

Novel Synthesis of Monodispersed Pd/Ni Nanoparticles

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Pd is an attractive element from the viewpoint of magnetism, because Pd does not polarize magnetically in bulk metal, but has a giant magnetic moment in the presence of a small amount of a ferromagnetic 3d transition metal. The appearance of the giant magnetic moment was first found by the measurements of paramagnetic susceptibility and ferromagnetic saturation magnetization.^{1–3} For example, 1 mol % of Fe induces a strong polarization of Pd in a Pd/Fe alloy, resulting in a giant magnetic moment of $\sim 10 \mu_B$ per Fe atom⁴ and the polarized region of $\sim 10 \text{ \AA}$ around the Fe atom.⁵ This magnetic enhancement can be investigated in detail by using nanoscopic materials. The nanoscale metal particles, so-called nanoparticles, show the quantum size effect, derived from the dramatic reduction of free electrons,⁶ which causes their new magnetic, electronic, optical, and thermal properties.^{7–10} In particular, the preparative methods of nanoparticles and thin layers for 4d metals, mainly Pd, and their magnetic properties have been vigorously investigated during the past decade.^{10–17} In contrast, research on the Pd/3d transition metal alloy nanoparticles is just beginning. The Pd/Fe,¹⁸ Pd/Ni,^{19,20} and Pd/Cu^{21–23} alloy particles have been prepared by the conventional gas evaporation method,¹⁸ the sol–gel method,¹⁹ the simultaneous alcohol reduction of the corresponding metal salts in the presence of

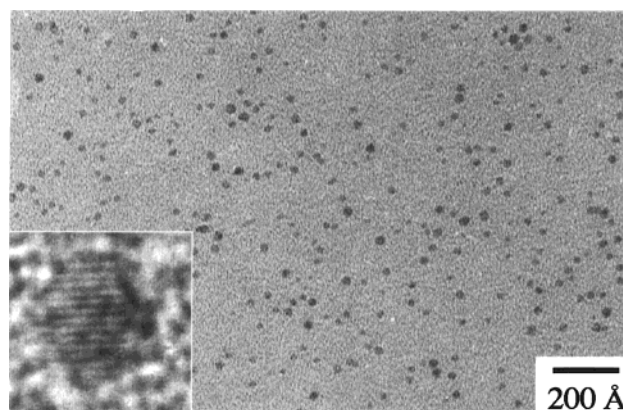


Figure 1. TEM and HRTEM (inset) images of 25 Å PVP–Pd nanoparticles.

the linear polymer,^{20–22} and the decomposition of metal salts.²³ For an accurate measurement of the giant magnetic moment induced on the Pd atoms by the 3d metal impurities, it is important to prepare the particles with an equal size to a series of the Pd/3d metal nanoparticles of various compositions, although this is quite difficult to achieve with previously reported techniques. We recently developed a stepwise growth reaction to obtain the Pd and Pt nanoparticles with larger sizes and narrow size distributions, which cannot be established in a one-step reaction.²⁴ In this communication, we describe a novel synthetic method of a series of the monodispersed Pd/Ni nanoparticles of the similar size by adopting a stepwise growth technique to the monodispersed Pd nanoparticles of 25 Å in mean diameter. The structures and electronic features of a series of Pd/Ni nanoparticles are clarified by XRD and XPS measurements.

The monodispersed Pd nanoparticles of 25 Å in size were prepared as described previously.^{24a} The mixture of 80 mL of 2.0 mM H_2PdCl_4 aqueous solution (160 μmol), 560 mL of water, 160 mL of ethanol, and 178 mg of poly(*N*-vinyl-2-pyrrolidone) (PVP ($M_w = 40\,000$), 1.60 mmol as a monomeric unit) was refluxed in a 1000-mL flask for 3 h under air to synthesize the homogeneous colloidal dispersion of PVP-protected Pd nanoparticles (PVP–Pd), whose TEM and HRTEM images are shown in Figure 1. The 25 Å in diameter Pd nanoparticles correspond to the “magic number” of 561 atoms with a 5-shell structure. After the solvent was evaporated, the PVP–Pd nanoparticles were redissolved in 200 mL of

