Silver-induced Enhancement of Magnetic Properties of $CoPt_3$ Nanoparticles

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The influence of Ag on the magnetic properties of $CoPt_3$ nanoparticles has shown that the addition of Ag (5.0 mol %) can not change the size and crystal structure (i.e., fcc structure) of $CoPt_3$ nanoparticles. However, SQUID studies have revealed that the addition of Ag can notably improve the magnetic properties of $CoPt_3$, which could result from the interaction between Ag and $CoPt_3$ nanoparticles.

CoPt and FePt nanocomposites have attracted a great deal of attention lately due to their application in ultrahigh-density recording media.[1] As-prepared nanoparticles of equiatomic alloys FePt and CoPt possess a disordered fcc structure with relatively low magnetocrystalline anisotropy and are unsuitable for storage purposes. An increase in anisotropy is achieved by annealing the particles at temperature of 600–800 °C, thereby transforming them into a tetragonal phase with anisotropies of $5–7 \times 10^7$ erg/cm^3.[1,2] Several approaches have been proposed to reduce the ordering temperature of Fe–Pt and Co–Pt alloys and optimize their magnetic properties. Kang et al.[3] and Sato et al.[4] reported that the addition of Ag was effective in reducing the ordering temperature in FePt nanoparticles. In the case of CoPt alloy, it was found that the addition of Sn, Pb, Sb, and Bi into sputtered CoPt thin films promoted a disorder–order transformation, resulting in an appreciable reduction of the temperature for ordering.[5] Recently, the use of a silver underlayer was effective in reducing the ordering temperature in $L1_0$ CoPt alloys.[6–8] Shern and co-workers reported that magnetic enhancement was observed after Ag ultrathin film deposited on Co/Pt(111).[9] It was recently demonstrated that the addition of copper reduced the fcc-disordered to fct-ordered phase transition temperature by 250 °C compared with pure $CoPt_3$ nanoparticles.[10]

We have prepared $CoPt_3$ nanoparticles by a two-stage procedure.[11] In this paper, we propose an effective procedure to improve the magnetic properties of $CoPt_3$ nanoparticles, namely, the addition of silver to $CoPt_3$ nanoparticles during chemical synthesis.

Under nitrogen atmosphere, 100 mL of $NaBH_4$ ethanol solution (0.066 M) was dropped into 100 mL of $CoCl_2$ ethanol solution (3.6 mM) containing 0.5000 g of PVP under vigorous stirring at 0 °C. The color of the solution changed from blue to brown, indicating the formation of the suspension of cobalt nanoparticles. Then, 100 mL of H_2PtCl_6 ethanol solution (10.8 mM) containing 0.0165 g of $AgClO_4$ was dropped into the above suspension. After keeping vigorous stirring for 30 min, 100 mL of $NaBH_4$ solution (0.066 M) was slowly added. The mixtures were kept stirring at 40 °C for 3 h. Afterwards, the colloid dispersions were filtered by an ultrafine membrane filter in nitrogen atmosphere and washed by dehydrated ethanol for three times. The residual ethanol of the colloid was removed by using of a rotary evaporator. $CoPt_3$/Ag powders were finally obtained by vacuum drying at 40 °C for 48 h.

XRD patterns of $CoPt_3$/Ag nanoparticles were given in Figure 1. The sample was assigned to fcc crystal phase of $CoPt_3$ from the diffraction lines of (111), (200), and (220) planes in the XRD profile. Super lattice peak of (110) place was too weak to be detached on $CoPt_3$/Ag nanoparticles as well as on $CoPt_3$ nanoparticles prepared by the present method. A trace of hexagonal B_2O_3 found resulted from $NaBH_4$. It was demonstrated that the addition of Ag with a specific quantity cannot change the crystal structure of $CoPt_3$ nanoparticles.

Figure 2 shows the TEM micrographs of $CoPt_3$ nanoparticles and $CoPt_3$/Ag nanoparticles, where spherical nanoparticles of average sizes of 2.6 and 2.5 nm, respectively. The shapes and average size of $CoPt_3$ extremely approach to those of $CoPt_3$/Ag nanoparticles, implying that the addition of Ag has little influence on the shapes and size of the nanoparticles. In order to confirm the presence of Ag in $CoPt_3$/Ag nanoparticles, energy-dispersive X-ray (EDX) spectrometric analysis was performed. The presence of Ag is qualitatively confirmed.

Figures 3a and 3b show hysteresis loops of as-synthesized $CoPt_3$ and $CoPt_3$/Ag nanoparticles, respectively.[12] The coercivity value of $CoPt_3$ nanoparticles at 1.85 K was 980 Oe, whereas the coercivity value of $CoPt_3$/Ag nanoparticles increased up to 3000 Oe, which is much higher than that of $CoPt_3$/Au (415 Oe at 10 K) prepared via microemulsion technique.[13] This remarkable improvement could be related to the effect of Ag on the spin reversal of Co.[9]

In order to reveal the reason for silver improving the magnetic properties of $CoPt_3$ nanoparticles, XPS studies were performed to verify the chemical valences of all elements for $CoPt_3$/Ag nanoparticles, and the results were given in Table 1.

