

ESR Study on Palladium Nanoparticles

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ESR study on monodispersed palladium nanoparticles with the mean diameters of 25 Å corresponding to the “magic atom number” of 561 atoms (five-shell nanoparticle) and smaller than 25 Å (22 and 23 Å) was carried out to investigate their electronic structures. Two broad absorption peaks corresponding to $\Delta S = 1$ and 2 and a sharp one with $\Delta S = 1$ were observed in the ESR spectra of palladium nanoparticles. The broad and strongest spectrum with $\Delta S = 1$ may arise from the spin on the large orbital moment state of the nanoparticles. The relatively strong second harmonic spectrum with $\Delta S = 2$ is characteristic of the nanoparticles, and its low-field shift compared with bulk palladium implies the existence of the effective field from the orbital moment of the electron. On the other hand, the sharp ESR signal with $\Delta S = 1$ may be derived from the nanoparticles that have the electronic structure with one s-state electron outside the closed electron shell core with the “magic atom number”.

Introduction

The properties of metallic nanoparticles is different from those of metal in bulk.^{1,2} It was found from vigorous mass studies on metallic nanoparticles that the binding energies of metallic particles consisting of less than 1000 atoms varied periodically due to the quantum size effect,³ so it was clarified that the metallic nanoparticles were not just aggregates of metallic atoms. Recently, Volokitin et al. clarified that the quantum size effects strongly influenced the thermodynamic properties of metallic nanoparticles.⁴ Therefore, elucidating the electronic structures of metallic nanoparticles is very attractive to scientists. Under these circumstances, ESR study on metallic nanoparticles, which can reveal their electronic structure much more directly than the other methods such as NMR, has been required.⁵ The development of the preparative method to obtain enough amount of the monodispersed metallic nanoparticles is essential for the observation of the ESR signal. Many researchers have developed the synthetic methods of monodispersed metal nanoparticles in the presence of linear polymer,^{6–11} ligand,^{12–15} and so on.^{16–19} Recently, we successfully synthesized the monodispersed palladium nanoparticles²⁰ as well as the platinum particles²¹ in our systematic research. In this communication, taking the periodical change of the binding energies of palladium nanoparticles into consideration, ESR experiments of the palladium nanoparticles with 10–30 Å in diameter were carried out. Here, we discuss the difference in the electronic structures between the 25 Å five-shell palladium nanoparticles corresponding to the “magic atom number” of 561 atoms and those smaller than 25 Å.

Synthesis and Characterization

Homogeneous colloidal dispersions of palladium nanoparticles were synthesized by alcohol reduction of 10 μmol of $\text{H}_2\text{-PdCl}_4$ in 50 mL of ethanol/water mixed solvent in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP, average molecular weight 40 000) under air.^{6–8,22} The preparative conditions are shown in Table 1. The dispersions of palladium nanoparticles protected

TABLE 1: Preparative Conditions of PVP-Protected Palladium Nanoparticles

sample	H_2PdCl_4 (μmol)	PVP ^a (μmol)	EtOH (mL)	H_2O (mL)	[Pd] (wt %)
1	10	200	20	30	4.6
2	10	100	15	35	8.7
3	10	100	10	40	8.7

^a Calculated as a monomeric unit.

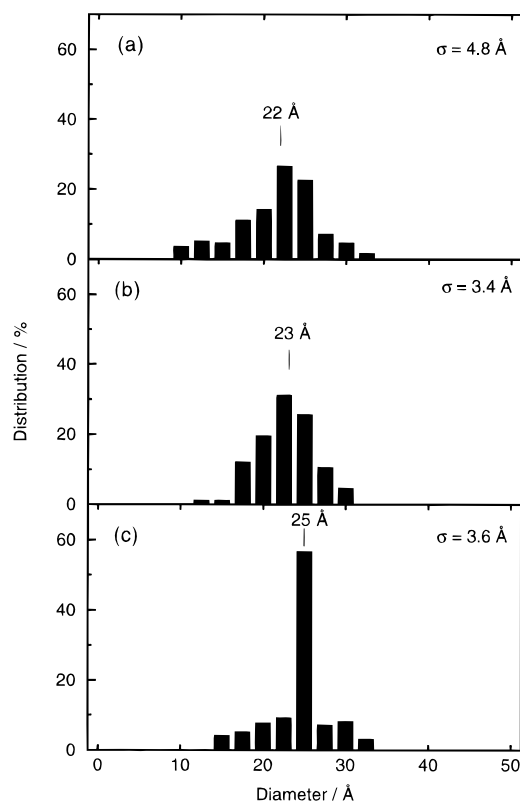


Figure 1. Size distributions of monodispersed palladium nanoparticles protected by PVP. (a) PVP/Pd = 20, EtOH/ H_2O = 2/3, (b) PVP/Pd = 10, EtOH/ H_2O = 3/7, (c) PVP/Pd = 10, EtOH/ H_2O = 1/4.

