Sonochemical preparation and characterization of composite noble metal nanoparticles

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Colloidal nanoparticles of noble metals were prepared from solutions containing noble metal ions by the ultrasound irradiation which provides unique reaction sites. Two kinds of noble metal ions, Au(III)/Pd(II), Au(III)/Pt(IV) and Pt(II)/Pd(II), were simultaneously reduced in the presence of surfactants (SDS or PEG-MS) by the ultrasound irradiation of argon-saturated aqueous solutions. Reducing radicals were produced mostly from the surfactants. Except for Pt(II)/Pd(II)/SDS system, the rates of reduction of Au(III), Pd(II) and Pt(IV) were much faster than those of Pt(II). Synthesized nanoparticles were characterized by UV-vis spectra, XRD measurements and TEM and EDX analyses. Three types of morphologies of a core-shell structure, a random alloy structure and a mixture of monometallic nanoparticles were observed. Core-shell structures were made from Au(III)/Pd(II)/SDS, Au(III)/Pt(IV)/PEG-MS. In the system of Au(III)/Pd(II)/PEG-MS and Pt(II)/Pd(II)/SDS, random alloy nanoparticles were obtained and Au(III)/Pt(IV)/SDS system provided mixtures of monometallic nanoparticles. The particle sizes were of the order of ten nanometers or lower. Core-shell structured particles had narrower size distributions than monometallic or random alloy nanoparticles.

"Keywords:" gold-palladium alloy, gold-platinum alloy, platinum-palladium alloy, ultrasound irradiation, nanoparticles.

1. INTRODUCTION

Nanostructured metal materials have been widely studied in recent years because their physical and chemical properties are often quite different from those of the bulk. Such nanostructured materials are also applied to various fields of industry, such as optical, electronic and magnetic devices as well as catalysts and sensors⁽¹⁾. Various methods to prepare nanoparticles have been employed; they are controlled chemical reactions⁽²⁻⁵⁾, photochemical or radiation chemical reactions⁽⁶⁻⁷⁾ and metal vaporization techniques⁽⁸⁻⁹⁾. The preparation of</sup> nanoparticles from noble metal ions by application of ultrasound is worthy of attention because of many unique properties induced by acoustic cavitation, the formation, growth and collapse of bubbles in a liquid⁽¹⁰⁻¹²⁾. High-pressures (hundreds of atmosphere) and high-temperatures (several thousand of degrees) were generated during the collapsing of the cavitation bubbles⁽¹³⁾. So far, there have been a few investigations on the reduction of noble metal ions by a sonochemical method⁽¹⁴⁻²⁰⁾.

In this paper, we report the formation mechanisms and morphologies of nanoparticles formed by the sonochemical reduction of noble metal ions, such as Au(III), Pt(IV or II) and Pd(II). The products were characterized by using UV-vis spectra, XRD measurements, TEM and EDX analyses.

2. EXPERIMENTAL

A multiwave ultrasonic generator with a barium titanate oscillator was used for the sonication and operated at 200 kHz with an input power of 6 W/cm². A

cylindrical glass vessel was used for the ultrasonic irradiation, which had a silicon rubber septum for gas bubbling or sample extraction without exposing the sample to air. The argon-purged aqueous solutions containing noble metal complexes (AuCl₄⁻, PdCl₂, PtCl₆²⁻ and PtCl₄²⁻) were sonicated in the presence of surfactants (SDS; sodium dodecyl sulfate, PEG-MS; polyethylene glycol monostearate). During the sonication the vessel was closed. The sonication was carried out in a water bath (about 20°C). TEM specimens were prepared by placing droplets of the colloidal dispersion onto a carbon film supported copper grid and drying in a vacuum.

