

Nano-sized Effect on the Magnetic Properties of Ag Clusters

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We have prepared crystalline Ag nanoparticles with an average size of 4 nm in diameter by using an inductively coupled plasma reactor equipped with the liquid nitrogen cooling system. Our magnetic data show that the nano-sized effect of Ag nanoparticles on the magnetic properties is ferromagnetic, instead of a diamagnetic component of the Ag bulk and a superparamagnetic component of magnetic nanoparticles. We have also studied the magnetic properties of Ag-Cu nanocomposites with an opposite concentration profile between surface and core. These comparisons indicate that the ferromagnetic component strongly depends on the surface of Ag nanoparticles, while the paramagnetic component is strongly affected by the outer oxide layer, with the background of a diamagnetic component from the core of Ag.

Keywords : Ag nanoparticle, ferromagnetism, core-shell, plasma technique

1. Introduction

Research in the synthesis and functionalization of nanoparticles has received considerable interest in recent years because of a variety of potential applications [1]. The synthesis of nanoscale materials with desired properties is difficult and presents a great challenge to the scientific community. The frequently encountered obstacle is the spontaneous production of oxides. Due to very high surface to volume ratio, nanoparticles have high reactivity and can easily be environmentally degraded. The oxide close to the metallic core is almost stoichiometric whereas that at the surface consists of atoms with a reduced coordination number. This can modify the magnetic and other related properties to an appreciable extent. Particular interest lies in the fabrication of magnetic nanoparticles, which are promising materials for ultrahigh-density magnetic storage devices and sensors. Most of the studies on such magnetic nanoparticles are currently focusing on the nanoparticles based on the synthesis of ferromagnetic metals such as Fe, Co, and Ni [2]. However, the magnetic properties of the nanoparticles are very complicated due to the presence of oxide coated layer and magnetic impurities. On the other hand, there are a few reports on

nonmagnetic 4d elements in nanoparticles such as Pd and Au [3-6], which exhibit unexpected d^0 ferromagnetism. Here, attempts are being made to synthesize nonmagnetic nanoparticles and the nano-sized effect is being studied to search new magnetic properties and applications.

2. Experimental Details

The nano-sized composites of Ag and Ag-Cu were produced by an inductively coupled plasma reactor equipped with the liquid nitrogen cooling system. The nano-sized Ag and Ag-Cu were prepared by thermolysis of single molecular precursor in hexadecylamine. The reaction was carried out at relatively low temperatures without reducing agent under inert atmosphere condition. The SEM and HRTEM images showed nearly spherical shape and average size of 4 nm in diameter. This enables us to study the effect of particle size and surface anisotropy on magnetic interaction in the nanocomposites. The x-ray diffraction patterns of all of the alloys could be indexed with a cubic structure. The diffraction peaks show a trend of broadening, which results from the reduced size of the particles. Magnetic measurements were performed using a commercial SQUID magnetometer (MPMS7, Quantum Design). The temperature dependence of magnetization was measured in an applied field of 1 kOe between 2 and 350 K and the hysteresis loop was measured at room

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temperature.

3. Results and Discussion

Among the various synthesis techniques, plasma method is used for producing Ag nanoparticles. Three kinds of Ag nanoparticles are prepared by an inductively coupled plasma reactor equipped with the liquid nitrogen cooling system. Figure 1(a) represents a typical high-resolution TEM image of a Ag nanoparticle with a diameter of 4 nm, providing the highly crystalline nature of the single nanoparticle. In Fig. 1(b), the highly crystalline cubic structure is demonstrated by the electron diffraction pattern of the Ag nanoparticle. For Ag-Cu nanoparticles, the size of core is almost same to the pure Ag nanoparticles. The diameter of core is about 4 nm and the thickness of shell is between 2 and 3 nm.

The magnetic properties of the Ag nanoparticles have

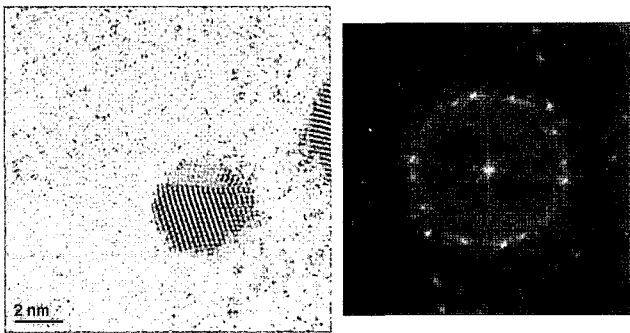


Fig. 1. (a) HR-TEM image of Ag nanoparticles. (b) Electronic diffraction pattern for Ag nanoparticles.