by PVP (abbreviated as PVP-Pd) have brown color and are stable for months at room temperature. The formation of

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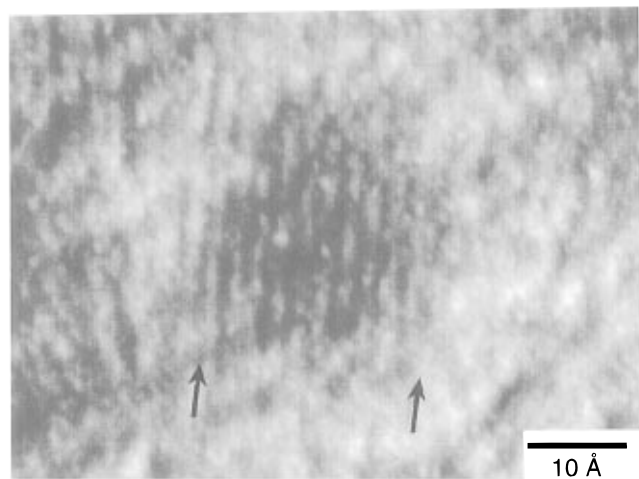


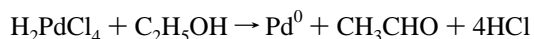
Figure 2. HRTEM image of 25 Å five-shell palladium nanoparticles with fcc structure.

palladium nanoparticles was confirmed by the electronic spectra and the TEM photographs. Figure 1 presents the size distributions of PVP-Pd together with the mean diameters and standard deviations. We obtained the PVP-Pd smaller than 25 Å, i.e., 22 and 23 Å, in mean diameter with similar size distribution (Figure 1a,b) and those of 25 Å in mean diameter with extremely narrow distribution (Figure 1c). The latter corresponds to so-called "magic atom number" of 561 atoms, i.e., five-shell nanoparticles.^{13,14,23} On the other hand, it is difficult to synthesize the nanoparticles consisting of non-magic atom number with very narrow distribution, probably because they do not exist so stably in the synthetic process. In our systematic research on the size control of Pd nanoparticles,²⁰ which involves numerous control experiments by changing the amount of PVP and the concentration and/or kind of alcohol, we obtained 22 and 23 Å PVP-Pd nanoparticles of non-magic atom number with narrow distribution, which have enough content of palladium to obtain sensitively the ESR signal and have standard deviation smaller than 5 Å. Therefore, these three samples employed here are most adequate to the ESR measurement so far. It was found from the HRTEM images that all the palladium nanoparticles showed the lattice images, indicating that they are single crystals. Figure 2 shows the HRTEM image of 25 Å five-shell PVP-Pd, in which 11 {111} layers can be observed. The electron beam diffraction and XRD investigations indicate the fcc structures of PVP-Pd nanoparticles. The colloidal dispersions of PVP-Pd were evaporated, redispersed in ethanol, precipitated with

diethyl ether, filtered, and dried in vacuum at 90 °C to obtain the PVP-Pd powders, which were stored under nitrogen. According to the measurement by SQUID magnetometer, the magnetic moment per one Pd atom in these sample is 0.014 μ_B . Such a small value shows that the moment arises from the magnetic polarization of the conduction electron in nanoparticles.

ESR Analysis

Figure 3 shows the ESR spectra of these samples. Two broad absorption peaks and one very sharp peak are found on the quite broad back ground. The PVP-Pd nanoparticles were synthesized by using ultrapure water (18.8 M Ω ·cm) free from the 3d metal ions such as Fe³⁺ responsible for the ESR signals. The precursor, H₂PdCl₄, was completely reduced, and HCl generated by the following formula was removed by washing the sample with diethyl ether, which was confirmed by XPS measurement.



