Morphology and Surface Plasmon
of Platinum Fine Particles Formed with a Surfactant

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Platinum fine particles were formed in an aqueos solution of chloroplatinic acid by hydrogen-reduction using sodium dodecyl sulfate as a surfactant. The morphology of fabricated platinum particles quenched in a vitreous ice was studied by cryogenic transmission electron microscopy. The surfactant was found to work as a stabilizing agent which regulates particle size and isolates the formed nm-size platinum particles from each other. In electronic spectrum from the solution, a weak absorption peak appeared around 400 nm in wavelength after full reduction, which can be considered to be originated from surface plasmon resonance of platinum particles.

1. INTRODUCTION

Interest in the physicochemical properties of colloidal metal particles has been ongoing since the time of Faraday, who demonstrated that colloidal gold particles can be produced by reduction of an aqueous gold salt solution [1]. Current efforts are focused on a number of different areas and applications. One is the area of catalysis, where reactivity of colloidal metal particles on oxide supports is examined, and the others are of the active species in various reactions including biological applications. On the fundamental level, the issue of quantum size effects is an actively debated topic, with various experimental and theoretical approaches currently being utilized [2].

A characteristic feature of metal colloids is the discrete band that can be observed in the ultraviolet-visible (UV-VIS) electronic spectrum of the particles and the surface plasmon resonance. For the surface plasmon, in particular, gold and silver particles have been intensively studied on the peak positions in electronic spectrum and their full width of half maximum. However, it has not been studied so much on surface plasmon for platinum fine particles in solution. Moreover, the structural aspects of particles in solutions have not been observed directly, which can make clear the particle sizes and the aggregation states in solution. Usually dried samples have been examined by conventional electron microscopy. However, the drying process often introduces artificial aggregations so that it is indispensable to observe metal particles as they are in solution. The particle aggregation states in solution are expected to be an important factor for understanding the optical absorption spectrum as well as size distribution of particles. In this study, we will report an observed results on platinum particles formed in a solution by cryogenic transmission electron microscopy (Cryo-TEM) to clarify the morphology of particles in the solution and discuss the UV-VIS spectrum in relation with the structure.

There have been many attempts to prepare fine platinum clusters by physical, chemical or other techniques. Among them, the chemical synthesis in solution with some dispersion stabilizing agent is known to be a familiar method to fabricate fine metal particles [3]. Recently Toshima *et al.* have reported about preparation of colloidal dispersions of platinum clusters through hydrogen-reduction by using surfactants [4]. They have demonstrated that well-controlled platinum particles of some nm size in diameter can be prepared by this method.

Following their method, we prepared platinum particles in an aqueous solution with a surfactant to control the particle size in nm order. By comparing the aggregation states in solutions with and without the surfactant, we will discuss the surface plasmon resonance in UV-VIS electronic spectra of the solutions.

2. EXPERIMENTAL

An aqueous solution of 0.2 mmol/dm^3 chloroplatinic acid (HPtCl) containing a regulated amount of sodium dodecyl sulfate (SDS) of 10 - 100 mmol/dm^3 was reduced with hydrogen gas. At room temperature, platinum sol formed in less than 10 min. With SDS, the color of solution changed from light yellow to light brown by reduction, but without SDS to black due to the following precipitation.

Direct observation method of platinum particles in solution is illustrated in Fig.1. A droplet of solution at an intended time of reduction was placed on a microgrid, the excess solution on the grid was drained off with a filter paper, and then the grid was immediately plunged into liquid propane maintained at about 100 K in an immersion cryofixation apparatus to achieve quick cooling for preventing rearrangement of platinum particles and crystallization of the water molecules. By this preparation, particles in solution can be frozen in vitreous ice which provides almost no contrast in transmission electron microscopy (TEM) observation [5]. Then it was placed in a compartment of a specially designed cryotransfer system

attached to a Cryo-TEM (JEOL 4000SFX). This instrument has a helium stage to keep specimens around 4 K. Fine particles formed in the solution, therefore, can be observed directly in transparent vitreous ice as they are in water solution. By this method, artificial aggregation can be avoided for TEM observation.

