Direct Evidence of Ferromagnetic Spin Polarization in Gold Nanoparticles

It is believed that bulk gold metal is chemically inert and the most stable metal in nature. However, its properties in the nanosize region might be different from its bulk nature because the electronic structure may be modified significantly. In fact, recent experiments have shown that gold nanoparticles exhibit an enhancement in catalytic activity at a diameter of approximately 2 nm [1]. Moreover, superparamagnetic behavior has been reported for gold nanoparticles stabilized by a polymer (Fig. 1) for diameters below 3 nm [2], although bulk gold metal has non-magnetic (diamagnetic) properties. This indicates that individual Au particles possibly have ferromagnetic moments. However, no clear evidence has been provided showing that the ferromagnetism of Au particles is intrinsic because conventional magnetometry may include magnetization from trivial origins, such as magnetic impurities. Therefore, it is essential to measure the element-specific magnetization of gold atoms to confirm that their magnetism is intrinsic.

In this study, we have presented direct evidence of the intrinsic ferromagnetism of Au nanoparticles protected by polyallyl amine hydrochloride (PAAHC) (abbreviated as PAAHC-Au) by means of element-specific magnetization (ESM) measurements based on the X-ray magnetic circular dichroism (XMCD) technique. The XMCD technique allows the detection of the magnetic moments of a particular element through sensitivity to the difference between the up- and down-spin densities at approximately the Fermi level. This element selectivity is the most important advantage of this technique over conventional magnetometry and is essential in the present study of extracting the magnetization of Au nanoparticles.

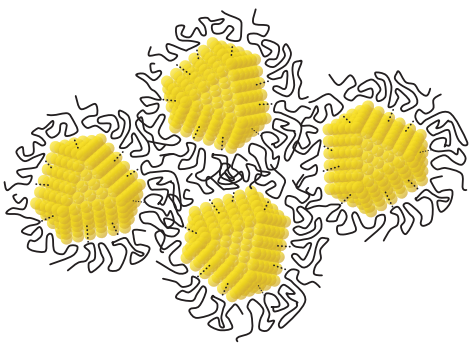

Fig. 1. Schematic of gold nanoparticles protected by linear polymer. Each nanoparticle (cluster of Au metal) is surrounded by a matrix polymer, which prevents further aggregation and oxidation of Au nanoparticles.

XMCD spectra were recorded using a highly sensitive spectrometer installed at beamline **BL39XU**. External magnetic fields up to 10 T were applied along the X-ray beam direction using a split-type superconducting magnet. The experimental resolution was high enough to detect XMCD signals of 10^{-5} parts of the spin-averaged X-ray absorption coefficients. This high sensitivity is achieved through the helicity modulation technique based on lock-in detection [3], and the high brilliance of a third generation synchrotron radiation source. We emphasize that the modulation technique is crucial for the detection of very small ferromagnetism in Au nanoparticles because this technique markedly improves the signal/noise ratio of the XMCD signal.

Figure 2 shows the X-ray absorption spectroscopy (XAS) and XMCD spectra of Au at the L_3- ($2p_{3/2} \rightarrow 5d_{5/2}$, $6s_{1/2}$ dipole-allowed transitions) and L_2-edge ($2p_{1/2} \rightarrow 5d_{3/2}$, $6s_{1/2}$) at 2.6 K in an applied magnetic field of 10 T. A negative XMCD signal was clearly observed at the L_3-edge (11.917 keV), whereas the XMCD signal at the L_2-edge (13.730 keV) was positive. As shown by the dotted line in Fig. 2, the sign of the XMCD signal reversed when the magnetic field direction was changed. This result confirms that the observed signal is truly of magnetic origin and does not arise from any artificial effects. To the best of our knowledge, this is the first observation of an evident XMCD signal arising from Au within a nonmagnetic matrix.

Considering the XMCD signal to be proportional to the magnetization, ESM is obtained by recording the peak amplitude of the XMCD spectra at the Au L_3-edge as a function of external magnetic field and temperature. Figure 3 shows ESM measurements scaled arbitrarily for comparison with the magnetic field variation of SQUID magnetization in the same figure. ESM increases with increasing magnetic field without saturation. This behavior is similar to the magnetization process obtained by SQUID magnetization measurements. The temperature dependence of ESM was also investigated and compared to the temperature variation of SQUID magnetization. ESM increases rapidly with decreasing temperature, although it seems that a finite constant value remains at high temperatures. The steep increase in ESM at low temperatures is consistent with the temperature variation of SQUID magnetization and does not