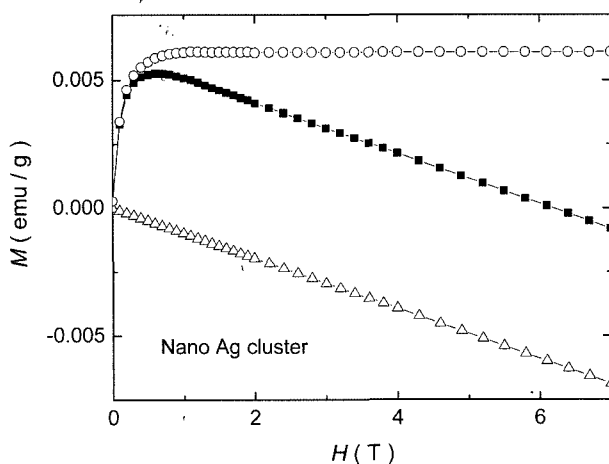


Fig. 2. Magnetization $M(H)$ of the Ag nanoparticles as a function of the applied field measured at room temperature. The symbols of solid square, open circle, and open triangle represent the measured data, the separated ferromagnetic and diamagnetic components, respectively.

been studied by measuring the magnetization at room temperature. It is clear that the magnetization data of the Ag nanoparticles are very different from that of the bulk. The bulk of Ag is well known to be diamagnetic, providing the negative slope of $M-H$ curve. As evident from the initial magnetization curve (Fig. 2), the magnetization at lower fields shows a rapid increase with field, followed by a maximum and then by a linear behavior suggesting the existence of two different magnetic phases in each particle – a ferromagnetic and a diamagnetic phase. The first is responsible for the rapid increase of the magnetization at low fields, while the second is responsible for the negative slope of the magnetization at higher fields. Each particle can thus be considered as a magnetically heterogeneous system consisting of a diamagnetic Ag core and a ferromagnetic outer shell, probably in the form of silver oxides. However, no significant oxides could be detected in the XRD patterns as well as HRTEM analysis. An attempt to separate the ferromagnetic component from the initial magnetization curve has been made by subtracting the diamagnetic component from the total magnetization in the high field region. Reasonably good linear fit to the high field region of the initial magnetization curve has been obtained with the saturation magnetization $M_S = 0.006$ emu/g. The ferromagnetic state may be attributed to small particle dimensions, which can modify the magnetic exchange interactions of the nanoparticles.

In order to check this issue, we have studied the magnetic properties of the Ag nanoparticles with a copper core. In Fig. 3, a clear ferromagnetic component is present with the saturation magnetization $M_S = 0.287$ emu/g and the

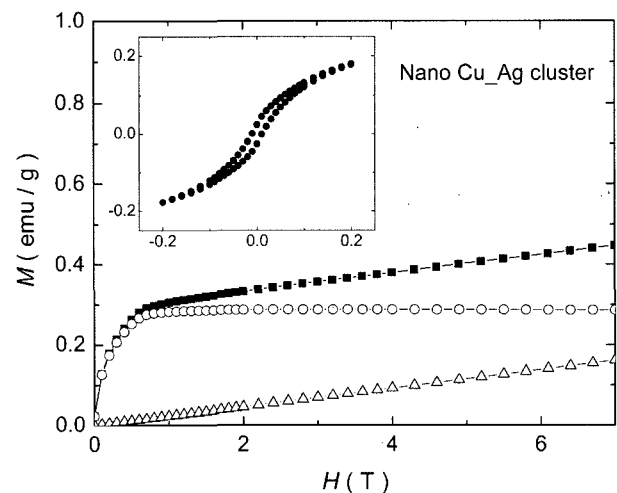


Fig. 3. Magnetization $M(H)$ of the Ag nanoparticles with a copper core as a function of the applied field measured at room temperature. The symbols of solid square, open circle, and open triangle represent the measured data, the separated ferromagnetic and paramagnetic components, respectively.