UV-VIS electronic spectra were measured as a function of reduction time with a spectrophotometer (Shimadzu UV-2200) in the wavelength range of 190 - 900 nm.
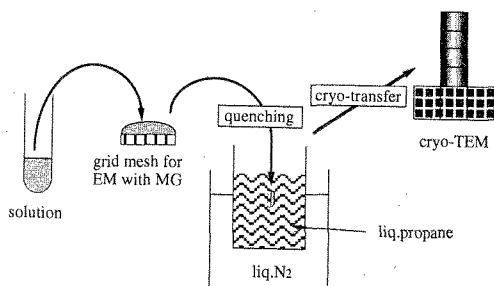

Fig.1 Sample preparation for Cryo-TEM. Objects in solution were frozen in vitreous ice by quenching into liquid propane at 100 K and they were cryotransferred into a Cryo-TEM with a liquid helium stage of 4 K.

3. RESULTS AND DISCUSSION

Without SDS, black precipitates, which were resulted soon after the reduction time of 6 min, were formed in the HPtCl aqueous solution. This indicates that the reduced metal particles are considerably aggregated as large particle in the solution. Correspondingly a typical Cryo-TEM image of platinum particles thus formed without SDS is observed as in Fig.2(a), where one can find large aggregated particles with several tens nm in size formed in the solution. From detailed inspection of the image as shown in Fig.2(b), however, the large particles are found to be composed of finer particles with a size of about 2 nm in diameter, which can be named as primary particles. The size distribution of the primary particles was estimated from a histogram of particle sizes observed in the images showing the aggregates. From the histogram, the diameters are found to be distributed over 1 to 4 nm with the maximum at 2 nm. The width of size distribution is narrow, independent of the sizes of aggregates which are large and widely distributed.

On the other hand, when SDS of 10 - 100 mmol/dm^3 was added as a surfactant to the aqueous solution, the reduced platinum particles were formed as isolated clusters as shown in Cryo-TEM image of Fig.3, where the dark contrasts with the diameter of about 2 nm are recognized sporadically in the matrix of vitreous ice for the fully reduced sample. The size distribution is similar as that of the primary particles described in the previous paragraph (without SDS). Even when SDS concentrations were changed in the range between 10 - 100 mmol/dm^3, the platinum sol formed by hydrogen-reduction was observed in the same feature as shown in Fig.3. Though it is not clear in this figure, each particle
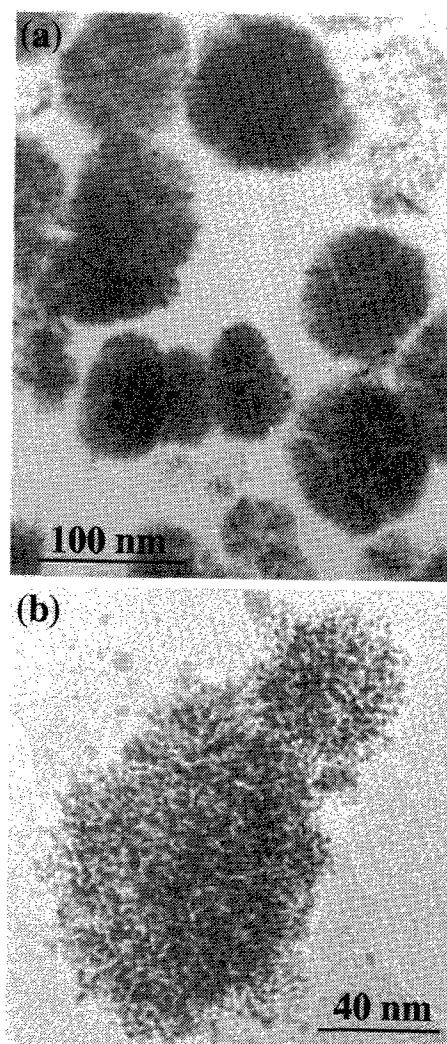

Fig.2 Cryo-TEM images of Pt particles reduced without SDS. (a) Aggregated state of Pt particles, and (b) magnified image of (a), where the aggregate is composed of many fine particles (primary particles) with the diameter of about 2 nm.

was found to be covered with SDS monolayer when observed at higher magnification. The fine platinum particle was observed to be covered with a low contrast layer with a thickness of 1 - 2 nm. Therefore, the particles are considered to be coated with SDS monolayer as schematically illustrated in Fig.4. The structural details of the platinum particles covered with SDS will be reported elsewhere. As a result, platinum particles are suspended isolatedly from each other in the aqueous solution when formed with SDS. However, they aggregated without SDS, where each primary particle has almost the same size as the case reduced with SDS.