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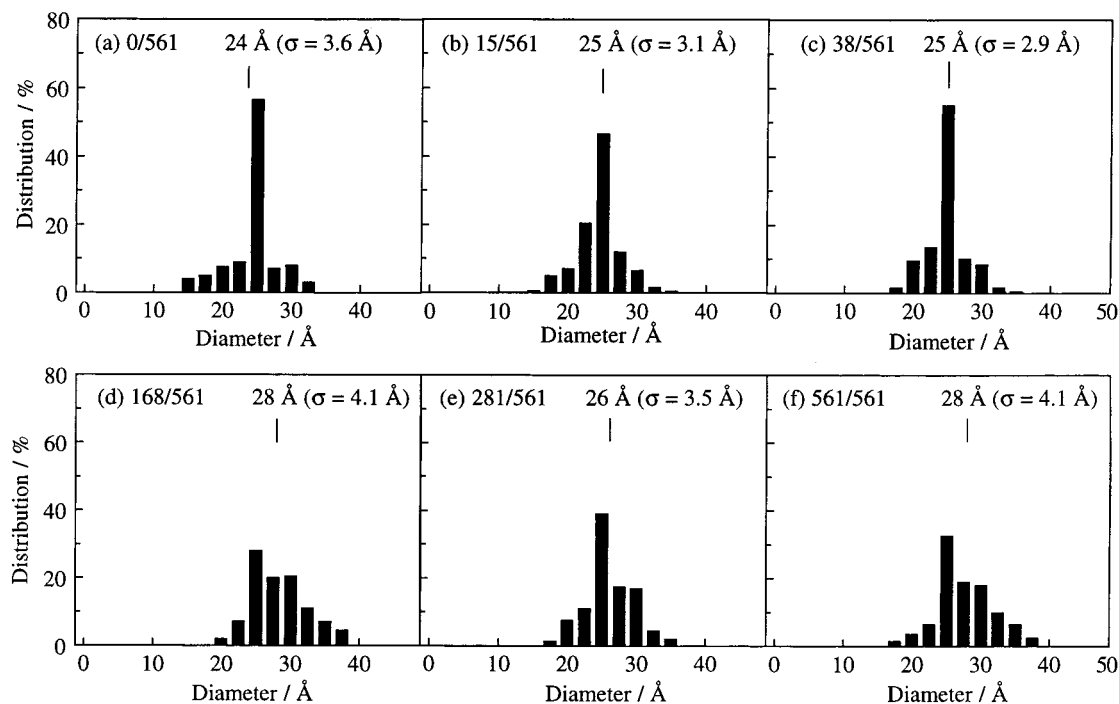


Figure 2. Size distributions of the PVP-Pd and a series of PVP-Pd/Ni nanoparticles. Ni/Pd = (a) 0/561, (b) 15/561, (c) 38/561, (d) 168/561, (e) 281/561, and (f) 561/561.

1-propanol, followed by adding the prescribed amount of $(\text{CH}_3\text{COO})_2\text{Ni}\cdot 4\text{H}_2\text{O}$ to the solution. The molar ratios of $(\text{CH}_3\text{COO})_2\text{Ni}\cdot 4\text{H}_2\text{O}$ to H_2PdCl_4 employed here were 1/561, 2/561, 10/561, 15/561, 38/561, 168/561, 281/561, and 561/561. The mixed solution was degassed by the conventional freezing and thawing technique three times, and then refluxed for 3 h under nitrogen to synthesize Pd/Ni nanoparticles protected by PVP (PVP-Pd/Ni). The black precipitate was produced by adding 100 mL of degassed diethyl ether to the resulting solution, which was concentrated to ~ 20 mL, and then dried under vacuum for 12 h to obtain the PVP-Pd/Ni powder.

