

## Letter

# Preparation of Poly(Cyclodextrin)-Protected Platinum Colloids and Application as Catalysts for Visible-Light-Induced Hydrogen Generation

Yukihide SHIRAISHI <sup>a\*</sup>, Yoshimi NAKANISHI <sup>a</sup>, Tomoko KOTANI <sup>a</sup>, Shinichi HATA <sup>a</sup>, Yukou DU <sup>b</sup> and Naoki TOSHIMA <sup>c</sup>

**Abstract:** Metal colloids are attracting significant attention because of their uniform size, shape, size distribution in nanometers, and easy preparation process; their impact is evident in the recent developments in nanoscience and nanotechnology. Although protective colloids are often employed to prevent the aggregation of metal colloids, they also promote some of the special properties of metal colloids. Cyclodextrin (CyD) is known to form inclusion complexes with organic compounds in solution. However, platinum colloids are properly stabilized by poly(cyclodextrin) (PCyD) not CyD. Platinum colloids protected by PCyD were prepared by the photoreduction of hexachloroplatinic(IV) acid in the presence of PCyD. The PCyD-protected platinum colloids exhibited higher catalytic activities than the dextran-protected platinum colloids for visible-light-induced hydrogen generation.

**Key words:** Metal Colloids, Platinum, Poly(cyclodextrin), Visible-Light-Induced Hydrogen Generation, Catalyst

The fundamental materials required for nanoscience and nanotechnology research are expected to be afforded by organic-inorganic hybrid complexes. Metal colloids stabilized by organic molecules constitute a new class of materials that are different from conventional bulk materials or atoms, affording one of the smallest building blocks of matter.<sup>1-3)</sup> Most of the remarkable properties of metal colloids are based on their high surface areas and quantum size effect. Conventionally, metal colloids are prepared chemically by the reduction of the corresponding metal salts<sup>4)</sup> and physically by the pulverization of the metallic mass.<sup>5)</sup> The chemical method, wherein metal ions are reduced by various kinds of reductants to produce metal atoms and subsequently metal colloids by their aggregation, is advantageous for mass production. Silver and/or platinum colloids prepared by chemical methods are of interest in the photographic industry.<sup>6,7)</sup>

The conversion of solar photoenergy is an important step in realizing the sustainable development goals (SDGs). One of the most important and simplest routes is the visible-light-induced decomposition of water to produce oxygen and hydrogen.<sup>8)</sup> To realize this process, several approaches have been proposed, including the construction of heterogeneous photocatalytic systems composed of semiconductors, such as TiO<sub>2</sub>,<sup>9,10)</sup> and the use of homogenous aqueous solutions composed of photosensitizers, electron mediators, and oxidative/reductive catalysts. Dispersions of noble metals, particularly platinum colloids, are well known as reductive catalysts in aqueous solutions, producing molecular hydrogen from protons and electrons. Since platinum colloids are transparent in the visible light

range, they are effective as catalysts for photocatalytic reactions. Many studies on visible-light-induced hydrogen generation using platinum colloids have been reported.<sup>11-13)</sup> Metal colloids are protected by citrate ions, surfactants, polymers, and organic ligands.<sup>14)</sup> Protective colloids are often used to prevent the aggregation of metal colloids and promote some of their special functions.

*Alpha*-, *beta*- and *gamma*- cyclodextrins ( $\alpha$ CyD,  $\beta$ CyD, and  $\gamma$ CyD) are cyclic oligomers of 6, 7, and 8 glucose units, respectively, linked by  $\alpha(1-4)$  bonds with a central cavity. The external diameter at the secondary hydroxyl side of CyD is larger than that at the primary hydroxyl side of CyD. The cavity diameters of  $\alpha$ CyD,  $\beta$ CyD, and  $\gamma$ CyD are 4.7~5.2, 6.0~6.4, and 7.9~8.0 Å, respectively. The outside of the CyD molecule is hydrophilic, while the inside cavity contains a hydrophobic medium, such as diethyl ether; various hydrophobic substances can be included in the aqueous medium as "guests," by spatially fitting them in the cavity.<sup>15,16)</sup> The formation of inclusion complexes in solution is a dynamic process of equilibrium between the inclusion state and the free state of the substrate. Herein, we report the synthesis of poly(cyclodextrin)-protected platinum (PCyD-Pt) colloids by a chemical method and their application as novel catalysts for visible-light-induced hydrogen generation. The visible-light-induced electron-transfer system was constructed using tris(bipyridine)ruthenium(III), methyl viologen, and ethylenediaminetetraacetic acid as the photosensitizer, electron relay, and sacrificial electron donor, respectively.<sup>17,18)</sup>