UV-VIS spectra were measured on the solutions containing the platinum particles reduced with and without SDS. Typical spectra during the reduction without SDS are shown in Fig.5(a) and with SDS in Fig.5(b). In both cases, the strong absorption peaks at 210 nm (peak-A) and 260 nm (peak-B) decrease their intensities as the reduction proceeds. These peaks come from the absorptions due to PtCl$_4^{2-}$ and
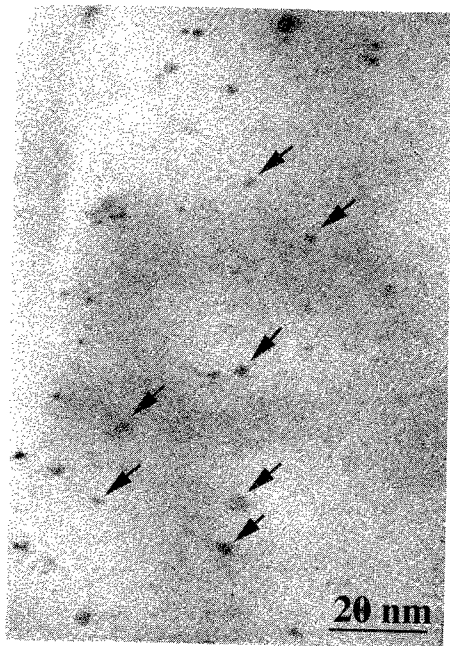
Fig.3   Cryo-TEM image of Pt particles prepared with SDS, where the Pt particles are well dispersed in vitreous ice. Several Pt particles with diameters of about 2 nm are indicated by the arrows.
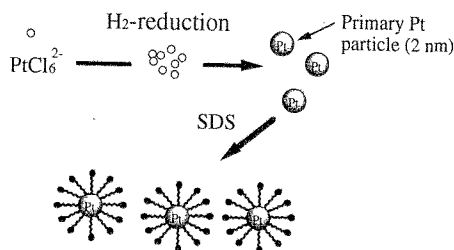

Fig.4   A model of Pt micelle formation process with SDS. Pt particles primarily formed by reduction are then covered with SDS molecules.

$PtCl_6^{2-}$ ions, respectively [6], so that they become weaker on reduction and finally disappear after about 6 min of the hydrogen full reduction. In particular, in the visible region, the background level of absorbance increases with proceeding the reduction disregarding with or without SDS, which indicates that the scatterers (platinum particles) increase in their numbers by the reduction. More interesting point in the spectra is that a weak but clear absorption peak was observed near the wavelength of 400 nm in the case with SDS. The enlarged spectra near 400 nm are shown in Figs.6(a) and (b). In the reduction with SDS, a new absorption appears around 400 nm (peak-D, 3.1 eV) in wavelength in Fig.6(b) after full reduction, but not observed without SDS. When considering the regular spherical shape with about 2 nm in diameter of platinum particles formed with SDS, this absorption can be originated from fine
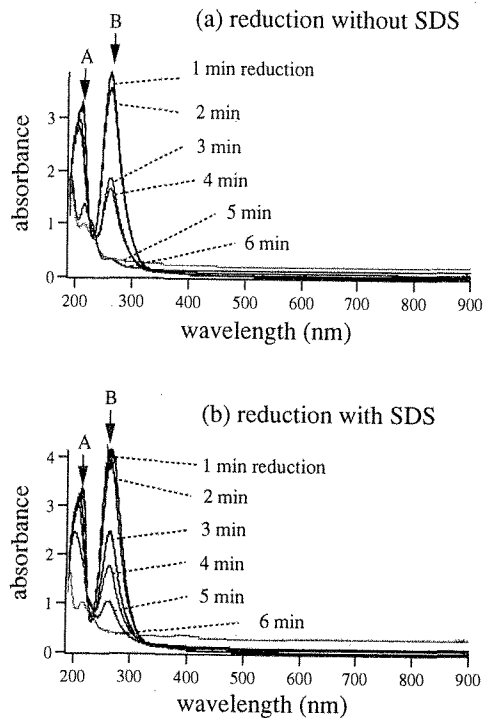

