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Properties of Au-Pd Nanoparticles Prepared by Sonochemical Technique

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Binary Au-Pd alloy nanoparticles were prepared by sonochemical reduction of solutions containing noble metal ions. When using SDS as an additive, the prepared Au-Pd nanoparticles exhibited a core-shell structure composed of a Au-core and a Pd-shell. Since core-shell structured Au-Pd nanoparticles were reported to exhibit superior catalytic activity to random alloy Au-Pd particles or pure Pd black, electronic states of Au atoms sitting at the interfaces of sonochemically prepared size-different Au-Pd nanoparticles were examined by ^{197}Au Mössbauer spectroscopy, and the results were compared with those of conventional Au-Pd foils. It was found that the Mössbauer apectra of core-shell structured Au-Pd nanoparticles included a subcomponent with positive isomer shifts which accounted for the Au atoms near the core-shell interfaces.

Key words: sonochemistry, gold-palladium alloy, nanoparticle, core-shell structure, Mössbauer spectroscopy

1. INTRODUCTION

Fine and ultrafine particles have been drawn intense attention as new functional materials because of their peculiar properties that have not been obtained in the bulk materials[1]. Although various methods have been developed to prepare nanoparticles, which are grouped in building-up and breaking-down processes[2], they have different problems such as production costs, preparing times and particle size control, respectively.

It is noteworthy that a sonochemical technique can produce nanoparticles more easily than those methods. Nanoparticles are prepared by sonochemical effects of the ultrasonic irradiation-induced cavitaion. Sonication of solutions yields a specific reaction field divided into three reaction sites; the bubbles, the interfaces and the bulk. Acoustic energies compress or expand the molecular of medium repeatedly, resulting in breaking down of the molecules to create cavitation bubbles. At points where the cavitation bubbles collapse, the extreme conditions are generated; they are high-temperatures of several thousand of degrees and high-pressures up to hundreds of atomosphere. Near the interfaces between the bubbles and the bulk solution, the regions are subjected to marked temperature and pressure gradients[3-6]. In this reaction field, water, surfactant, polyvalent alcohol and other polymeric compounds in the solution are pyrolytically decomposed to produce various reducing radicals, and they are associated with the reduction of ions involved in the solution. Furthermore additives such as surfactant play a role as not only sources of reducing radicals but also protective layers, which prevent particles from aggregating larger to generate nano-scale particles[7-8]. Sonicating aqueous solutions without additives are able to reduce ions only using the water-induced reducing radicals, and then additives were used to increase amounts of reducing radicals in this study. Preparation of bimetallic nanoparticles is also possible. When using solutions with Au and Pd ions, obtained Au-Pd nanoparticles were reported to have the morphology of a core-shell structure composed of Au-core and Pd-shell [9]. It was found that the core-shell structured Au-Pd nanoparticles exhibited superior catalytic activity to conventional Au-Pd alloy particles or commercially available Pd black[10]. This effect is considered to be associated with Au-Pd interfaces of the sonochemically prepared nanoparticles. With the aim of examining electronic states of Au atoms sitting at the core-shell interfaces, size-different Au-Pd nanoparticles prepared by sonochemical reduction and high-frequency induction molten Au-Pd alloys were examined by ^{197}Au Mössbauer spectroscopy.

2. EXPERIMENTAL

A multiwave ultrasonic generator with a barium titanate oscillator of 64mm diameter was operated for sonication at 200kHz with an input power of 4.2W/cm^2. A cyrindrical glass vessel with a silicon rubber septum which allows gas bubbling and sample extraction without exposing the sample to air was used for ultrasound irradiation. The planer bottom of the vessel was 1mm in thickness to prevent loss of the input ultrasonic energy. Aqueous solutions with a given concentration of $NaAuCl_4$ $2H_2O$, $PdCl_2$ 2NaCl $3H_2O$ and sodium dodecyl sulfate (SDS) were argon purged and sealed in glass vessels. They were sonicated in a water bath (about 20°C), and the products were examined by using UV-vis spectra, XRD, TEM, HRTEM and EDX. The obtained nanoparticles were also studied by ^{197}Au Mössbauer spectroscopy. The ^{197}Au Mössbauer source was prepared by thermal neutron irradiation of Pt plates enriched with ^{196}Pt. The measurements were performed at about 8K. For comparison, Au_3Pd, AuPd and $AuPd_3$ alloys were made by high-frequency induction melting. The alloys were cold-rolled, and the thin foils were also examined by ^{197}Au Mössbauer spectroscopy.

