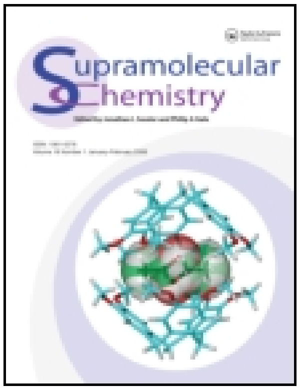

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Syntheses of poly(cyclodextrin)-stabilised metal nanoparticles and their quenching abilities of active oxygen species

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Metal nanoparticles have been developed to increase the catalytic activity of metals due to the larger surface area of smaller particles. We report the synthesis of novel cyclodextrin-stabilised metal nanoparticles and their application to catalysts for the quenching of active oxygen species. Platinum nanoparticles stabilised by poly(cyclodextrin) (PCyD-Pt) were prepared by UV irradiation of an aqueous solution of hexachloroplatinic(IV) acid in the presence of PCyD. Most PCyD-Pt nanoparticles were distributed in the range of 1–6 nm. PCyD-Pt nanoparticles have higher catalytic activity than a commercial platinum catalyst for quenching of superoxide anion radical. The PγCyD-stabilised Au/Pt bimetallic nanoparticles showed higher catalytic activity than the corresponding monometallic nanoparticles.

Keywords: poly(cyclodextrin); metal nanoparticle; platinum; colloid; active oxygen species

1. Introduction

Recently, much attention has been paid to bionanomaterials for the quenching of active oxygen species (*1*, *2*). Since some noble metal nanoparticles are reducing catalysts (*3*, *4*), they may be usable as antioxidants, which reduce active oxygen species in a living body. We have found that the colloidal dispersions of metal nanoparticles stabilised by organic molecules are generally active catalysts for reduction and that the stabilisers are often used not only to prevent metal nanoparticles from aggregation, but also to promote some special functions of metal nanoparticles (*5*, *6*). Surface modification of metal nanoparticles through assembly of functional molecules would lead to various possibilities for nanoparticle properties (*7*). Cyclodextrin is considered as one of the pioneers of supramolecules and has been widely applied in fields such as drug delivery, pesticide, foods, cosmetics and catalyst (*8–10*). Alvarez et al. (*11*) reported that thiolated β-cyclodextrin could be introduced in the synthesis of platinum and palladium nanoparticles. Methylated cyclodextrin-stabilised ruthenium nanoparticles were prepared by Nowicki et al. (*12*) by reducing ruthenium chloride with sodium borohydride in dilute aqueous solutions of methylated cyclodextrin. To the best of our knowledge, there are no reports on synthesis of poly(cyclodextrin)-stabilised metal nanoparticles and their quenching abilities of active oxygen species.

In this paper, we report the preparation of poly(cyclodextrin)-stabilised platinum nanoparticles under mild conditions by the photoreduction method. The poly(cyclodextrin)-stabilised platinum nanoparticles, thus obtained, are applied to the catalysts for quenching ability and against superoxide anion radical and hydrogen peroxide. The promotion effect of bimetallisation of platinum with gold on poly(cyclodextrin)-stabilised nanoparticles is described as well.

2. Experimental

2.1 Materials

Hexachloroplatinic (IV) acid was received from Wako Pure Chemical Industries, Ltd. (Chuoh-ku, Osaka, Japan) Poly(cyclodextrin) (PCyD, CycloLab R&D, Ltd, Budapest, Hungary) was used without further purification as the protective polymer for platinum nanoparticles. Other reagents employed here were of a commercial G.R. grade and were used as received. A superoxide dismutase (SOD) assay kit-WST was received from Dojindo Molecular Technologies, Inc., (Mashiki-cho, Kumamoto, Japan).

2.2 Synthesis and characterisation

PCyD-stabilised platinum nanoparticles were prepared by a photoreduction method. PCyD (2.6 mmol in monomeric

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units, 40 times the total amount of metal ions) and hexachloroplatinic (IV) acid (0.066 mmol) were mixed in water to form a 100 cm^3 solution. Mixed solutions in a quartz vessel were degassed by three freeze–thaw cycles, filled with pure nitrogen and then exposed to the light of an Ushio 500 W super-high-pressure mercury lamp for 1 h in a water bath maintained at 25°C.

