

液相還元법에 의한白金 나노粉末 製造[†]

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Preparation of Nano-sized Pt Powders by Solution-phase Reduction[†]

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요 약

백금은 물리화학적 특성에 기인하여 많은 분야에서 중요한 역할을 하고 있으며, 이러한 분야에서는 아주 미세한 백금의 사용을 요구하고 있다. 그러므로 본 연구에서는 액상에서 환원제를 사용하여 백금염을 환원시킴으로서 나노크기의 백금을 제조하는 방법에 대하여 알아보았다. 수용액상에서 C14TABr과 H₂[PtCl₆]의 상호작용은 [C1₄TA]₂[PtCl₆]의 유기백금염 화합물을 형성한다. 단분산 나노 백금입자를 얻기 위해서는 C1₄TABr과 H₂[PtCl₆] 농도가 각각 cmc와 0.32 mM 이상이 되어야 한다. H₂[PtCl₆]와 C14TABr 농도가 증가함에 따라 백금입자 크기가 증가하였으며, 백금입자의 형태는 C14RABr농도 증가에 따라 제어가 가능하였다.

주제어 : 액상환원, 백금, 나노분말, 계면활성제

Abstract

Platinum plays an important role in many applications because of its extraordinary physical and chemical properties. All these applications require the use of platinum in the finely divided state. Therefore the preparation of platinum nanoparticles by reducing platinum-surfactant salt with reducing agent in the solution was investigated in this study. The net interaction between C14TABr and H₂[PtCl₆] in aqueous solution results in the formation of [C1₄TA]₂[PtCl₆]. The concentration of C14TABr and the concentration of H₂[PtCl₆] has to be above cmc and 0.32 mM, respectively in order to obtain complex-micelle aggregation for mono dispersed Pt particles. Pt particle size increases with increasing H₂[PtCl₆] and C14TABr concentration. And the shape of Pt particles was well controlled with increasing surfactant concentration.

Key words : solution phase reduction, platinum, nano powder, surfactant

1. Introduction

In recent years, metallic nanoparticles of definite size have received considerable attention because of their fascinating properties and potential applications in microelectronics, catalysts, magnetic materials, and so on¹⁾. Especially, the studies of platinum nanoparticles have been very active with maturing synthetic and characterization techniques. Platinum plays an important role in many applications because of its extraordinary

physical and chemical properties. For instance, it serves as a major catalyst in the CO oxidation at low temperature, oil cracking, and direct methanol fuel cell²⁾. All these applications require the use of platinum in the finely divided state. It is obviously important to synthesis particular fine and shape-controlled platinum nanostructures.

A number of techniques have been proposed for the preparation of metallic nanoparticles, including electrochemical deposition³⁾, chemical vapor deposition⁴⁾, bimolecule-assited synthesis⁵⁾, and sono-chemical method⁶⁾. Among them, solution-phase reduction method appears to be particular interesting since they

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offer the potential of simple operation, controlling the size of the synthesized nanoparticles easily².

The chemical reduction of Pt(VI) precursor compounds to colloiddally stable Pt nanoparticles can be achieved in a variety of micellar systems, including normal micellar solutions, inverse micellar solutions, media containing swollen micelles, liquid crystals, inverse microemulsion, and biphasic oil/water systems⁷. The particle size and size distribution are determined by the relative rates of the individual steps of nucleation, growth, and particle stabilization.

Seed formation begins when the Pt precursor species incorporated in the micellar system in the oxidized state are reduced to zerovalent Pt atoms.

For surfactant-mediated synthesis, mechanistic considerations suggested that the limited aggregation of Pt nuclei to nanoscale particles may proceed via compartmentalization and via the arrested growth mechanism⁸. Compartmentalization implies that the interior of a micellar aggregate, with the inner pool either spherical in shape, or a network of interconnected channels, may be regarded as a micro-reactor in which the precursor molecules are dissolved and reduced. The finite aggregation of Pt nuclei is thought to be restricted to the size of the pool insofar as the primary particles are efficiently stabilized by surfactant molecules adsorbed from the surrounding micellar micro-environment.

