Size Control of Au@Pt Core-shell NPs using Ultrafine Bubbles and Ultrasound, and Evaluation of Catalytic Activity

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1. Introduction

Pt nanoparticles (Pt NPs) serve as catalysts for various reactions such as methanol oxidation. However, since Pt is a rare metal, core-shell nanoparticles with the shell composed of Pt have been actively investigated in an effort to reduce the amount of Pt^{1} . It is desirable to control the size of core-shell NPs, including the Pt shell thickness, to improve the catalytic activity.

In this study, Au@Pt core-shell nanoparticles (Au@Pt NPs) were synthesized by sonochemical and chemical reduction in the presence of non-ionic surfactant and ultrafine bubbles (UFBs), which are defined as fine bubbles whose diameter is less than 1 μ m. After the synthesis, the effects of surfactant and UFBs on the morphology of Au@Pt NPs were investigated. Furthermore, the catalytic activity of Au@Pt NPs for the reduction of 4-nitrophenol (4-NP) was evaluated by UV-Vis spectroscopy.

2. Experimental

Fig. 1 shows the outline of the experimental apparatus. The transducer was a disk-type one (Honda Electronics) and driven by a power amplifier, which amplified a continuous sine wave generated by a signal generator. With the bottom of the reaction vessel approximately 6 mm away from the transducer, the vessel position was adjusted by Z-Stage to maximize the impedance of the transducer²). The ultrasonic frequency and the input electric power applied to the transducer were set at 488 kHz and 30 W, respectively. The temperature of the sample solution was maintained at 283 K by a low temperature circulation bath.

 $6.0 \text{ mL of HAuCl}_4$ aq (20 mM) and 0.3-6.0 mL of H₂PtCl₆ aq (20 mM) were mixed, and surfactant (either Pluronic F127 (PF127), a non-ionic triblock copolymer, or sodium dodecyl sulfate (SDS), anionic surfactant) was added to the solution. Then the solution was irradiated with ultrasound for 20 minutes, which was followed by the addition of enough ascorbic acid to the solution as a reducing agent. After this operation, the solution was mixed with either UFB water or ultrapure water. Then the

sample stood still for 24 h. UFB water was produced from ultrapure water by a pressurized dissolution method (ultrafineGalf FZ1N, IDEC).

The synthesized NPs were observed using transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). The size and concentration of UFBs were measured by nanoparticle tracking analysis.

To evaluate the catalytic activity of Au@Pt NPs for the reduction of 4-NP, 4-NP aq was mixed with NaBH₄ aq as a reducing agent and the Au@Pt NP solution in an optical cell. The molar ratio of each chemical species was 4-NP : NaBH₄ : Au and Pt atoms = 1 : 63.75 : 0.15. The decrease in absorbance at a wavelength of 400 nm was measured over time.



- 1. Signal generator 2. Power amplifier
- 3. Oscilloscope 4. Transducer
- 5. Reaction vessel 6. Z-Stage
- 7. Low temperature circulation bath

Fig. 1 Outline of experimental apparatus.

3. Results and discussion

Fig. 2 (a) and **(b)** show TEM images of the NPs (Pt/Au = 1.00, UFB concentration (a): 0 /mL, (b): 1.85×10^{10} /mL) synthesized in the presence of PF127 (M.W. 12500). The result of EDS confirmed the formation of the Au@Pt core-shell structure. Thus, Au@Pt NPs were successfully synthesized. In the synthesis, [AuCl₄]⁻ was first reduced to Au NPs by ultrasound. Following the formation of Au NPs, the surface of Au NPs was adsorbed on by hydrophobic parts of PF127. Due to the hydrophilic interaction between [PtCl₆]²⁻ and hydrophilic parts of PF127, [PtCl₆]²⁻ was attracted near the surface of Au

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NPs. Then, immediately after the chemical reduction of $[PtCl_6]^{2-}$ to Pt NPs, Pt NPs adsorbed on the Au NP surface, which prevented the aggregation of Pt NPs. On the other hand, in the presence of SDS $(C_{12}H_{25}-SO_3Na, M.W. 288.38)$, Pt NPs aggregated, and Au@Pt NPs were not synthesized. This indicates that $[PtCl_6]^{2-}$ was not attracted near the surface of Au NPs. It could be attributed to either the weak hydrophobicity of SDS, which prevented SDS from adsorbing on the Au NP surface, or the electrostatic repulsion between $[PtCl_6]^{2-}$ and $C_{12}H_{25}-SO_3^{--}$ adsorbed on the Au NP surface.

Comparison of both TEM images (Fig. 2 (a) and (b)) shows that the Pt shell was thickened in the presence of UFBs. Fig. 2 (c) shows the relationship between the UFB concentration and the mean thickness of the Pt shell. At the molar ratios of Pt/Au = 1.00 and 0.33, the Pt shell thickness increased with the UFB concentration. This is because UFBs, whose surface is hydrophobic, provided additional Pt NPs onto the surface of Au NPs during the growth process of the Pt shell. Therefore, it is possible to control the Pt shell thickness and reduce the Pt loading by changing the UFB concentration.

Next, the catalytic activity of Au@Pt NPs for the reduction of 4-NP was evaluated. Fig. 3 shows the temporal change in $\ln (A_t/A_0)$. Here, the absorbances at a wavelength of 400 nm immediately (0 s) and t s after the initiation of the reduction are denoted as A_0 and A_t , respectively. Upon mixing 4-NP aq and NaBH₄ aq, an absorbance peak of 4nitrophenolate (conjugate base of 4-NP) was observed at 400 nm. The reduction of 4-NP to 4aminophenol resulted in the decrease in absorbance at 400 nm and the increase in absorbance at 300 nm. This shows that the reduction behavior of 4-NP can be evaluated from the decrease rate of absorbance at 400 nm. Since the amount of NaBH₄ was excessive compared to that of 4-NP, this reaction followed a pseudo-first-order reaction. Therefore, the rate constant was determined from a slope of $\ln (A_t/A_0)$.

Fig. 4 shows the rate constant of the 4-NP reduction reaction using several Au@Pt NPs as catalysts. The rate constant increased as the Pt/Au molar ratio decreased. Note that in the case of Pt/Au = 0.05, the catalytic activity of Au@Pt NPs synthesized in UFB water was higher than that of Au@Pt NPs synthesized in ultrapure water. This might be due to the decrease in the exposed surface area of Au NPs in the presence of UFBs, since UFBs increased the Pt NP coverage on the surface of Au NPs during the growth of the Pt shell.

References

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Fig. 2 TEM images of Au@Pt NPs synthesized in the presence of PF127 at different UFB concentrations ((a): 0 /mL, (b): 1.85×10^{10} /mL), (c) Relationship between UFB concentration and mean thickness of Pt shell.



Fig. 3 Temporal change in $\ln (A_t/A_0)$.



Fig. 4 Relationship between Pt/Au molar ratio and rate constant.