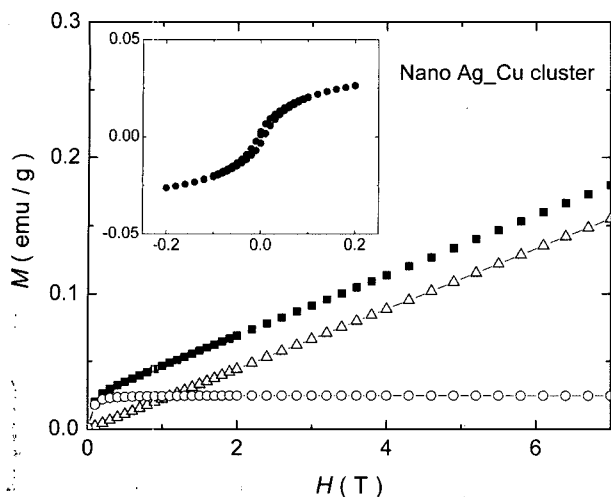


Fig. 4. Magnetization $M(H)$ of the Ag nanoparticles with a copper shell as a function of the applied field measured at room temperature. The symbols of solid square, open circle, and open triangle represent the measured data, the separated ferromagnetic and paramagnetic components, respectively.

coercive field $H_C = 100$ Oe at room temperature. On similar way above, we consider each particle of the Cu core and Ag shell nanostructure consisting of a nonmagnetic Cu core, ferromagnetic Ag shell, and any other paramagnetic impurities in the form of copper oxides. The paramagnetic term is responsible for the no saturation of the magnetization in the high field region. It should be noted that the M_S value is highly enhanced because of the presence of paramagnetic impurities instead of the diamagnetic Ag core. It is then reasonable to anticipate that the Ag shell gives rise to the ferromagnetic component as a result of the nano-sized effect at the surface of Ag nanoparticles.

More clear evidence could be found in studies on magnetic states of opposite nanostructure. Figure 4 shows the room temperature M - H curve of the Ag nanoparticles with a copper shell. The Ag core can be described as a diamagnetic component, while the copper shell can be described as an surface oxide layer as a paramagnetic component. The presence of small ferromagnetic component, with the M_S value of 0.025 emu/g and the H_C value of 60 Oe, can be interpreted in terms of ferromagnetic Ag impurities at the surface. Such an absence of large ferromagnetic component in the Ag nanoparticles with the outer copper oxide layer is an indication of strong ferromagnetic component of nano-sized Ag surface.

The temperature dependence of the magnetization has been measured at a constant dc field of 1 kOe. In Fig. 5, a ferromagnetic component, independent of the temperature, for the Ag nanoparticles with a copper shell is much larger than that for the pure Ag nanoparticles and exhibit

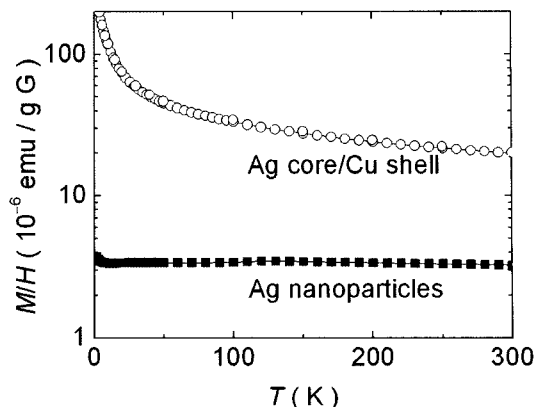


Fig. 5. Magnetization $M(T)$ of the Ag nanoparticles and Ag nanoparticles with a copper shell as a function of the temperature measured with $H=1$ kOe. The symbols of solid square and open circle represent the measured data of Ag nanoparticles and Ag core/Cu shell, respectively.

a paramagnetic behavior. The large value of magnetic moment could be related with possible mixing phase at the boundary of core and shell, which can play a role in enhancing the magnetic moment. On the other hand, the paramagnetic temperature dependence indicates that the copper shell acts as a paramagnetic layer in the form of copper oxides. Here the absolute value of the magnetization may not be valid because of the unknown boundary phase.

4. Conclusion

From our experiments described above, the nature of magnetism of the Ag nanoparticles is quite different from that in the bulk sample of Ag. A large ferromagnetic component is observed in the nanoparticles with a surface Ag layer, compared with a paramagnetic component of the nanoparticles with a surface copper layer. In addition, there is observed an intrinsic bulk character of diamagnetism from the core of Ag. This is a new report about the ferromagnetism in the form of metallic Ag nanoparticles. When the particles are reduced to be nanosized, there have been many studies on an enhancement of magnetization and/or an appearance of superparamagnetism. For ferromagnetic nanoparticle systems, the presence of magnetic oxide layer is expected to show the characteristic of a superparamagnet. Such explanations can be extended to the metallic nanoparticles and might suggest the existence of some special spin polarization mechanism in the Ag nanoparticles.

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