3. RESULTS AND DISCUSSION

3.1 Preparation of core-shell structured nanoparticles

The color of the aqueous solution containing NaAuCl₄ (0.5 mM), PdCl₂ (0.5 mM) and SDS (8 mM) was found to turn from pale yellow originated from noble metal complexes, into reddish-violet at first and then into brown in the progress of the irradiation. Since it is known that the formation of colloidal Au and Pd nanoparticles shows reddish-violet and dark brown color respectively^(17,15), it was assumed that Au nanoparticles are produced first and then Pd nanoparticles followed. An improved colorimetric method using saturated NaBr solution was employed to determine Au(III) and Pd(II) concentrations. By the addition of saturated NaBr solution, the absorption bands of Au(III) and Pd(II) were shifted to suitable positions for the determination. At the same time Au and Pd nanoparticles aggregated and removing of them became possible by filtration through a membrane filter. It was found that Au(III) began to be consumed, and their

depletion was followed by Pd(II) consumption. When comparing the spectra of the mixtures of monometallic Au and Pd nanoparticles with those of simultaneously sonicated Au/Pd solutions with the corresponding compositions, it was shown that the surface plasmon of Au absorption was proportional to its molar ratio in case of the mixtures nanoparticles, but not in the case of the simultaneously sonicated solution. This suggests that Pd deposits onto the pre-formed Au cores, and the morphology of these product is core-shell structure.

Figure 1 shows the XRD patterns of binary Au/Pd nanoparticles. The lattice constant was 4.06 Å, that is almost the same value of Au (4.07 Å). It is considered that the pattern reflects the core-shell structure, because if the nanoparticles are Au/Pd solid solutions the diffraction peaks should appear between Au and Pd, depending on the composition⁽²¹⁾. However, when the molar ratio of Au/Pd was 1/1, the diffraction peaks only from Au were detected. This may be because that Pd-shell is too thin to make significant diffraction intensities. When the molar ratio changed from 1/1 to 1/4, Pd 111 and 200 reflections were observed probably due to increase in the Pd shell thickness.



Fig.1 XRD patterns of sonochemically prepared Au/Pd (SDS). (a)Au/Pd=1/1 (b)Au/Pd=1/4.

HRTEM micrographs of Au/Pd binary nanoparticles and their corresponding EDX results are shown in Fig. 2 and Table 1. They clearly show that the products consist of Au-core and Pd-shell. The average diameter was about 8 nm, and the size distribution was fairly narrow. When the molar ratio of Au/Pd was changed from 1/1 to 1/4, the average diameter remained unchanged.





Fig.2 HRTEM micrographs of binary Au/Pd nanoparticles (SDS). (a)Au/Pd=1/1 (b)Au/Pd=1/4.

Table 1 EDX results of nanoparticles of (a) and (b).

| | ١ | whole | center | edge |
|------------|-----|-------|--------|------|
| Pd content | (a) | 50.4 | 24.0 | 96.4 |
| atom% | (b) | 75.1 | 44.2 | 99.3 |
| Au content | (a) | 49.6 | 76.0 | 3.6 |
| atom% | (b) | 24.9 | 55.8 | 0.7 |

Similar core-shell structured nanoparticles were obtained from the sonication of a solution containing NaAuCl₄ (0.25 mM), H₂PtCl₆ (0.25 mM) and PEG-MS (0.4 mM). UV-vis spectra showed that Au surface plasmon absorption dismissed when the both ions were reduced. Comparison of UV-vis spectra and XRD patterns showed similar tendency as the case of Au/Pd/SDS system. HRTEM observations revealed that the formed nanoparticles consist of Au-core and Pd-shell and their average diameter was about 5 nm both in the cases of Au/Pt = 1/1 and 1/4.

3.2 Preparation of random alloy nanoparticles

A solution containing NaAuCl₄ (0.5 mM) PdCl₂ (0.5 mM) and PEG-MS (0.4 mM) was sonicated under argon atmosphere. In this case, the surface plasmon absorption of Au nanoparticles appeared quickly, grew and reached maximum at 3 min of the sonication. A rapid increase of absorbance after the time of the maximum, especially in the shorter wavelength region, is considered to be a tail of a large absorption band due to Pd nanoparticles.