3. RESULTS AND DISCUSSION

Table I summarizes the sample preparation conditions of the present experiments.

The color of the solution turned from pale yellow of Au and Pd ions to reddish-violet indicating the formation of Au nanoparticles, finally to dark brown originated from Pd nanoparticles. Correspondingly the absorption of about 313nm coming from Au and Pd ions before irradiation gradually disappeared with sonication, then the surface plasmon absorption of Au nanoparticles (around 530nm) arose and followed by that of Pd nanoparticles and eventually the Au peak was hidden, as shown in Fig.1. This UV-vis absorption spectra indicate that this reaction is successive; Pd ions are begun to be reduced after reduction of Au ions is completed with the duration of sonication. The final disappearance of the surface plasmon absorption of Au nanoparticles suggests that the surfaces of preformed Au nanoparticles are coated by Pd, resulting in the formation of Au cores and Pd shells.

Table I Summary of sample preparation conditions.

	(a)	(b)	(c)	(d)
Au^{3+}	0.5mM	0.5mM	0.25mM	0.25mM
Pd^{2+}	0.5mM	0.5mM	0.25mM	0.25mM
SDS	8mM	12mM	8mM	12mM
Irradiation time	20min	21min	11min	12min

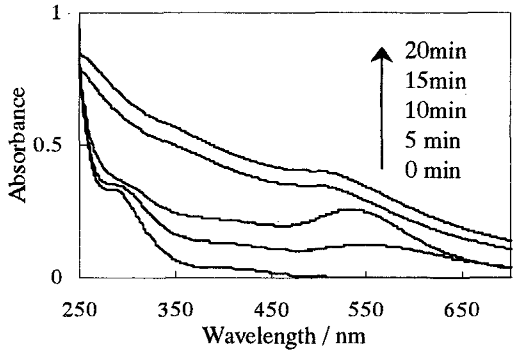

Fig.1 Absorption spectra change with irradiation times for the solution containing Au^{3+}:0.5mM , Pd^{2+}: 0.5mM and SDS 8mM. Cell length: 1cm.

Fig.2 shows an XRD pattern of Au-Pd nanoparticles. This spectrum seems to indicate the existence of Au diffraction peaks which shift only slightly to a high angle side, in addition to small peaks of an adhesive material used to attach the nanoparticles to the sample holder. Therefore, it is suggested that the prepared Au-Pd nanoparticles are not random alloys, because the diffraction peaks should appear between the Au and Pd peaks in this case[11]. Taking into consideration of the results of UV-vis spectroscopy that the initial Au peak gradually disappeares and the Pd peak emerges subsequently with sonication, the reason why no clear Pd peaks are observed could be due to thinness of the Pd layer. Accordingly it is considered that the XRD measurement supports the possibility of the core-shell structure of the particles.

TEM and HRTEM micrographs of Au-Pd nanoparticles are shown in Fig.3 (a) and (b), respectively. It was confirmed that the nanoparticles have spherical shapes with a nearly monodispersion, and the morphology is a core-shell structure with a Au-core and

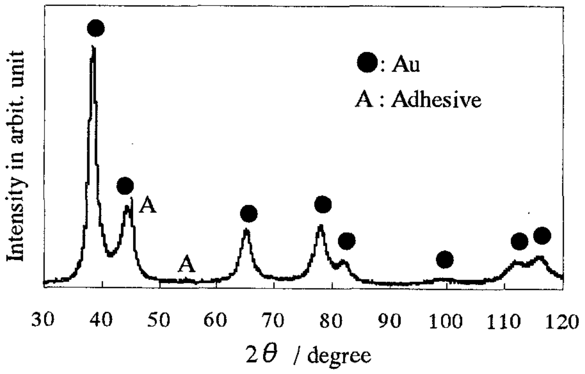

Fig.2 XRD pattern of sonochemically prepared Au-Pd nanoparticles.

