Analytical TEM study of the core-shell structure of Au-Pd nanoparticles prepared by sonochemical technique

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Abstract. The structure of Au-Pd nanoparticles prepared by the sonochemical method was observed by an analytical TEM. The core (Au)-shell (Pd) structure was confirmed by ADF-STEM images. The ratio of Au and Pd contents was controlled by adjusting the ratio of precursors, and the Pd-shell thickness was also controlled by the ratio of Au and Pd contents. The electron diffraction patterns showed that the lattice constant of the Pd shell is quite larger than that of bulk Pd and rather similar to that of bulk Au even in the systems with larger ratios of Pd, which supports the pseudomorphic growth of the Pd shell on the Au core.

Introduction
Bimetallic nanoparticles are widely used for various catalytic reactions. Recently, it is reported that the Au-Pd bimetallic particles exhibit high catalytic activity for various reactions. For example, Au-Pd particles supported on metal oxides exhibit high activity for the synthesis of hydrogen peroxide from H2 and O2 or the oxidation of alcohols to aldehydes with O2 [1-3]. It was predicted from the result of analytical transmission electron microscopy (TEM) that the bimetallic Au-Pd particles have a Pd–rich surface [3].

Recently, the sonochemical technique is successfully applied to prepare the Au-Pd or Au-Pt bimetallic nanoparticles more efficiently [5-9]. And the Au-Pd core–shell particles exhibited higher catalytic activity for hydrogenation of 4-pentenoic acid in comparison to Au particles or Pd particles alone. The structure of the bimetallic particles depends on the preparation conditions, and the core–shell structure is considered to be formed when the sodium dodecyl sulfate (SDS) is used for surfactant. The detailed structure of the bimetallic core–shell nanoparticles is not yet understood well, because atomic-scale characterization is difficult for the inside of nanoparticles. It is essential to elucidate the detailed atomic and electronic structure of bimetallic Au-Pd nanoparticles in order to understand the catalytic properties. The core-shell structure was confirmed by annular dark field–scanning transmission electron microscopy (ADF-STEM) image and energy dispersive X-ray spectroscopy (EDS) analyses in previous report [10]. The analytical TEM observations suggest the lattice constant of a Pd shell is changing. In this study, Au-Pd nanoparticles with various Au/Pd ratios are prepared in order to control

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the Pd-shell thickness and examine the lattice constant of Pd shells with various thickness by the electron diffraction method.

**Experimental**

Bimetallic Au-Pd particles were prepared by the sonochemical techniques [6,7]. A multi-wave ultrasonic generator with a barium titanate oscillator of 64mm diameter was operated for sonication at 200 kHz with an input power of 200 W. The solutions of NaAuCl$_4$·2H$_2$O and PdCl$_2$·2NaCl·3H$_2$O were used as precursors of Au$^{3+}$ and Pd$^{2+}$ ions, respectively. The Au and Pd contents were adjusted from 0.1 mmol/l to 0.9 mmol/l. The total amount of Au and Pd precursors was fixed to 1 mmol/l in these experiments. The 60 ml aqueous solutions containing Au and Pd ions with an additive of SDS were sonicated in a water bath for 20 min at approximately 293 K [8].

The structure of the Au-Pd particles was observed by the analytical TEM, JEOL JEM-3000F, equipped with EDS, and ADF-STEM systems. The Au-Pd nanoparticles were dispersed on a carbon film supported on Cu-mesh of 3 mm in diameter by dropping the solution including the Au-Pd particles. The EDS analyses were carried out by using Thermo Noran VANTAGE EDS analysis system. The ADF-STEM images were obtained with a collection angle of 65 to 255 mrad with 0.2-0.3 nm electron probe.

**Result and Discussions**

A typical TEM image of prepared Au-Pd nanoparticles with a Au/Pd ratio of 3:7 is presented in figure 1. Bimetallic Au-Pd nanoparticles are successfully prepared by the sonochemical method. The mean diameter is 9-10 nm. The bimetallic Au-Pd nanoparticles have polyhedral shapes with low index facets such as \{111\} or \{100\}. The EDS analyses confirmed that each nanoparticle is really composed of Au and Pd. The amount of residual Na and Cl contained in the Au-Pd nanoparticles is below the detection limit of the EDS analysis. The nanoparticles are stable under electron beam irradiation of 300 kV during the conventional HRTEM observation. No obvious structure changes of the particles are observed during the TEM observation and EDS measurements.