Fig.3 XRD pattern of sonochemically prepared Au/Pd (PEG-MS).

In Fig. 3 is shown the XRD pattern of the Au/Pd nanoparticles. The diffraction peaks were observed to appear between Au and Pd peaks, indicating that a random solid solution was formed, not a core-shell alloy. TEM micrographs of the Au/Pd nanoparticles are shown in Fig. 4. The average diameter was about 6 nm when the molar ratio was Au/Pt=1/1, and size distribution was broader than those of the Au/Pd nanoparticles prepared in the SDS system. The average diameter became small (about 4 nm) with decreasing molar ratio of Au and then constant.



Fig.4 TEM micrographs of random alloy Au/Pd nanoparticles (PEG-MS). (a)Au/Pd=1/1 (b)Au/Pd=1/4.

An aqueous solution containing $PdCl_2$ (0.25 mM) K_2PtCl_4 (0.25 mM) and SDS (8 mM) was sonicated under argon atmosphere. The color of the solution turned from light brown originated from noble metal complexes and then into dark brown in the progress of irradiation. Similar colorimetry to that used in the Au(III)/Pd(II)/SDS system using saturated NaI solution instead of saturated NaBr solution, Pt(II) and Pd(II) were determined without interference of the formed particles. The rates of reduction of Pt(II) was faster than that of Pd(II) and both reductions proceeded simultaneously. It was found that this fact contradicts the report that the reduction rate of Pd(II) is faster than the Pt(II)^(17,22). It seems that Pd nanoparticles are produced first and then, majority of the formed Pd nanoparticles reduce Pt(II) as follows:

$$Pd(II)+R \rightarrow Pd(0)+R'+H^{+}$$
(1)

 $Pd(0)+Pt(II) \rightarrow Pd(II)+Pt(0)$ (2) (R: reducing radicals)

Figure 5 shows TEM micrograph of Pt/Pd nanoparticles. The average diameter was about 7 nm with broad size distribution. It was shown from EDX analyses that they were solid solutions.



Fig.5 TEM micrograph of Pt/Pd solid solution nanoparticles (SDS).

3.3 Preparation of mixtures of monometallic nanoparticles UV-vis spectra of a solution containing NaAuCl₄ (0.25 mM), H₂PtCl₆ (0.25 mM) and SDS (8 mM) showed that Au(III) ions were consumed at first, and after the completion of reduction, Pt(IV) ions were consumed. The Au plasmon absorption was remained until the end of the reduction. This suggests that Au and Pt nanoparticles exist separately. Fig. 6 shows a TEM micrograph of Au/Pt/SDS nanoparticles. It clearly shows that there are two kinds of products; large Au nanoparticles with a high contrast, with circular, triangular or hexagon –shape and small Pt nanoparticles with a low contrast. The average diameters of Au and Pt were about 10 nm and 2 nm, respectively.



Fig.6 TEM micrograph of the mixture of monometallic Au and Pt nanoparticles (SDS).

4. SUMMARY

Three kinds of products with core-shell and random alloy structures and monometallic mixtures were obtained by the sonochemical reduction of aqueous solutions

Table 2 Summarized data of sonochemically prepared products.

| Surfactant | | Structure | Average diameter | |
|------------|-------|------------|--------------------|--|
| | Au/Pd | core-shell | 8 nm | |
| SDS | Au/Pt | Mixture | Au 10 nm / Pt 2 nm | |
| | Pt/Pd | random | 7 nm | |
| | Au/Pd | random | Au/Pd=1/1 6 nm | |
| PEG-MS | | | Au/Pd=1/4 4 nm | |
| | Au/Pt | core-shell | 5 nm | |

containing two kinds of noble metal complexes and surfactants. The morphologies of the products are

summarized in Table 2.

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