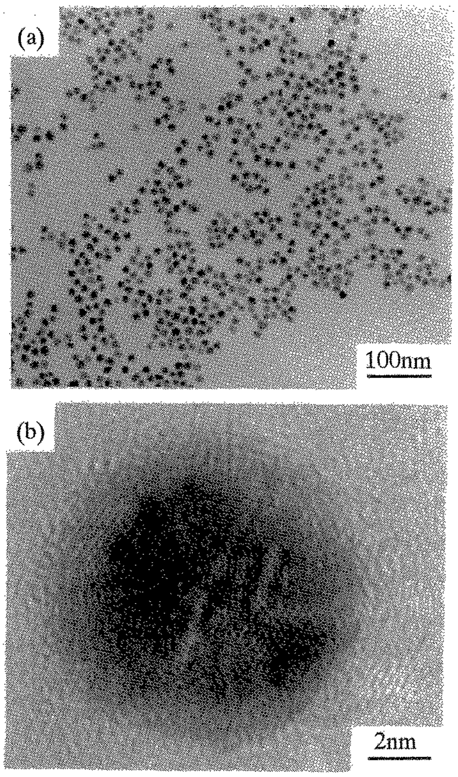

Fig.3 Electron micrographs of sonochemically prepared bimetallic Au-Pd nanoparticles, (a) TEM and (b) HRTEM.

a Pd-shell. The widths of Au-core and Pd-shell determined by HRTEM images were in good agreement with calculated values based on the ratio of Au to Pd concentrations is unity. It was confirmed that all the nanoparticles have the identical core-shell structures.

In Fig.4 is shown the results that the nanoparticles prepared by various sonochemical reduction conditions have narrow size distributions, and the average particle diameters are decreased by 18% or 16% with increasing SDS concentrations or decreasing initial noble metal concentrations, respectively. The former effect is considered to be protection effect of SDS.

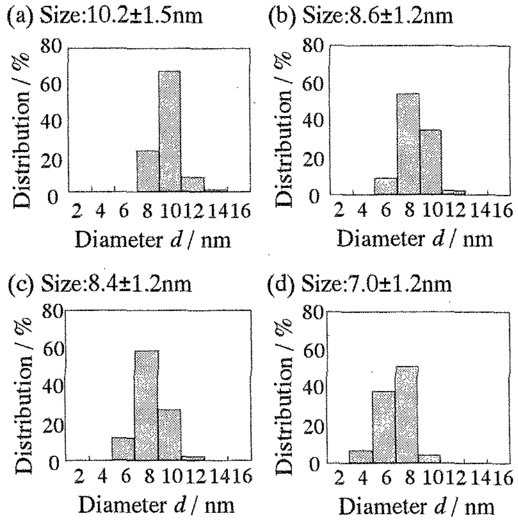

Fig.4 Size distributions of AuPd nanoparticles prepared by ultrasound irradiation. The symbols correspond to that of Table I.

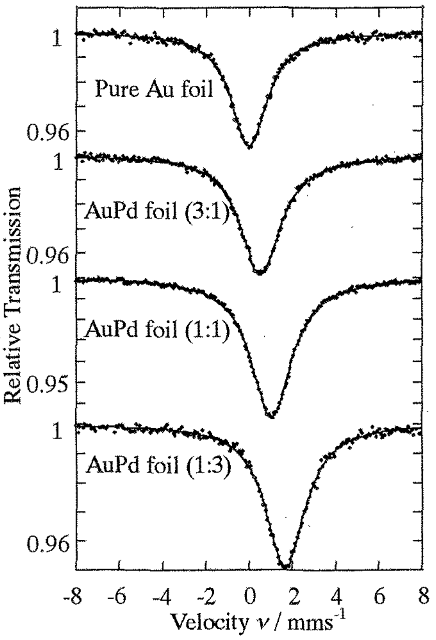

Fig.5 ^{197}Au Mössbauer spectra of AuPd alloy foils.