Ultraviolet and visible (UV–vis) spectra were obtained at room temperature using a Shimadzu 2500PC recording spectrophotometer equipped with a 10 mm quartz cell. PCyD-Pt nanoparticles employed here were characterised by transmission electron microscopy (TEM) at 80 kV on a JEOL JEM-1230 electron microscope. The mean diameter and standard deviation were calculated by counting 200 particles from the 100,000 × TEM photograph magnified 10 times by a magnifier.

2.3 *Quenching abilities of active oxygen species*

Quenching of hydrogen peroxide was determined by a spectrophotometric method (*13*). H_2O_2 (20 mM, 2880 μl) was placed in a quartz cuvette and 120 μl of a sample solution was added to initiate the quenching of hydrogen peroxide. After 5 min incubation, the concentration of residual hydrogen peroxide was calculated from absorbance measured at 240 nm by the spectrophotometer.

Quenching of superoxide anion radical was estimated by a formazan formation using a SOD assay kit-WST. The superoxide anion radical was generated by the enzymatic reaction with xanthine and xanthine oxidase. The assay was performed according to the manufacturer's manual. Twenty microlitres of a sample solution in water containing nanoparticles were mixed with 200 μl of WST working solution and the reaction was initiated with addition of 20 μl of enzyme working solution. A water soluble WST-1 formazan was spectrophotometrically determined at 450 nm.

3. Results and discussion

3.1 *Synthesis of PCyD-platinum nanoparticles*

Colloidal dispersions of platinum nanoparticles, stabilised by PCyD, were prepared by photoreduction of the mixed solution of hexachloroplatinic(IV) acid and PCyD in water, having a dark brown colour and being stable for months at room temperature. Figure 1 depicts UV–vis absorption spectra of the dispersions of PαCyD-Pt, PβCyD-Pt and PγCyD-Pt nanoparticles. The dispersions of PCyD-Pt nanoparticles obtained after photoreduction show broad absorption spectra without structure from the visible region to the near UV. The absorption peak due to $PtCl_4^{2-}$ completely disappeared on photoreduction, showing completion of the reduction of the platinum ions (*14*).

Figure 2 shows transmission electron micrographs and the corresponding histograms indicating the particle size distributions of colloids. Most PCyD-Pt nanoparticles distributed were in the range of 1–6 nm, suggesting that the size of PCyD-Pt is homogeneous. The average diameter of PαCyD-Pt, PβCyD-Pt and PγCyD-Pt nanoparticles is 1.8, 2.3 and 3.6 nm, respectively, with a narrow size distribution.

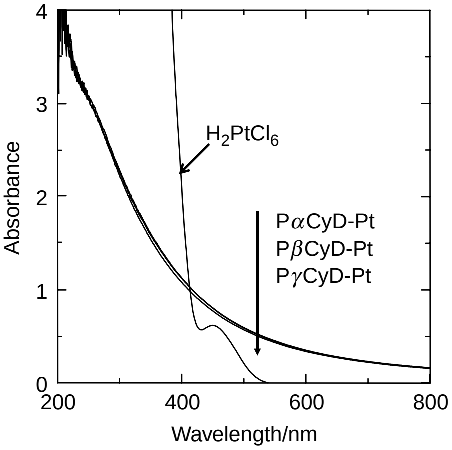

Figure 1. UV–vis absorption spectra of an aqueous solution of hexachloroplatinic (IV) acid and colloidal dispersions of PCyD-Pt nanoparticles.

3.2 *Quenching of active oxygen species by nanoparticles*

PCyD-Pt nanoparticles were applied to the catalyst for quenching of superoxide anion radical. Figure 3 exhibits the relationship between concentration of PCyD-Pt nanoparticles and the residual superoxide anion. The PαCyD-Pt, PβCyD-Pt and PγCyD-Pt nanoparticles at 50 μM quenched 82, 63 and 95%, respectively, of superoxide anion radical. The PαCyD-Pt and PγCyD-Pt nanoparticles have higher catalytic activity than a commercial platinum catalyst (poly (acrylic acid)-protected Pt nanoparticles with average diameter in the range of 1.6–2.4 nm). The low catalytic activity of poly (acrylic acid)-protected Pt nanoparticles is probably because the substrate may not easily approach active site on the surface of Pt nanoparticles, because poly (acrylic acid) molecules coordinate strongly to the metal and cover the surface of Pt particles. In fact, we reported the stability of poly (acrylic acid)-protected Ag nanoparticles by thermogravimetric analyses of the protective polymers and the Ag-containing polymers (*15*). On the other hand, PCyD-stabilised nanoparticles are normally quite stable and effective as catalysts, because the coordination of PCyD to the metal surface is relatively weak, but the total adsorption of PCyD to the metal particle is strong enough to stabilise the colloid.