Hexachloroplatinic(IV) acid was obtained from FUJIFILM Wako Pure Chemical Corporation, Ltd. Poly( $\alpha$ -cyclodextrin) (P $\alpha$ -

Received 17th April, 2021; Accepted 22nd May, 2021 ; Published 27th May, 2021

<sup>a</sup> Department of Applied Chemistry, Sanyo-Onoda City University, Daigakudori, Sanyo-Onoda, Yamaguchi 756-0884, Japan.

<sup>b</sup> College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China.

<sup>c</sup> Professor Emeritus, Tokyo University of Science Yamaguchi, Japan.

\* shiraishi@rs.socu.ac.jp

CyD), poly ( $\beta$ -cyclodextrin) (P $\beta$ CyD), and poly ( $\gamma$ -cyclodextrin) (P $\gamma$ CyD) (CycloLab R&D. Ltd.) were used without further purification as the protective polymers for the platinum colloids. The other reagents employed in this study were of commercial general reagent grade. The PCyD-Pt colloids were prepared using a photoreduction method. PCyD (0.528 mmol in monomeric units, 40 times the total amount of metal ions) and hexachloroplatinic(IV) acid (0.0132 mmol) were mixed in ethanol/water (1/1, v/v) to form a 20 cm<sup>3</sup> solution. The mixed solutions in a quartz vessel were degassed by three freeze-thaw cycles, filled with pure nitrogen, and subsequently exposed to light supplied by an Ushio 500 W super-high-pressure mercury lamp for 1 h in a water bath maintained at 30 °C. The dextran-protected Pt colloids were prepared by the same photoreduction method.

Ultraviolet-visible (UV-Vis) spectra were obtained at room temperature using a Shimadzu 2500PC recording spectrophotometer equipped with a 10 mm quartz cell. The PCyD-Pt colloids employed here were characterized by transmission electron microscopy (TEM) at 80 kV on a JEOL JEM-1230 electron microscope. The samples for TEM were prepared by placing a drop of the PCyD-Pt colloid dispersion onto a carbon-coated copper microgrid for high-resolution TEM, followed by natural evaporation of the solvent. The mean diameter and standard deviation were calculated from the TEM photograph by measuring the diameters of 200 particles 10 times with a magnifier at 100,000 magnification.

The typical visible-light-induced hydrogen generation was performed as follows: a 20 cm<sup>3</sup> Pyrex Schlenk tube was charged with 10 cm<sup>3</sup> of an aqueous solution containing 0.1 mol dm<sup>-3</sup> of an ethylenediaminetetraacetic acid disodium salt (Na<sub>2</sub>EDTA, the sacrificial electron donor), 1.4×10<sup>-4</sup> mol dm<sup>-3</sup> of tris(bipyridine)ruthenium dichloride ([Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>, the photosensitizer), and 1.4×10<sup>-3</sup> mol dm<sup>-3</sup> of 1,1'-dimethyl-4,4'-bipyridium dichloride (methyl viologen, MVC<sub>2</sub>, the electron relay). The PCyD-Pt colloids were added last to obtain the above-mixed solution at the designed concentrations. The mixtures were degassed by three freeze-thaw cycles, after which the

tubes were filled with nitrogen at 1 atm. Photoirradiation was carried out with an Ushio 500 W super-high-pressure mercury lamp through a UV-39 cut filter in a water bath maintained at 30 °C. The products in the gas phase were analyzed with a Shimadzu model GC-14A gas chromatography (GC) apparatus using an MS13X column at 60 °C.

