters are superior as catalysts to those protected by monomeric micelles or linear polymers. This effect is clear in the case of anionic protective materials. The large difference in activity is probably due to the stability of the clusters. Since the CMC of sodium undecenoate ($C_{10}COO^-$) is quite high, the clusters protected by it (Pt-MC₁₀-COO⁻) could be destroyed when aqueous dispersions of Pt-MC₁₀COO⁻ were added to the reaction mixtures containing EDTA·2Na, Ru(bpy)₃²⁺, and MV²⁺ with high ionic strength. In comparison to polymerized micelles with linear polymers, polymerized micelles (PC'₁₀COO⁻) form hydrophobic cores which interact with hydrophobic platinum clusters more strongly than do linear polymers (PAA⁻).

TABLE 1. Catalytic Activities of Platinum Cluster Catalysts for Photochemical Hydrogen Generation from Water in the System EDTA/Ru(bpy)₃²⁺/MV²⁺/Pt

Pt cluster ^a	Protective material	R _{rel} ^b
Pt-PC' ₁₁ EO	Nonionic polymerized micelle	306
Pt-MC ₁₂ EO	Nonionic monomeric micelle	302
Pt-PC' ₁₁ N ⁺	Cationic polymerized micelle	267
Pt-MC ₁₂ N ⁺	Cationic monomeric micelle	250
Pt-PC' ₁₀ COO ⁻	Anionic polymerized micelle	105
Pt-MC ₁₀ COO ⁻	Anionic monomeric micelle	8
PT-PVP	Nonionic linear polymer	100
Pt-PAA ⁻	Anionic linear polymer	60

^aPrepared by the photoreduction method. See text for the abbreviations.

^bRelative activities in comparison with Pt-PVP as 100.

For nonionic protective materials, platinum clusters protected by polymerized micelles (Pt-PC'₁₁EO) and those protected by monomeric micelles (Pt-MC₁₂EO) show nearly the same catalytic activity, in contrast to the anionic protective materials. This is probably due to the low CMC of the nonionic surfactant molecules. Nevertheless, the polymerized micelles are superior to the nonionic linear polymers (PVP). This result again depends upon the strong interaction of the hydrophobic core of the micelle with the platinum clusters.

The electric charge of protective materials affects the catalytic activities of platinum clusters strongly. The activity increases in the order anionic < cationic < nonionic in every series of polymerized micelles, monomeric micelles, and linear polymers. This would be the effect of charge separation between methyl viologen cation radicals (MV^{•+}) and tris(bipyridine)ruthenium(III) [Ru(bpy)₃³⁺] which are generated by electron transfer from excited Ru(bpy)₃²⁺ to MV²⁺. Thus, for anionic protective micelles, cationic MV²⁺ or Ru(bpy)₃²⁺ strongly interacts with the anionic surface of the micelles by electrostatic forces. Thus it is likely that reverse electron transfer from MV^{•+} to Ru(bpy)₃³⁺ can occur. Furthermore, since a number of MV^{•+} radical ions accumulate around the surface of the protective materials, it is

TABLE 2. Relative Rate of Decay of Accumulated Methyl Viologen Cation Radicals in the Presence of Various Polymers and Surfactants

Protective material ^a	Relative rate
C ₁₂ EO	0.77
PVP	0.68
C ₁₂ N ⁺	1.23
None	1.00

^aSee text for the abbreviations.

not likely that MV^{•+} can enter into the hydrophobic inner core and make contact with the platinum cluster catalyst. In contrast, the catalytic activities for cationic protective micelles are higher than for anionic protective micelles, but they are less active than nonionic ones. This is thought to be due to the electrostatic repulsion between MV^{•+} and protective micelles. Reverse electron transfer occurs less than in the case of anionic protective micelles, but MV^{•+} can hardly be in contact with the platinum clusters. For the nonionic protective materials, the catalytic activity is higher than for the other protective materials, probably because there are no such electrostatic effects to interfere with the light-induced electron transfer from MV^{•+} to platinum clusters, and MV^{•+} radical ions are likely to be in contact with the platinum particles.

Table 2 collects the rates of decay of accumulated MV^{•+}. For nonionic protective materials, both linear polymers and surfactants, the lifetimes of MV^{•+} are longer than for the other protective materials. The decrease in absorbance at 605 nm seems to be caused by both the decay of the methyl viologen cation radical itself and reverse electron transfer to Ru(bpy)₃³⁺. This result supports the above discussion on the effect of electric charge of the protective materials.

From the above considerations it is clear that the polymerized micelles dispersed in an aqueous solution and three key components, Ru(bpy)₃²⁺, MV²⁺, and Pt clusters, are located in the aqueous phase near the surface of the micelles and near the center of the micelles, respectively. As is well known, the redox potentials of the excited Ru(bpy)₃²⁺, MV²⁺, and Pt clusters decrease in this order, and at the same time they are located in this order. Both the potential and the location (so-called "sequential potential field") are very important for smooth electron transfer. This is illustrated in Fig. 7.

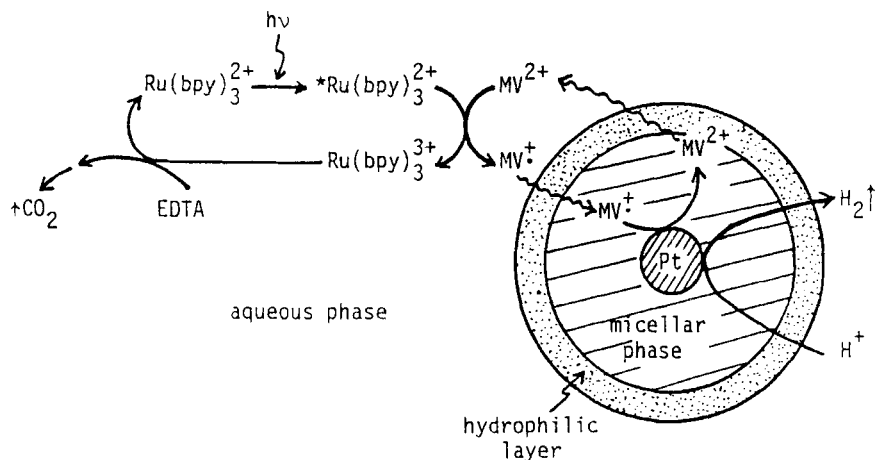


FIG. 7. Illustration of the proposed scheme of visible light-induced electron transfer and hydrogen generation in a polymerized micelle-protected platinum cluster system.

ACKNOWLEDGMENTS

The present work was financially supported by the Iwatani Naoji Foundation, the Asahi Glass Foundation for Industrial Technology, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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