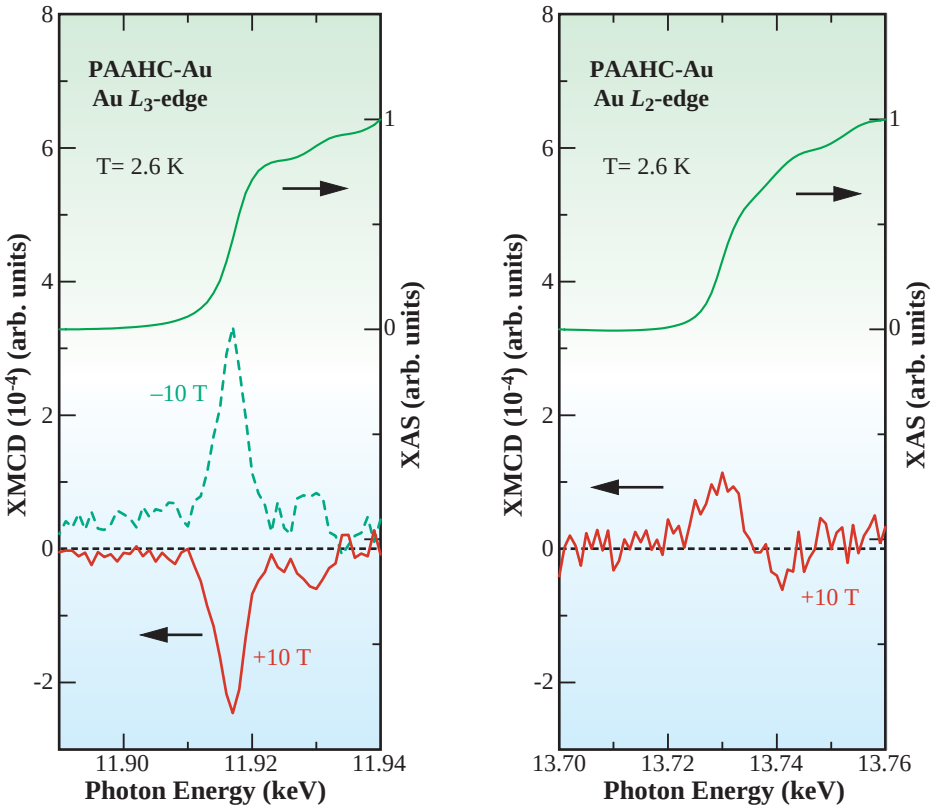

Fig. 2. XMCD and XAS spectra at Au L_3- and L_2-edge with applied magnetic fields of 10 T (red solid line) and –10 T (broken line). The XMCD and XAS spectra include the same scale factor so that the heights of the edge jumps of the XAS spectra (solid lines) are unity.

contradict the characteristics of the superparamagnetic model. If one assumes that superparamagnetism and Pauli paramagnetism arise from surface atoms and core atoms in Au nanoparticles respectively, the observed mixture of superparamagnetism and Pauli paramagnetism is reasonably explained.

In summary, our XMCD and ESM experiments have revealed the intrinsic magnetic polarization in Au nanoparticles with a mean diameter of 1.9 nm [4]. The external magnetic field and temperature dependences of the ESM signal suggest that the magnetization of Au nanoparticles consists of a superparamagnetic part and a temperature-independent Pauli paramagnetic part. The mixture of these components is reasonably explained by the picture that the surface atoms are ferromagnetic and the core atoms are Pauli paramagnetic.

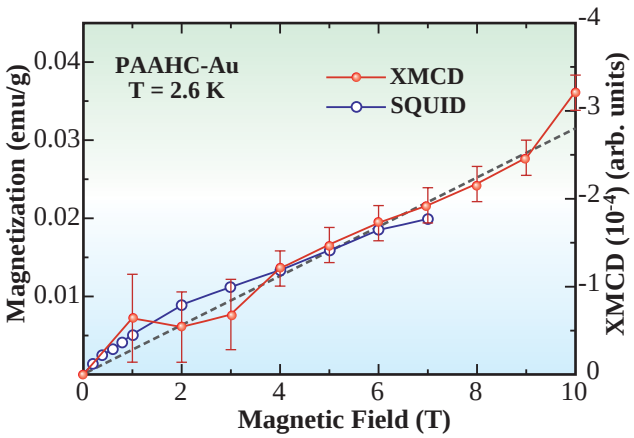

Fig. 3. ESM of PAAHC-Au as a function of applied magnetic field and magnetization process obtained using SQUID magnetometer. The integral of the peak intensity yields similar results. The dashed line is the fit to the data assuming a Langevin function plus a linear field-dependent term.

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