Dispersions of platinum colloids protected by PCyD were prepared by the photoreduction of a mixed solution of hexachloroplatinic(IV) acid and PCyD in ethanol/water, which had a dark brown color and was stable for months at room temperature. Figure 1 shows the UV-Vis absorption spectra of the dispersions of the P $\alpha$ -CyD-Pt, P $\beta$ CyD-Pt, and P $\gamma$ CyD-Pt colloids. The dispersions of the PCyD-Pt colloids obtained after photoreduction show broad absorption spectra without a structure from the visible to the near-UV regions. The absorption peak due to PtCl<sub>6</sub><sup>2-</sup> completely disappeared upon photoreduction, indicating the completion of the reduction of the platinum ions.<sup>13)</sup>

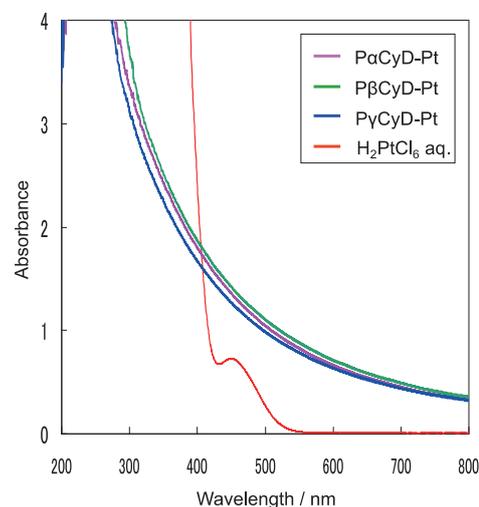


Figure 1. UV-Vis absorption spectra of an aqueous solution of hexachloroplatinic(IV) acid and PCyD-Pt colloids.

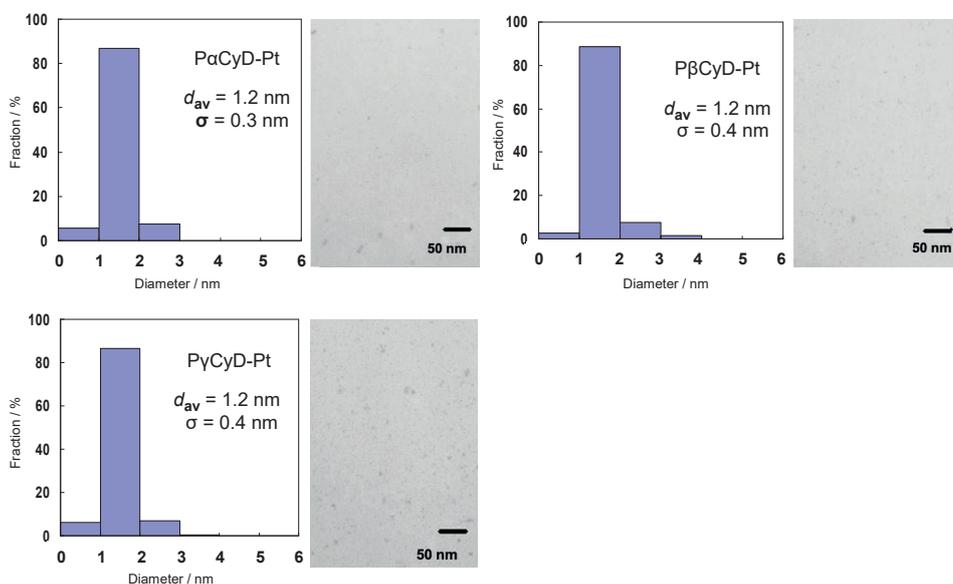


Figure 2. Transmission electron micrographs and particle size distribution histograms of PCyD-Pt colloids.  $d_{av}$  = average diameter,  $\sigma$  = standard deviation.

Figure 2 depicts the transmission electron micrographs and the corresponding histograms, indicating the particle-diameter distributions of the colloids. Most of the PCyD-Pt colloids were distributed in the diameter range of 1–3 nm, suggesting that they are homogeneous. The average diameters of the P $\alpha$ CyD-Pt, P $\beta$ CyD-Pt, and P $\gamma$ CyD-Pt colloids are  $1.2 \pm 0.3$ ,  $1.2 \pm 0.4$ , and  $1.2 \pm 0.4$  nm, respectively. When  $\beta$ CyD was used instead of PCyD, rapid precipitation occurred and the colloidal dispersion was not obtained. When  $\alpha$ CyD and  $\gamma$ CyD were used instead of PCyD, some aggregates, several times larger in diameter than the single particle, were observed. The polymer molecule could coordinate to the metal particle at multiple sites.<sup>19</sup> Even though each coordination bond was weak, the multicoordination resulted in the strong chemical adsorption of polymer molecules on the metal colloid surface. The coordination to the platinum surface at multiple sites of PCyD may account for the stability of the PCyD-Pt colloids.