Fig.5 shows the ^{197}Au Mössbauer spectra of Au-Pd alloy foils. The absorption peaks shift to the positive velocity side as Pd concentrations increase. It is found from the Mössbauer spectra of the core-shell structured Au-Pd nanoparticles of Fig.6 that a subcomponent with a positive isomer shift appears. Because of the HRTEM results that no other structured nanoparticles coexisted, the Mössbauer spectra are considered to reflect the structure of the core-shell structured nanoparticles. Therefore the positive isomer shift of Fig.6 may be concluded to be associated with the Au atoms near the core-shell interfaces. The observed isomer shifts of the spectra of the AuPd alloy foils, and the isomer shifts and the area ratios of the subspectra of the AuPd nanoparticles are listed in Table II. Assuming that only Au atoms of one interface layer of the core-shell structure are affected by Pd atoms, the area ratio is calculated to be about 10 and a few %. However, the observed ratios (about 20~30%) were considerably larger than the calculated value. Hence it was considered that several layers of Au atoms of the interfaces interact with Pd atoms between Au-core and Pd-shell, which might hold the key of high catalytic activity in core-shell structured Au-Pd nanoparticles.

Table II Summarized results of ^{197}Au Mössbauer spectroscopy for the AuPd foils and the AuPd nanoparticles.

Spectra of AuPd foil		Subspectra of AuPd nanoparticle		
Au:Pd	Isomer shift / mms^{-1}	$Au^{3+}/Pd^{2+}/SDS$ (mM)	Isomer shift / mms^{-1}	Area ratio / %
3:1	0.539	0.5/0.5/8	0.861	30.0
1:1	1.037	0.5/0.5/12	0.839	21.9
1:3	1.659	0.25/0.25/12	0.709	28.2

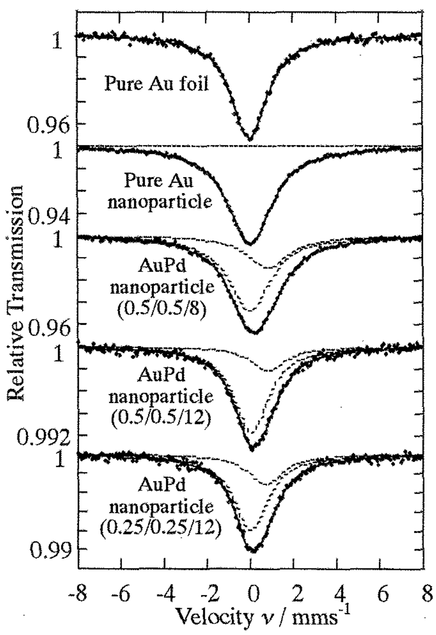

Fig.6 ^{197}Au Mössbauer spectra of Au and AuPd nanoparticles prepared by sonication.

4. SUMMARY

Sonochemically prepared core-shell structured Au-Pd nanoparticles exhibit narrow size distributions. The particle sizes were reduced by increasing SDS concentration or decreasing initial noble metal concentrations. The ^{197}Au Mössbauer spectra of Au-Pd foils shifted to the positive velocity side as Pd concentration increased, and the subscomponent with positive isomer shifts of core-shell structured Au-Pd nanoparticles were considered to be associated with Au atoms at the core-shell interfaces. Provided that Au atoms of a single layer of the Au core are influenced by the adjoining Pd shell, the observed area ratios of the subpeaks to the main peaks are larger than calculated one. Accordingly, it is considered that there exists several layers of Au atoms interacting with Pd atoms between the Au-core and the Pd-shell.

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