A similar catalytic tendency was observed in the case of PCyD-Pt nanoparticles for the quenching of hydrogen peroxide. Figure 4 exhibits the relationship between the

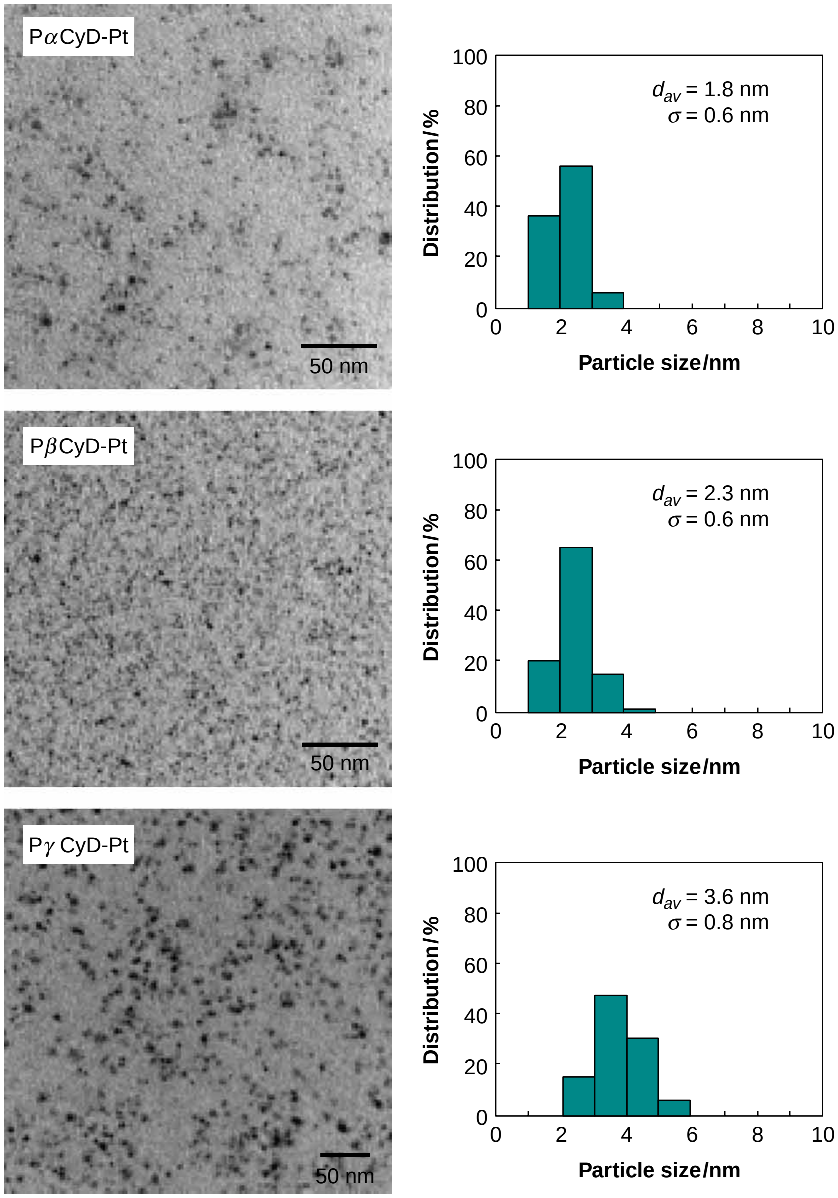

Figure 2. Transmission electron micrographs and particle size distribution histograms of PCyD-Pt nanoparticles. d_{av}, average diameter and σ, standard deviation.

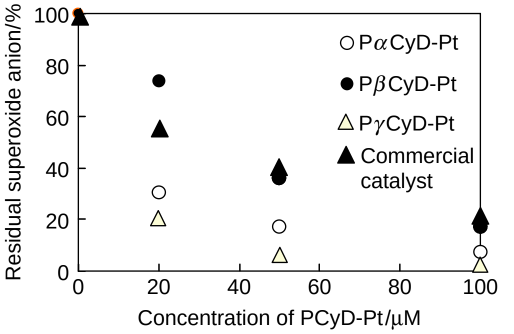

Figure 3. Relationship between concentration of PCyD-Pt nanoparticles and the residual superoxide anion.

concentration of PCyD-Pt nanoparticles and the removal ratio of hydrogen peroxide. The PαCyD-Pt and PγCyD-Pt nanoparticles have higher catalytic activity than PβCyD-Pt nanoparticles. The volubility of αCyD, βCyD and γCyD in water is 14.5, 1.85 and 23.2 g/100 ml, respectively (*16*). The low activity of PβCyD-Pt nanoparticles may be due to the low solubility of PβCyD in water.