The PCyD-Pt colloids were used as catalysts for visible-light-induced hydrogen generation. The reductive production of hydrogen was observed by GC upon irradiation with visible light in the electron relay system of EDTA/Ru(bpy)<sub>3</sub><sup>2+</sup>/MV<sup>2+</sup>/Pt colloids. In the steady state of the reaction, the hydrogen-generation amount increased linearly in proportion to the irradiation time of visible light. A typical hydrogen-generation curve for the catalyzed P $\beta$ CyD-Pt colloids is shown in Figure 3. The total amount of hydrogen generation is limited, probably because of the degradation of methyl viologen by the reduction.<sup>20</sup> The hydrogen-generation rate ( $r_{\text{H}_2}$ ), measured from the initial slope for 20 min of the hydrogen-generation curve in Figure 3, is proportional to the metal concentration. Figure 4 exhibits the relationship between the hydrogen-generation rate and the metal concentration. The hydrogen-generation rate can be expressed by Eq. 1 using the hydrogen-generation rate coefficients ( $k_{\text{H}_2}$ ).

$$r_{\text{H}_2} = k_{\text{H}_2} [\text{Metal}] \quad (1)$$

The hydrogen-generation rate coefficients of the P $\alpha$ CyD-Pt, P $\beta$ CyD-Pt, and P $\gamma$ CyD-Pt colloids were 1.22, 1.04, and 1.31 s<sup>-1</sup>, respectively. The hydrogen-generation rate coefficient of commercial platinum black (0.0008 s<sup>-1</sup>) was considerably lower than those of the PCyD-Pt colloids. The commercial platinum black (< 10 nm) is composed of relatively large particles and their aggregates. The P $\gamma$ CyD-Pt colloids exhibited a higher catalytic activity than the P $\alpha$ -

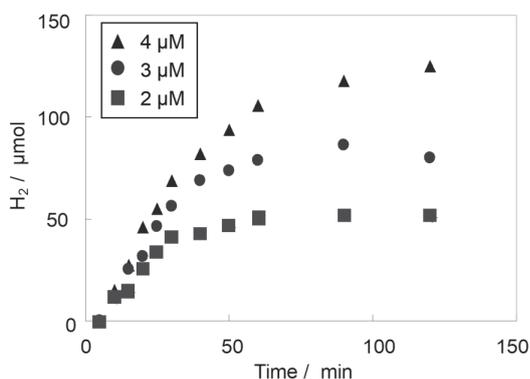
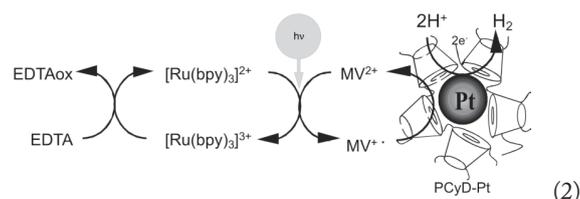


Figure 3. The typical hydrogen generation curve catalyzed by P $\beta$ CyD-Pt colloids.

CyD-Pt and P $\beta$ CyD-Pt colloids. The solubilities of  $\alpha$ CyD,  $\beta$ CyD, and  $\gamma$ CyD in water are 14.5, 1.85, and 23.2 g/100 mL, respectively.<sup>21</sup> The high hydrogen-generation activity of the P $\gamma$ CyD-Pt colloids may be due to the high solubility of P $\gamma$ CyD in water. On the other hand, Osa *et al.* reported that the formation constants of the CyD-methyl viologen cation radical were 10, 30, and 40 M<sup>-1</sup> for  $\alpha$ CyD,  $\beta$ CyD, and  $\gamma$ CyD, respectively.<sup>22</sup> Methyl viologen ion, as an electron relay, transformed into the methyl viologen cation radical, as represented by Eq. 2. The P $\gamma$ CyD-Pt colloids may include more methyl viologen cation radicals than the P $\alpha$ CyD-Pt and P $\beta$ CyD-Pt colloids.