Fig. 5   Changes in UV-VIS electronic spectra during the reduction. (a) Reduction without SDS and (b) with SDS where the peaks A and B decrease their absorption intensities with the reduction times.
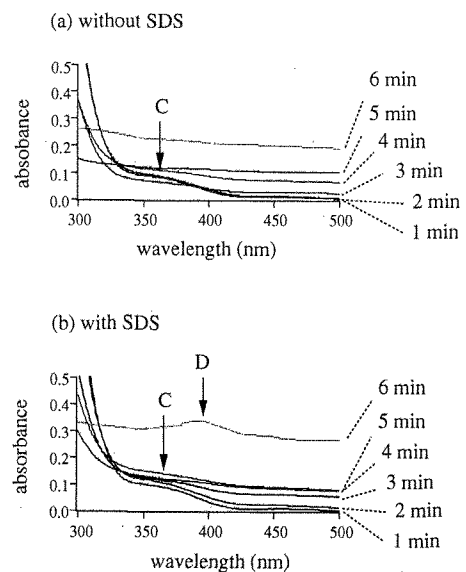

Fig.6   Changes of UV-VIS spectra near 400 nm. Without SDS, the peak C disappears according to the reduction as shown in (a), and also with SDS the peak C disappears (b), but a new peak D appears after full reduction at about 400 nm as shown in (b) when used SDS.

particles; surface plasmon resonance in platinum particles. In the cases of metal particles in aqueous solutions, the surface plasmon peaks are often observed in the wavelength region. However, the peak becomes broaden when particles aggregate. For example, from a comparison of spectra obtained for silver particles having different degrees of particle aggregation, it has been concluded that the surface plasmon resonance exhibits considerable broadening in spectra [7]. This may be related to various surface excitation modes in the aggregates [8]. In the present case, since the 400 nm absorption was not observed for the aggregated platinum particles when reduced without SDS, the high broadening of the surface plasmon resonance absorption peak is expected and then not observed as a peak. From the above results, the peak at 400 nm can be plausibly attributed to the surface plasmon resonance. Another absorption peak around 370 nm (peak-C) was observed at the beginning of reduction but disappears when the reduction was completed. Therefore, it can be certainly attributed to an absorption due to some platinum complex ion, but detailed assignment is still under consideration.

A theoretical calculation by means of Mie theory [9] has been carried out for the absorption peaks by surface plasmon resonance in 10 nm diameter spherical particles of several metals in dielectric medium of water [10]. They have reported the resonance peaks at 520 nm (2.4 eV) for gold and 400 nm (3.1 eV) for silver, for example. The calculation succeeds to reproduce roughly the experimental peak positions of 2.4 eV in the case of gold and of 2.8 eV in the case of silver, which have been observed experimentally for the metal particles with the diameter between 5-26 nm [11]. On the other hand, the surface plasmon resonance of platinum spherical particles with 10nm diameter in water solution has been evaluated theoretically to be occur around 5.4 eV (230 nm in wavelength) [10]. Although the calculated peak position

does not agree with the 400 nm peak observed in this study, it is known that the surface plasmon peak depends on the dielectric constant of surrounding medium. In the present case, the platinum particles are covered with SDS, so that the dielectric constant should be larger, unfortunately not known the value, than the case of water. Accordingly it is expected that the surface plasmon resonance happens at lower energy (longer wavelength) from 5.4 eV.

In conclusion, the peak at 400 nm (3.1 eV) from the fine platinum particles can assign to the surface plasmon resonance which appeared clearer owing to the regularity of the particle sizes by the hydrogen reduction under the existence of the SDS surfactant.

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