In contrast, the arrested growth mechanism assumes that geometric constraint is not a prerequisite for nanoparticle formation, but the particle growth is limited by the rapid adsorption of surfactant molecules at a very early stage of the aggregation process, and in this way a colloiddally stable hydrosol is formed⁹.

Alkyltrimethylammonium bromides are prototypes of cationic surfactants whose solution properties have been thoroughly investigated¹⁰. Thus the size-controlled preparation of monodisperse Pt nanoparticles in $H_2[PtCl_6]/C14TABr$ normal micellar solutions was investigated in this study.

2. Experimental

2.1. Materials

Hexachloroplatinic(IV) acid [$H_2PtCl_6 \cdot nH_2O$, $n=5.6$] was guaranteed reagent of Kojima Chemicals Co., LTD. C14TABr(Tetradecyltrimethylammonium bromide,

99%, Aldrich) as surfactant, and sodium borohydride ($NaBH_4$, 99%, Aldrich) as reducing agent were used as received. Reagent-grade water was produced by a Milli-Q filtration system.

2.2. Preparation of Pt nanoparticles

Nanosized Pt particles were prepared by reduction of H_2PtCl_6 in the presence of cationic surfactant, C14TABr. A series of aqueous solutions of the H_2PtCl_6 and the C14TABr surfactant were prepared separately and then mixed to give desired concentrations. The interaction between the precursor metal anions [$PtCl_6^{2-}$] and the surfactant cations [$C14TA^+$] in aqueous solutions results in the formation of organic metal salt. The reaction system was subjected to vigorous stirring when the reducing agent, an aqueous solution of $NaBH_4$, was introduced into the reactor in a 20-fold excess over the precursor metals.

Interaction between H_2PtCl_6 and C14TABr in the surroundings of the cmc [critical micelle concentration, cmc of C14TABr = 3.9 mM] were investigated by UV-Vis spectroscopy at room temperature.

The size and shape of the Pt particles was determined by transmission electron microscopy in a Philips CM12 analytical TEM.

3. Results and Discussion

3.1. Binding in the Premicellar and the Post-micellar Regions

Transition metal complexes in media containing surfactants often display peculiar behavior. Specific complex-surfactant interactions have been described in both organic and aqueous media⁷. This present work includes the binding of $[PtCl_6]^{2-}$ to an oppositely charged surfactant in aqueous solution. Our visual observations during the preparation of Pt hydrosols likewise indicated that $[PtCl_6]^{2-}$ interact with cationic surfactants before the reduction process is induced.

Fig. 1 shows the appearance of solution with increasing surfactant. Upon addition of an excess of $H_2[PtCl_6]$ to C14TABr, first dissolved in water, the transparent solution turned the translucent in the premicellar [formation of complex-surfactant] region, and yellow color in the postmicellar [formation of complex-micelle] region. These observations are attributed to the formation



Fig. 1. The appearances of solutions with increasing surfactant.

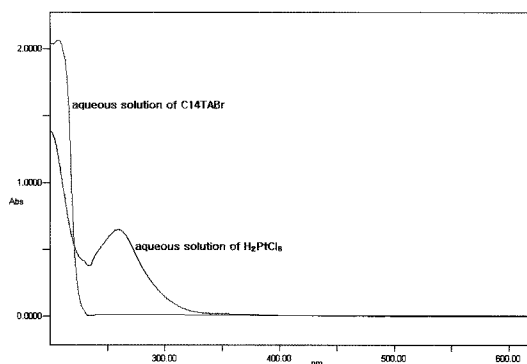


Fig. 2. UV-Vis spectrum graph of $H_2[PtCl_6]$ and C14TABr aqueous solution.

of complex-surfactant premicellar and complex-surfactant post-micellar aggregates below and above the cmc, respectively⁷⁾.

UV-Vis spectroscopy is a versatile tool with which to elucidate the binding of charged molecules to oppositely charged, single surfactant molecules in the premicellar region and oppositely charged micelle in the postmicellar region¹¹⁾. This method was used to investigate the progressive spectral change in the $H_2[PtCl_6]/C14TABr$ system in this study.