Figure 2a-d shows ADF-STEM images of the Au-Pd particles prepared with Au/Pd ratios of 0.7:0.3, 0.5:0.5, 0.3:0.7, and 0.1:0.9, respectively. The Au-Pd particles are observed as bright contrast in the ADF-STEM images. The weak bright contrast appears around the strong bright contrast in the centre part. This means a Au particle exists as a core and a Pd shell is covering the Au core, because the image intensity depends on the Z-number of the scattering objects in ADF-STEM images [11]. Although Au and Pd form solid solutions for almost all compositions in the phase diagram, the Au core and Pd shell seem to be almost separated because the intensity in the ADF-STEM images is rapidly changing at the interface. Of course, further precise investigation must be carried out to decide whether the Au core contains Pd atoms or not. And the effect of surfactants should be also examined for the details of the core-shell structure.

The Au core and Pd shell are clearly distinguished in the ADF-STEM images, which is difficult in the TEM images formed mainly by diffraction contrast and phase contrast. Thus, the Pd-shell thickness is measured precisely in the ADF-STEM images compared to conventional TEM images.
The mean diameter of the Au-Pd particles is almost constant, and the Pd-shell thickness increases with the increment of the contents of Pd for Au while the Au-core diameter decreases.

Figure 3 shows the relation between the Pd-shell thickness and the mean Pd contents for Au. The mean Pd contents were measured by the EDS analysis for Au-Pd particles with a low magnification containing many particles in a measurement area so as to obtain mean values. The Pd-shell thickness is successfully controlled by the adjustment of the Au/Pd ratio for starting solution. Controlling the Pd thickness is important in order to investigate the effects of the thickness on the catalytic activity associated with the changes of the lattice constant mentioned below.

Figure 4 shows electron diffraction patterns from the Au-Pd, pure Au and pure Pd particles. The electron diffraction pattern of Au particles was obtained from the Au particles deposited on the carbon micro-grid by vacuum deposition and the electron diffraction pattern of Pd was obtained from the aggregates of Pd particles. The all electron diffraction patterns are obtained with the same lens condition of TEM for precise comparison. The differences in the diffraction patterns of pure Au and pure Pd particles caused by the lattice constant difference of about 5% are detectable in this experimental condition. But, there is no diffraction rings corresponding to the diffraction from bulk Pd (pure Pd particles) in the diffraction patterns of Au-Pd particles in figure 4c-f. It seems that the lattice of the Pd shell is expanded and coincides with the lattice spacing of the Au core [12]. The diameter of the diffraction rings shift slightly to a smaller lattice constant for the sample of Au:Pd = 0.1:0.9, but the position of the diffraction rings does not coincide with that of the bulk Pd (pure Pd particles) in spite of the larger ratio of Pd. The mean lattice constants are estimated for Au(0.5):Pd(0.5), Au(0.3):Pd(0.7) and Au(0.1):Au(0.9) samples as 0.408nm, 0.403nm and 0.396nm, respectively, based on the position of (111) ring compared to the lattice constants of Au (a=0.40786nm) and Pd (a=0.389019nm). From these experimental results, it is concluded that the Pd shell pseudomorphically grows on the Au core with the same lattice spacing and gradually relaxes to the lattice spacing of bulk Pd. The lattice space of the Pd shell with 2nm thickness is still deviated from the value of bulk Pd. In the present experiments, the thickness of the Pd shell is successfully controlled, which means the control of the Pd lattice constant. Thus it is interesting to examine the effects of...
both the Pd shell thickness and the lattice constant change on the catalytic properties in near future.

**Conclusion**
The Au-Pd core–shell particles prepared with various Au/Pd ratios were observed by analytical TEM.
1. The thickness of Pd shell was controlled by adjusting the Au and Pd precursor ratio.
2. The results from HRTEM and electron diffraction analyses indicate that the Pd shell pseudomorphically grows on the Au core.

![Electron diffraction patterns of the standard sample of Au (a) and Pd (b) and the Au-Pd particles of the Au/Pd ratio, 0.5:0.5(c), 0.3:0.7(d) and 0.1:0.9(e).](image)

**Figure 4.** Electron diffraction patterns of the standard sample of Au (a) and Pd (b) and the Au-Pd particles of the Au/Pd ratio, 0.5:0.5(c), 0.3:0.7(d) and 0.1:0.9(e).

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