To examine the electron transfer of methyl viologen cation radicals, viologen molecules with several alkyl chain lengths (ethyl viologen, propyl viologen, butyl viologen, pentyl viologen, hexyl viologen, and octyl viologen) were synthesized. 4,4'-Bipyridine (21.2 mmol) and 42.4 mmol of the corresponding alkyl bromides (ethyl bromide, propyl bromide, butyl bromide, pentyl bromide, hexyl bromide, and octyl bromide) were mixed in acetonitrile to form a 100 cm<sup>3</sup> solution. The mixed solutions were stirred and heated to reflux at 90 °C under a nitrogen atmosphere for 5 h. The various viologen molecules synthesized were purified by recrystallization. Hydrogen production was also observed by GC upon irradiation with a visible-light-induced electron transfer system of EDTA/Ru(bpy)<sub>3</sub><sup>2+</sup>/viologen molecules/P $\beta$ CyD-Pt colloids. Figure 5 exhibits the relationship between the hydrogen-generation rate coefficient and the viologen molecules with varying alkyl chain lengths by P $\beta$ CyD-Pt colloids (■). The hydrogen-generation rate coefficients for the ethyl viologen (1.17 s<sup>-1</sup>), propyl viologen (1.61 s<sup>-1</sup>), and butyl viologen (1.21 s<sup>-1</sup>) were higher than that of methyl viologen (1.04 s<sup>-1</sup>). Furthermore, as the alkyl chain length increased, the hydrogen-genera-

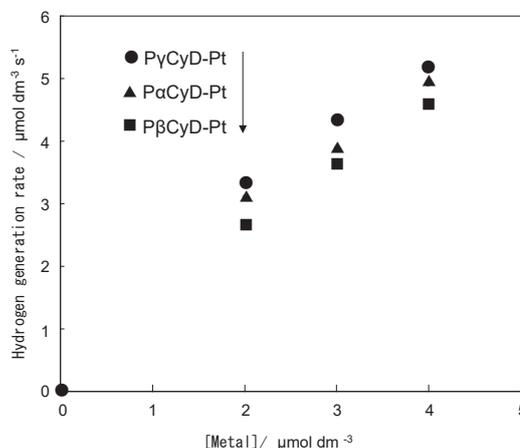


Figure 4. Hydrogen generation rate ( $r_{\text{H}_2}$ ) vs. [Metal] in the presence of PCyD-Pt colloids.

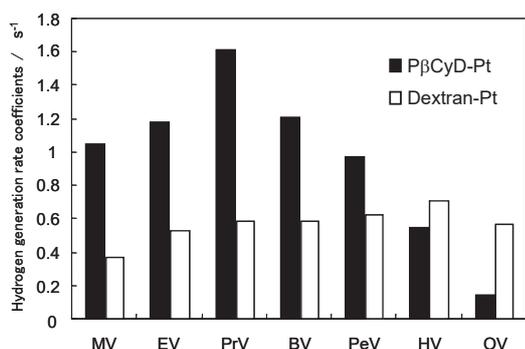


Figure 5. Relationship between hydrogen generation rate coefficient ( $r_{H_2}$ ) and viologen molecules with varying alkyl chain length (ethyl viologen; EV, propyl viologen; PrV, butyl viologen; BV, pentyl viologen; PeV, hexyl viologen; HV, and octyl viologen; OV).

tion rate coefficients decreased. In contrast, the dextran-protected Pt colloids ( $4.4 \pm 1.1$  nm) with a linearly bound glucose frame did not show a significant difference regarding the alkyl chain length. The P $\beta$ CyD-Pt colloids exhibited a higher catalytic activity than the dextran-protected Pt colloids ( $\square$ ). CyD exhibits remarkable catalytic activities owing to the following effects:<sup>23)</sup> (1) the solubilization of insoluble compounds, (2) protection of intermediates, (3) conformation effect, (4) microscopic solvent effect, and (5) control of molecular size. Due to the CyD moieties of PCyD-Pt, the viologen cation radical is placed near the platinum colloids and it readily transfers the electron from the viologen cation radical to the platinum colloids. Thus, the high catalytic activity of the P $\beta$ CyD-Pt colloids can be explained by the protective stability of the methyl viologen cation radical as intermediates by the formation of P $\beta$ CyD-methyl viologen cation radical inclusion complex.