The aqueous solutions of $H_2[PtCl_6]$ and C14TABr were analyzed by UV-Vis spectroscopy, and each UV-Vis absorption spectrum was showed in Fig. 2. The absorption spectrum of $H_2[PtCl_6]$ aqueous solution has intensity at 258 nm due to the absorption of Pt(IV) species²⁾, and in the case of C14TABr aqueous solution, the absorption spectrum has the intensity at 207 nm.

Fig. 3 shows the absorption spectrum of mixed aqueous solution of $H_2[PtCl_6]$ (0.04 mM) and C14TABr with increasing C14TABr, which displayed two predominant peaks, at 210 nm and 270 nm. Generally the interaction between the precursor metal anions and surfactant cations in aqueous solutions results in the formation of organic metal salt¹²⁾.

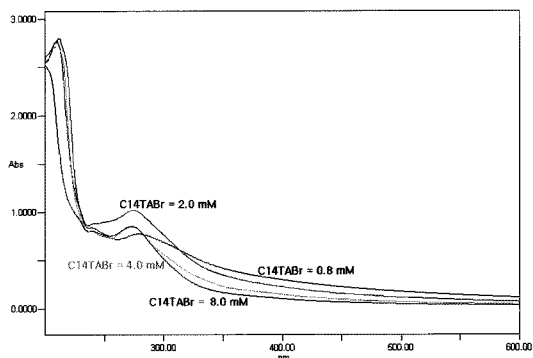


Fig. 3. UV-Vis spectrum graph of mixed aqueous solution of $H_2[PtCl_6]$ and C14TABr with increasing C14TABr.

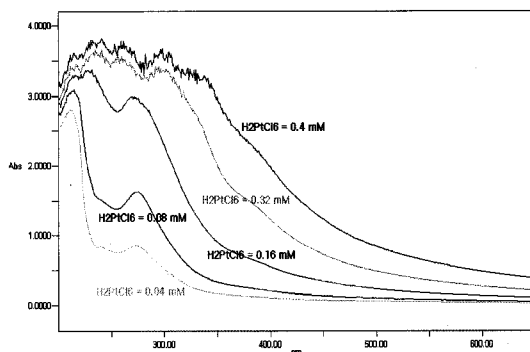


Fig. 4. UV-Vis spectrum graph of mixed aqueous solution of $H_2[PtCl_6]$ and C14TABr with increasing $H_2[PtCl_6]$.

Therefore it seemed that two predominant peaks, at 210 nm and 270 nm was due to the formation of organic metal salt, $[C14TA]_2[PtCl_6]$. As the surfactant concentration is increased at constant concentration of $H_2[PtCl_6]$, 0.04 mM, the absorbance at 210 nm and 270 nm, attributed to complex-surfactant premicellar aggregates, gradually decrease. Upon storage, micro-phase separation occurred below the cmc and a milky white salt precipitated slowly. Above the cmc, the apparent solubility of the organic salt increased with increasing surfactant concentration. Therefore the concentration of C14TABr has to be above cmc.

Fig. 4 shows the absorption spectrum of mixed aqueous solution of $H_2[PtCl_6]$ and C14TABr (8 mM) with increasing $H_2[PtCl_6]$. As the $H_2[PtCl_6]$ concentration increased at constant concentration of C14TABr, 8 mM, the absorbance at 210 nm and 270 nm increase. New predominant peaks above 220 nm appeared when

the concentration of $H_2[PtCl_6]$ is above 0.32 mM. The intensity of these peaks increased with increasing $H_2[PtCl_6]$ concentration due to a further color intensification in the postmicellar region. Namely as a result of the formation of complex-micelle aggregation, the translucent solution turned yellow color with increasing $H_2[PtCl_6]$ concentration⁷⁾. Therefore the concentration of $H_2[PtCl_6]$ has to be above 0.32 mM at the C14TABr concentration of 8 mM in order to obtain complex-micelle aggregation for monodispersed Pt particles in this study.

