Magnetic properties of the noble metal nanoparticles protected by polymer

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Abstract

Platinum metal nanoparticles having diameter ranging from 2.3 to 3.8 nm with quite narrow diameter distribution have been synthesized by chemical reaction method and their diameter dependences of the magnetizations were measured. Pt nanoparticles having the diameter below 3.8 nm exhibited superparamagnetic behavior in the magnetization process and enhanced magnetization was observed compared to the paramagnetic moments in the bulk state. With decreasing the diameter, the magnetic moment increases and reaches 5.0 μ_B / Pt-particle at 2.3 nm.

Key words: nanoparticles ; chemical synthesis ; superparamagnetism ; quantum size effect

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Metallic nanoparticles or clusters have been recently fascinating many physicists, chemists and engineers in respect to the practical application for the next generation devices such as single electron transistor as well as their fundamental physical problems [1]. The size of the particle is smaller, the splitting of energy levels is larger and the so-called quantum size effect (QSE) dominates in the properties of these systems at low temperatures. In this regime, the material properties differ considerably from those in the bulk state. In the past decade, metallic nanoparticles stabilized by chemical materials were extensively studied. For these samples, remarkable reduction of the magnetic susceptibility and deviation of the specific heat from the bulk dependence with the decrease of the diameter have been observed experimentally [2]. Recently, chemical size adjustment method for Pt nanoparticles was developed [3]. This method ensures the generation of the metal nanoparticles having a quite sharp diameter distribution. In this study, we have performed systematical investigation of the diameter dependence of the magnetic properties using these well-characterized nanoparticle samples.

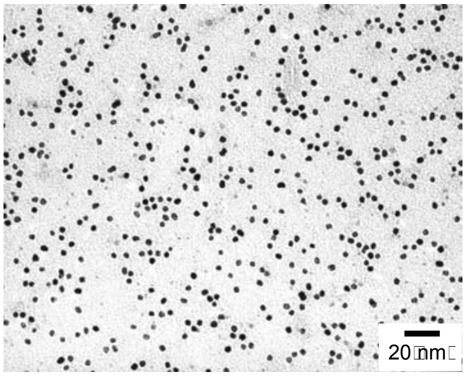

Fig. 1. TEM image for PVP-Pt nanoparticles with mean diameter of 3.8 nm. The scale is indicated in the photograph.

Pt nanoparticles protected by poly-N-vinyl-2-pyrrolidone (PVP) samples (abbreviated as PVP-Pt) are synthesized by methanol reduction of Hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) in the presence of PVP. The matrix polymer prevents from further aggregation and the oxidation of the Pt nanoparticles. The details of the sample preparation technique and growth mechanism are described in Ref.

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[3]. Fig. 1 shows the transmission electron microscopy (TEM, Hitachi H-7100) image of the PVP-Pt as a typical example. Size distribution histograms of the particles were obtained by counting 200 particles from the TEM image. The mean diameter and standard deviation of the diameter of four samples used in this work were 2.3 ± 0.3, 2.6 ± 0.5, 3.0 ± 0.4 and 3.8 ± 0.4 nm. Magnetization measurements for Pt nanoparticles were performed using commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-2) at temperatures ranging from 1.8 to 300 K and in magnetic fields up to 5.5 T. The diamagnetic component arising from coating polymer and sample holder was subtracted by measuring the polymer PVP separately.

Fig. 2 shows the field dependence of the magnetization for PVP-Pt nanoparticles with the mean diameter of 2.3, 2.6, 3.0 and 3.8 nm measured at 1.8 K. The observed curves almost follow the classical superparamagnetic process contrary to the bulk paramagnetism of Pt shown as dotted line in the same figure. The inverse magnetic susceptibility versus temperature shows a linear behavior below 50 K and the curve intersects the origin, although a slight deviation is found above 50 K. Furthermore, temperature dependence of the magnetization in both the zero field cooling and field cooling condition coincides with each other, suggesting that the interactions between each particle are negligible. Therefore, we assume that the individual particles have ferromagnetic spins and the model of superparamagnetism is employed for the analysis.

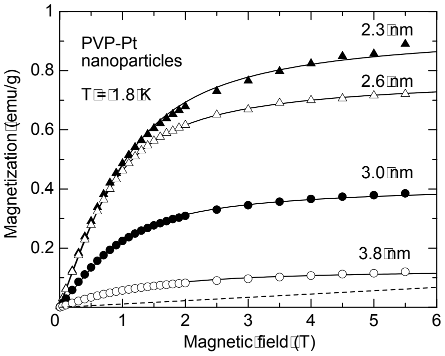

Fig. 2. Magnetic field dependence of magnetization at 1.8 K for PVP-Pt nanoparticles with mean diameter of 2.3, 2.6, 3.0 and 3.8 nm. The solid lines represent the fitting curves of Langevin function. The broken line represents the magnetization process of the bulk Pt metal.

The saturation magnetization was estimated by fitting the classical Langevin function. The magnetic moments per particle were estimated to be 5.0, 6.3, 5.4 and 3.9 μ_B for the diameter of 2.3, 2.6, 3.0 and 3.8 nm samples, respectively. These relatively large moments deny the possibility of observation of the even/odd particle number effect because the latter produces at most 1 μ_B change per particle. The saturation magnetization decreases rapidly with the increase of diameter. The magnetization curves seem to approach to that of the Pt bulk metal as the diameter increases.

These experimental results imply the occurrence of the ferromagnetic polarization in Pt nanoparticles. However, one might attribute it to the spin polarization of the surface of these nanoparticles because it has been predicted theoretically that the ferromagnetic or antiferromagnetic spin polarization takes place in transition metals with reduced dimension such as clusters or thin films. In the case of nanoparticles we studied here, the number of the atoms on the surface is comparable to that exists in the core, so that the effect of surface should be considerable. On the other hand, the polymer as an agent of the stabilization of the nanoparticles also interacts with the surfaces of the nanoparticles. The ligand molecule with large affinity to the metal is likely to diminish the magnetic moment at the surface of the nanoparticles [4]. In order to investigate the role of the surface on the magnetic polarization, we have also carried out the electron spin resonance (ESR) measurement on Au, Pd, and Pd/Ni nanoparticles [5]. The main absorption line consists of two lines, which can be indexed to the signal from core and surface of the nanoparticles and the intensity ratio of the signals between the surface and the inside core is almost unity. Preliminary ESR result for PVP-Pt also shows similar characteristic absorption lines. These experimental results indicate that the magnetization of the surface is approximately same with the magnetization produced in the inside of the particles. It is suggested that the surface magnetism model in nanoparticles is not so reasonable and other novel spin correlation mechanism should be considered for these systems.

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