The organic solvents, such as ethanol and acetaldehyde generated by the oxidation of ethanol, should be completely removed by drying the sample under vacuum at 90 °C for 1 day. Therefore, three peaks in Figure 3 substantially arise from the palladium nanoparticles. The background signal of the integral curves depends on the amount of H₂O in the sample, which makes us believe that the signal arises from the dielectric dispersion effect of the H₂O molecules contained in PVP. The relatively broad ones have two spectral positions corresponding to $\Delta S = 1$ and 2, respectively. The *g*-values of the signal with $\Delta S = 1$ and $\Delta S = 2$ are 1.97 and 2.06, respectively. The *g*-value of a sharp one with $\Delta S = 1$ is 1.93. The particle distribution of each sample reflects on the width of the broad ESR signal with $\Delta S = 1$. The absorption intensity of higher harmonic position is anomalously strong in comparison with the bulk samples. The similar result was also reported in Au nanoparticles.²⁴ Then, the relatively strong second harmonic spectra are considered to be the common characteristics in nanoparticles.

In Figure 3a,b, very sharp spectra with the width of 0.7 mT are found at 340 mT, which corresponds to the position at *g* = 2.00. The result shows that the sharp resonance arises from the pure spins on the orbital singlet state of nanoparticles. The sharp line, however, is quite weak for the sample of 25 Å, as is seen in Figure 3c. Because the magic atom number corresponds to the closed electron shell or spin singlet state, ESR absorption

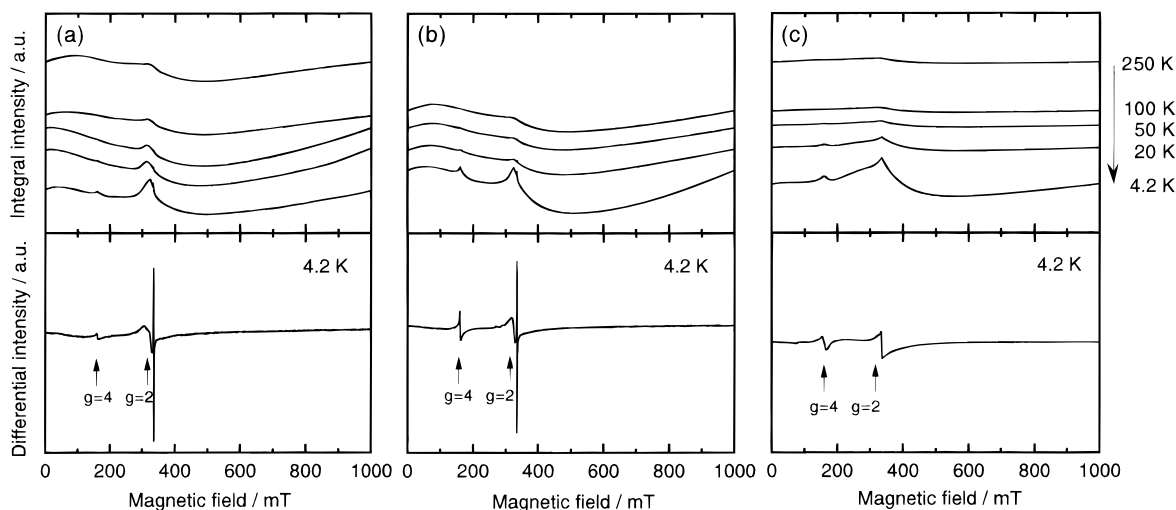


Figure 3. ESR spectra of PVP-protected palladium nanoparticles with diameters of (a) 22 Å, (b) 23 Å, and (c) 25 Å.

is not expected. Then, the broad ESR signal found in Figure 3c arises from the particles with the size except 25 Å, and the sharp spectrum may be masked by the ESR signal from the broadly distributed particles of the other sizes. In fact, the sharp spectrum could not be clearly observed in the broadly distributed samples prepared elsewhere.²⁰ One possible candidate of the sharp line is the ESR signal from the nanoparticles that have the electronic structures with one s-state electron outside the closed electron shell core with magic atom number.

The absorption peak corresponding to the second harmonics with $\Delta S = 2$ shows remarkably low field shift from the half-field position of the main peak. As is well-known in the ESR theory, the spectral shift is made from the spin-orbit coupling. The low-field shift means the existence of the effective field from the orbital moment of the electron and the broad main spectra arise from the spin on the large orbital moment state of nanoparticles. The details for the state, however, have not been known so far. In order to investigate the details of the state, other microscopic magnetic experiments such as MAFM measurement are required.

In addition, the magnetic property of palladium is also very attractive because it does not polarize magnetically in the bulk metallic state, but it has a so called "giant magnetic moment" in the presence of 3d transition metal impurity, such as Fe or Ni.²⁵⁻²⁷ The region of the giant moment polarization around the impurity is considered to be about 10 Å.²⁸ The present study will lead us to the next research on the "giant magnetic moment" of palladium nanoparticles in the presence of Fe or Ni.

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