3.2. Preparation of Pt nanoparticles in $H_2[PtCl_6]$ /C14TABr Micellar Solutions

The addition of reducing agent, $NaBH_4$ to a micellar solution of $H_2[PtCl_6]$ /C14TABr leads to nanosized Pt particles. In general, the reduction was complete in a matter of seconds, and the final size distribution was achieved in a matter of tens of minutes. Hydrosol samples that were stable for months were obtained in this way.

Fig. 5 shows the colloidal Pt particles prepared with

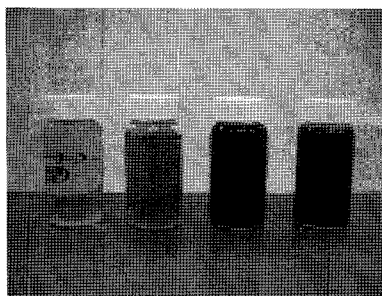


Fig. 5. The Pt colloidal solution prepared with exp. conditions.

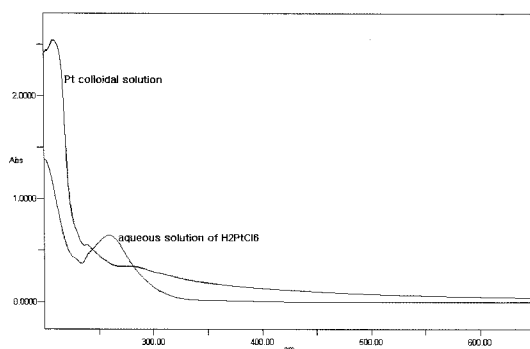


Fig. 6. UV-Vis spectrum graph of Pt colloid and H_2PtCl_6 .

different conditions. After reduction, the solution turned darkly golden with a further color intensification with increasing the concentration of $H_2[PtCl_6]$.

UV-Vis absorption spectrum of the colloidal solution showed in Fig. 6.

The absorption spectrum of H_2PtCl_6 aqueous solution at 258 nm due to the absorption Pt(IV) species disappeared completely, indicating Pt(IV) had been used up and colloidal Pt had been formed²⁾.

The size of Pt nanoparticles prepared with different conditions are displayed in Fig. 7. Pt particles in the size range from 3 to 5 nm were synthesized, and the Pt particle size increases with increasing $H_2[PtCl_6]$ and C14TABr concentration. And the shape of Pt particles was well controlled with increasing surfactant concentration.

4. Conclusions

The net interaction between C14TABr and $H_2[PtCl_6]$ in aqueous solution results in the formation of $[C14TA]_2[PtCl_6]$. This organic salt can be solubilized by the surfactant micelles to produce metallomicelles which are the real precursor entities for the $NaBH_4$ reduction of Pt^{4+} to Pt^0 . The concentration of C14TABr and the concentration of $H_2[PtCl_6]$ has to be above

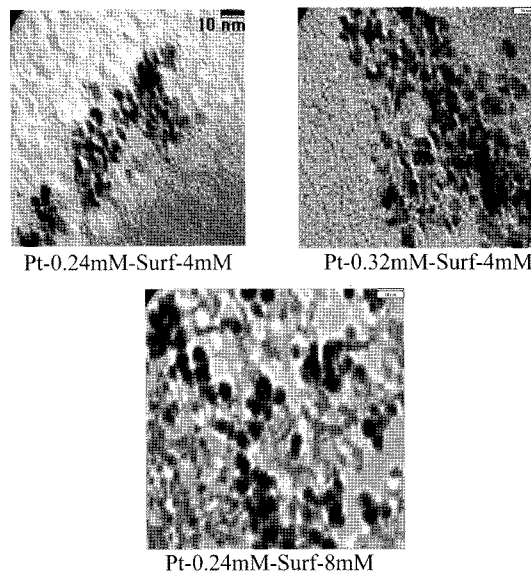


Fig. 7. TEM micrograph of Pt particles.

cmc and 0.32 mM, respectively in order to obtain complex-micelle aggregation for monodispersed Pt particles.

Pt particle size increases with increasing $H_2[PtCl_6]$ and C14TABr concentration. And the shape of Pt particles was well controlled with increasing surfactant concentration.

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