The reduction of two different precious metal ions by UV irradiation in the presence of PγCyD gave a colloidal dispersion of the so-called core/shell-structured bimetallic nanoparticles. In the case of Au and Pt ions, colloidal dispersions of bimetallic nanoparticles with an Au-core/Pt-shell structure are produced. PγCyD-Au/Pt

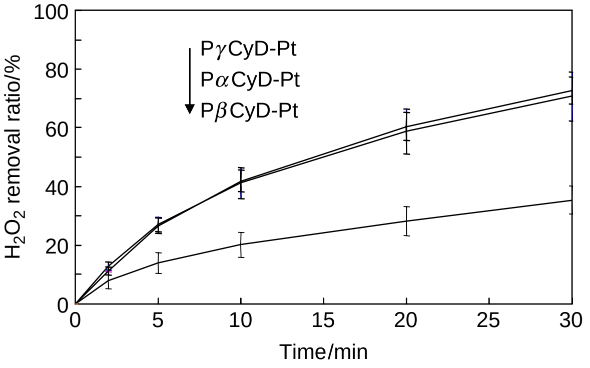

Figure 4. Relationship between concentration of PCyD-Pt nanoparticles and the removal ratio of hydrogen peroxide.

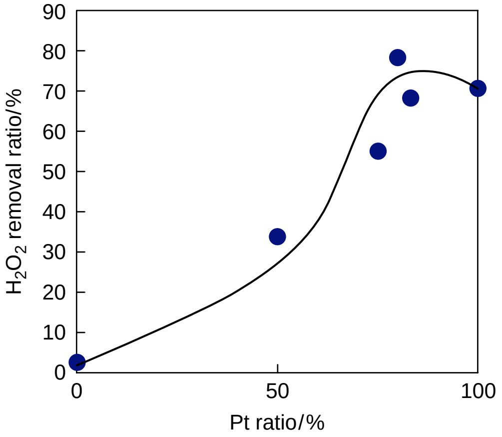

Figure 5. Plot of quenching activity of hydrogen peroxide vs. the metal composition of PγCyD-Au/Pt bimetallic nanoparticles.

bimetallic nanoparticles were applied to the catalyst for the quenching of hydrogen peroxide. Figure 5 exhibits the relationship between catalytic activity and the metal composition of PγCyD-Au/Pt bimetallic nanoparticles. Since gold has low activity and platinum has high activity for the quenching of hydrogen peroxide, PγCyD-Au/Pt bimetallic nanoparticles were thought to exhibit activities somewhere between the corresponding monometallic nanoparticles. PγCyD-Au/Pt(1/4) bimetallic nanoparticles show higher catalytic activity than the monometallic nanoparticles. Previous reports had shown that platinum nanoparticles containing a certain amount of other additional metals such as gold and palladium exhibit higher catalytic activity in hydrogen evolution and hydrogenation than platinum monometallic nanoparticles (*17*, *18*). In the series of the poly (*N*-vinyl-2-pyrrolidone)-stabilised Au/Pt bimetallic nanoparticles, the relation between catalytic activity and Pt content is expressed by the sigmoidal curve (*17*). The high catalytic activity was achieved at the position of 40% Au and 60% Pt. The same tendency was observed on our PγCyD-Au/Pt bimetallic nanoparticles. The high catalytic activity can be explained by an electronic effect of neighbouring Au on the surface of Pt.

4. Conclusion

PCyD-Pt nanoparticles were prepared by the photoreduction of hexachloroplatinic(IV) acid in the presence of PCyD. Catalytic properties of PCyD-Pt monometallic and PγCyD-Au/Pt bimetallic nanoparticles were studied for the quenching of active oxygen species. PγCyD-Au/Pt bimetallic nanoparticles are more active than PγCyD-Pt monometallic nanoparticles. The higher activity of the PγCyD-Au/Pt bimetallic nanoparticles can be understood by the electronic effect of the core upon the surface atoms.

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