PCyD-Pt colloids were prepared by the photoreduction of hexachloroplatinic(IV) acid in the presence of PCyD. These colloids exhibited excellent monodispersity and high stability at room temperature for several months. The catalytic properties of the PCyD-Pt colloids were studied for visible-light-induced hydrogen generation. The PCyD-Pt colloids are more active than the dextran-protected Pt colloids. The unprecedented PCyD-protected Pt colloids with clathration ability are expected to be applied to the development of new functional materials.

## Acknowledgements

This study was partially supported in part by the projects KAKENHI (Nos. 18K14017 to S.H. and 19K05633 to Y.S.) from the Japan Society for the Promotion of Science, Japan.

## References

- 1) G. Schmid, *Chem. Rev.*, 92, 1709 (1992).
- 2) J. H. Fendler, in *Nanoparticles and Nanostructured Films*, WILEY-VCH, Weinheim (1998).
- 3) H. Bönemann, W. Brijoux, in *Advanced Catalysts and Nanostructured Materials*, edited by W. Moser, Academic Press, New York (1996).
- 4) N. Toshima and Y. Shiraishi, in *Encyclopedia of Surface and Colloid Science*, edited by A. T. Hubbard, Marcel Dekker, New York (2002).
- 5) B.-J. Tan, K. J. Klabunde, P. M. A. Sherwood, *J. Am. Chem. Soc.*, 113, 855 (1991).
- 6) T. Tani, in *Silver Nanoparticles from Silver Halide Photography to Plasmonics*, Oxford University Press, Oxford (2015).
- 7) Y. Teshima, K. Ohzeki, *J. Soc. Photogr. Imag. Jpn.*, 76(6), 487 (2013).
- 8) N. Toshima, K. Hirakawa, *Polym. J.*, 31(11-12) 1127 (1999).
- 9) A. Fujishima, K. Honda, *Nature*, 238, 37 (1972).
- 10) A. Fujishima, T. N. Rao, D. A. Tryk, *J. Photochem. Photobio. C*, 1(1) 1 (2000).
- 11) J. Kiwi, M. Grätzel, *Nature*, 281, 657 (1979).
- 12) A. J. Frank, K. L. Stevenson, *J. Chem. Soc., Chem. Commun.*, 593 (1981).
- 13) N. Toshima, M. Kuriyama, Y. Yamada, H. Hirai, *Chem. Lett.*, 793 (1981).
- 14) N. Toshima, H. Yan, Y. Shiraishi, in *Metal Nanoclusters in Catalysis and Materials Science: The Issue of Size Control*, edited by B. Corain, G. Schmid, N. Toshima, Amsterdam, Elsevier (2007).
- 15) M. L. Bender, M. Komiyama, in *Cyclodextrin Chemistry*, Springer-Verlag, Berlin-Heidelberg- New York, 1 (1978).
- 16) Y. Shiraishi, *Kagaku To Kyoiku (Chemistry and Education)* 68, 224 (2020).
- 17) K. Kalyanasundaram, O. Micic, E. Pramauro and M. Gratzel, *Helv. Chim. Acta*, 62, 2432 (1979).
- 18) K. Yamada, M. Shakuto, K. Teshima, N. Kobayashi, K. Ikeda, R. Hirohashi, *J. Soc. Photogr. Imag. Jpn.*, 57(6), 445 (1994).
- 19) Y. Shiraishi, M. Hayashi, and N. Toshima, *Jpn. J. Polym. Sci. Tech.*, 64, 74 (2007).
- 20) P. Keller, A. Moradpour, E. Amouyal, H. Kagan, *J. Mol. Catal.*, 7, 539 (1980).
- 21) W. Saenger, *Angew. Chem. Int. Ed. Engl.*, 19, 344 (1980).
- 22) T. Matsue, T. Kato, U. Akiba, T. Osa, *Chem. Lett.*, 1825 (1981).
- 23) F. Toda, A. Ueno, *Cyclodextrin*, Sangyotosho, Tokyo, 92 (1995).