The UV-vis spectrum of the mixed solution containing Ni^{2+} ions and PVP-Pd was measured. After refluxing the solution, the absorption of the broad tailing peak from the ultraviolet to visible region increased, implying that Ni^{2+} ions were reduced to Ni^0 atoms to form the nanoparticles with the band structure. Such an increase in the UV-vis spectra was not observed without PVP-Pd, indicating that the Pd nanoparticles catalyzed the reduction of Ni^{2+} ions with 1-propanol. In preparing the bimetallic Pd/Cu nanoparticles by reducing the acetates of palladium and copper in a reducing alcohol solvent, Bradley et al. pointed out that the Cu^{2+} ions would be expected to be reduced at the surface of the growing Pd particle.^{22c} Moreover, the bimetallic Pd/Ni nanoparticles with 1–2 nm in size was successfully prepared by using a polyol reduction method by Toshima et al.,²⁰ although the generation of monometallic Ni nanoparticles has been proven to be very difficult, which suggests that the reduction of Ni^{2+} proceeds at the surface of the Pd particle. So, in our case, the Ni^{2+} ions are thought to be reduced at the surface of the Pd nanoparticles, presumably on the most catalytically active {111} surfaces,²⁵

and then deposited on the particle surface due to the formation of the strong metallic bond. The ICP measurement indicated that few Ni ions were left unreduced in 1-propanol. The selected-area HRTEM-EDX analysis of two kinds of PVP-Pd/Ni nanoparticles (Ni/Pd feed ratios = 168/561 and 281/561) showed that the Ni/Pd molar ratios coincided with the feed ones (169/561 and 299/561). Therefore, we concluded that almost all the charged Ni^{2+} ions were reduced to Ni^0 atoms and deposited on the surface of the Pd nanoparticles. Figure 2 shows the size distributions of the PVP-Pd and a series of PVP-Pd/Ni, which were estimated by counting 200 particles with a loupe from the TEM images of 400 000 magnifications. The size distributions and mean diameters of PVP-Pd/Ni (Ni/Pd < 38/561) are very similar to those of PVP-Pd, indicating that the size of Pd nanoparticles was maintained by PVP in 1-propanol under reflux and that the Ni atoms were uniformly deposited on every PVP-Pd nanoparticle. When the ratio of Ni/Pd was increased over 168/561, the nanoparticles with the increased size to ~ 30 Å were produced. There exists 362 surface atoms in 6-shell nanoparticles consisting of 923 atoms, whose diameter is 30 Å. The Pd/Ni nanoparticles prepared at the Ni/Pd molar ratios of 168/561–561/561 are thought to consist of 0.5–1.5 Ni atomic layers on the Pd nanoparticles, corresponding to the particle sizes of 27.5–32.5 Å, which is compatible with the experimental results.

The analysis of the giant magnetic moment of the Pd/Ni nanoparticles obtained here has already been reported elsewhere.²⁶ In the magnetization measurements

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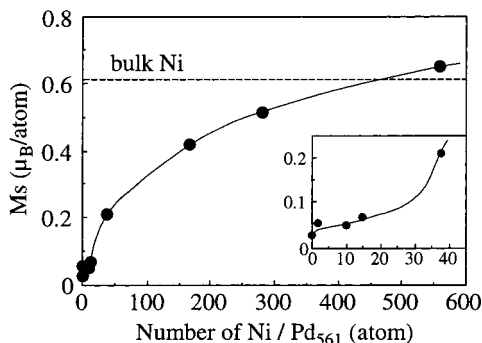


Figure 3. Saturation magnetization of a series of Pd/Ni nanoparticles. The dashed line shows a saturation magnetization of bulk Ni.