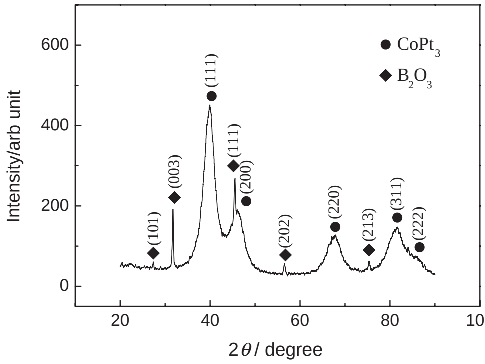

Figure 1. XRD pattern of $CoPt_3$/Ag nanoparticles.

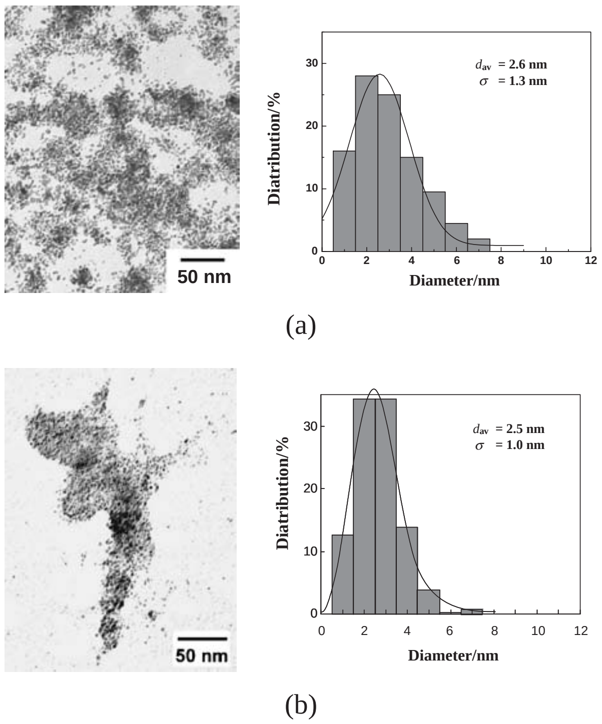

Figure 2. TEM micrographs and size distribution of (a) as-synthesized $CoPt_3$ nanoparticles and (b) $CoPt_3/Ag$ nanoparticles.

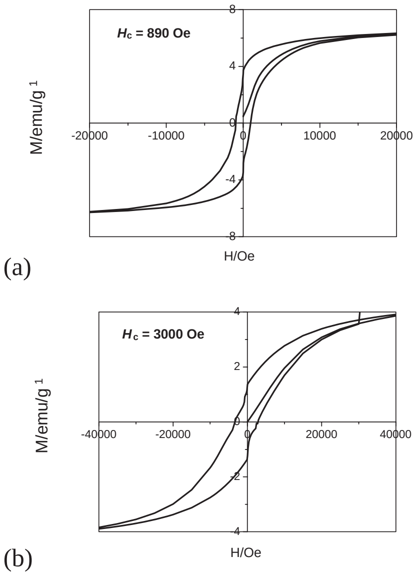

Figure 3. Hysteresis loops at 1.85 K of (a) as-synthesized $CoPt_3$ nanoparticles and (b) $CoPt_3/Ag$ nanoparticles.

Table 1. BE and the shift of $CoPt_3/Ag$ nanoparticles

Element	C 1s	Pt 4f	Ag 3d
Standard BE value/eV[a]	284.6	70.9	367.9
Observed BE value/eV	287.5	73.8	369.8
BE shift/eV	+2.9	+2.9	+1.9

[a] From ref 14.

The same binding energy (BE) shift value, 2.9 eV, of C 1s and Pt 4f indicates that Pt ions have been completely reduced to Pt metal. However, BE shift value of Ag 3d is only 1.9 eV, implying that Ag could form AgO or interact with other elements, such as Co, as reported by Wu and co-workers.[9] The great improvement of magnetic properties of the samples rules out AgO formation, thus, this suggests that Ag interacts strongly with $CoPt_3$ nanoparticles. BE of Co 2p cannot be obtained from the XPS spectrum due to its weak signals. It is clear that the investigation of the structure inside as-synthesized nanoparticles is a difficult task, especially in the case of element-specific methods such as EXAFS and WAXS.

The effects of Ag on the magnetic properties of $CoPt_3$ nanoparticles have been presented. $CoPt_3/Ag$ nanoparticles with average particle size of 2.5 nm formed a fcc $CoPt_3$ crystal structure, implying that the addition of Ag can not change the crystal structure of $CoPt_3$ nanoparticles. However, SQUID studies revealed that the addition of Ag can notably improve the magnetic properties of $CoPt_3$, which could result from the interaction between Ag and $CoPt_3$ nanoparticles.

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