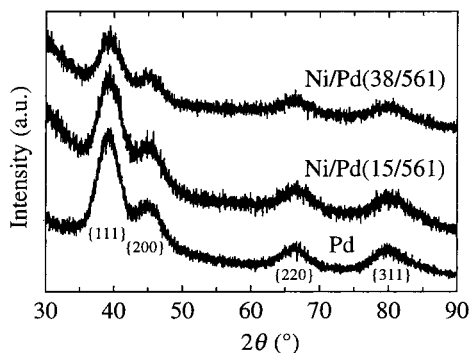


Figure 4. XRD patterns of the PVP-Pd and PVP-Pd/Ni (Ni/Pd = 15/561, 38/561) nanoparticles.

of a series of Pd/Ni nanoparticles, the remarkable threshold of the enhancement on the magnetic moment is observed at Ni/Pd = 38/561, and a large enhancement of the magnetic moment corresponding to a giant magnetic moment effect is found above this threshold, as shown in Figure 3. So we concentrated upon the XRD and XPS measurements of the PVP-Pd and PVP-Pd/Ni (Ni/Pd = 15/561, 38/561) to clarify the structures and electronic structures, respectively. The XRD patterns of these nanoparticles are presented in Figure 4. The diffraction angles of each pattern demonstrated the face centered cubic structures of the Pd cores in PVP-Pd and PVP-Pd/Ni nanoparticles, and the unchanged half-widths of the {111} peaks mean the similar sizes of these particles. In general, an alloy consisting of two kinds of metals shows the diffraction peaks between those of two pure metals.²⁰ However, the diffraction angle for {111} plane of the PVP-Pd (39.220°) is not shifted toward that for {111} plane of Ni (44.505°)²⁷ by depositing the Ni atoms, suggesting that the Pd cores are covered with the Ni atoms, and both elements are not mixed on an atomic level. Figure 5 shows the XPS

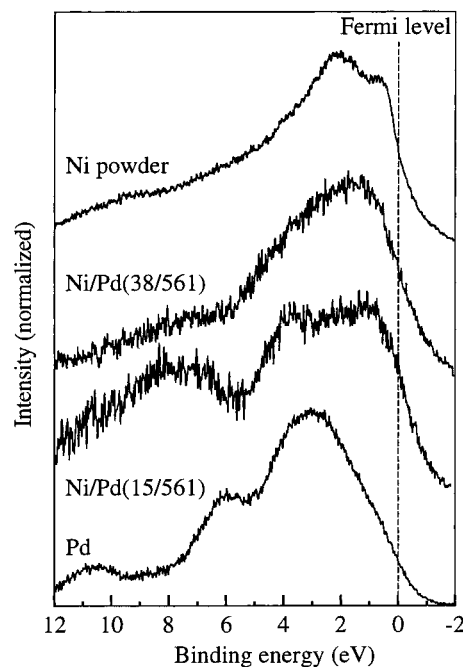


Figure 5. XPS spectra near the Fermi level of the PVP-Pd, PVP-Pd/Ni (Ni/Pd = 15/561, 38/561) nanoparticles, and bulk Ni powder. The broken line indicates Fermi level.

spectra near the Fermi level of the PVP-Pd, PVP-Pd/Ni (Ni/Pd = 15/561, 38/561), and bulk Ni powder. The spectra of the nanoparticles become close to the spectral profile of bulk Ni, as the amount of the deposited Ni increases. The change in the XPS spectrum near the Fermi level, i.e., the density of states, may be related to the variation of the band or molecular orbit structure. Therefore, the band structures of the Pd/Ni nanoparticles at Ni/Pd > 38/561 are close to that of the bulk Ni. The appearance of the giant magnetic moment induced on the Pd nanoparticles by the Ni impurity is considered to be closely related to the change in the band structure of the Pd/Ni nanoparticles.

In conclusion, we have demonstrated a novel method for the synthesis of the Ni-covered Pd nanoparticles of various compositions. These materials are suitable for an elucidation of the giant magnetic moment of the Pd/3d metal system, because they have the Pd cores of an equal size covered with the different amounts of Ni. Investigations on the giant magnetic moment of Pd/Co and Pd/Fe nanoparticles are in progress to develop the theoretical understanding.

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