Novel Synthesis of FePt Nanoparticles and Magnetic Properties of Their Self-assembled Superlattices

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The novel synthesis of FePt nanoparticle superlattices by polyol reduction of platinum acetylacetonate and iron acetylacetonate is reported. The compositions of FePt nanoparticle are readily controlled, and the particle sizes are not significantly affected by the compositions, retaining to be ca. 3 nm with a very narrow size distribution. The FePt nanoparticles self-assemble into 2-D and 3-D superlattices. Thermal annealing converts the crystal structure of FePt nanoparticle from fcc to $L1_0$ phase and transforms the superparamagnetic nanoparticle into ferromagnetic one.

The current sputtering technique to produce the magnetic recording media seems close to the limitation against the future high-density recording, because the thermal demagnetization has a remarkable effect as the size of the recording units becomes smaller. To overcome this problem, much attention has been paid to the perpendicular magnetic recording proposed by Iwasaki in 1975.[1,2] For this purpose, the FePt nanoparticle is the promising candidate, since it has both high coercivity and high uniaxial magnetocrystalline anisotropy ($K_u = 6.6$–$10 \times 10^6\ \mathrm{J/m^3}$).[3,4] The inorganic nanoparticles protected by the organic ligands have a big advantage for fabrication of nanodevices through a solution process making use of their solubility to the solvents[5–10] as well as easy handling as powders.[11] The control of primary structures of nanoparticles, such as size, shape, crystal structure, and composition, is of great importance because they determine the characteristics of nanoparticles including magnetic, electronic, optical, and catalytic properties.[12,13]

In 2000, Sun and co-workers pioneered the synthesis, self-assembly, and magnetic recording performance of FePt nanoparticles.[14] They succeeded in the synthesis of monodisperse FePt nanoparticles by the combination of the reduction of platinum acetylacetonate ($Pt(acac)_2$) and the decomposition of iron pentacarbonyl ($Fe(CO)_5$) in the presence of oleic acid and oleylamine stabilizers. Although many researchers have employed this synthetic procedure, $Fe(CO)_5$ is not only toxic and inflammable, but also has a low boiling point (103 °C), which makes it difficult to control the precise composition of FePt nanoparticles during the hot syntheses. In this paper, we report a novel synthesis of FePt nanoparticles using the polyol-reduction of $Pt(acac)_2$ and $Fe(acac)_3$ in place of $Fe(CO)_5$ in the presence of oleic acid and oleylamine. The resulting FePt nanoparticles of ca. 3 nm self-assemble into hexagonal close-packed (hcp) 2-D and fcc-stacking 3-D superlattices. The magnetic properties of the FePt nanoparticle assemblies annealed at ca. 600 °C are also presented.

The FePt nanoparticles were synthesized by a polyol-reduction of $Fe(acac)_3$ and $Pt(acac)_2$. First, both the precursors (total amount was 1.0 mmol) were added to di-*n*-octylether (13.5 mL), and the dissolved oxygen was removed from the solution under reduced pressure for 5 min. The vigorously-stirred solution was heated up to 150–170 °C under N_2 to completely dissolve the precursors. The solution color tuned from bright red to dark red when the mantle heater temperature reached at 280 °C. The solution was kept stirring for 30 min after an addition of reductant, 1,2-hexadecanediol (1.5 mmol), and the mixture of oleic acid (0.5 mmol) and oleylamine (0.5 mmol) was then injected into the solution and stirred for 30 min at this temperature (solution temperature was 220–230 °C). The solution was cooled down to room temperature and the resulting particles were precipitated with ethanol for purification. The black precipitate was redispersed in hexane (50 mL) containing oleic acid (100 μL) and oleylamine (100 μL).

The composition of FePt nanoparticles can be easily tuned by changing the initial feeding ratio of two precursors. Figure 1 shows the compositions of the resulting FePt nanoparticles determined by energy dispersive X-ray spectroscopy (EDX). Although the Fe contents of FePt nanoparticles are always lower than those of the precursors because of an incomplete reduction of Fe^{3+} ions, the Fe contents in FePt nanoparticles can be tuned from 23 to 67 atom %. The sizes of FePt nanoparticles are not significantly affected by their compositions, the sizes of $Fe_{23}Pt_{77}$ (lowest Fe content), $Fe_{53}Pt_{47}$ and $Fe_{67}Pt_{33}$ (highest Fe content) being 3.2 ± 0.3, 3.1 ± 0.2, and 3.2 ± 0.3 nm, respectively.

The dilute hexane solution of FePt nanoparticles was dropped onto a carbon-coated TEM grid and the solvent was evaporated to give a self-assembled superlattice. The FePt nanoparticles self-assembled into an hcp 2-D superlattice, where the interparticle spacing was about 3.5 nm maintained by the oleic

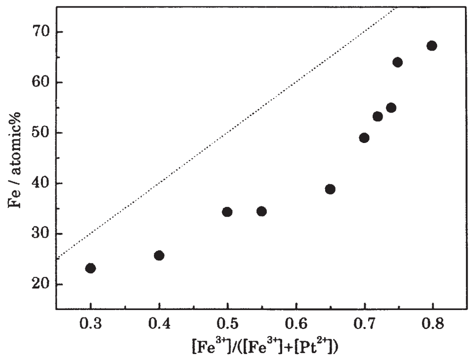

Figure 1. Influence of the molar ratio of precursors on the Fe content of FePt nanoparticles. The dashed line indicates the Fe content in feeding precursors.

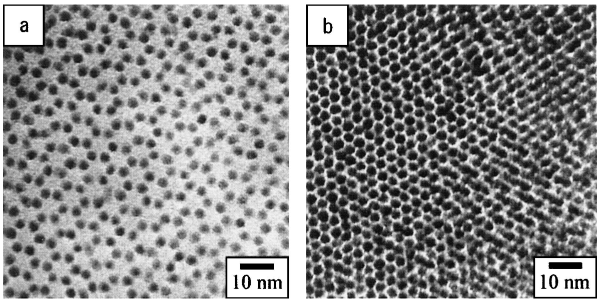

Figure 2. TEM images of (a) bilayer superlattice of $Fe_{34}Pt_{66}$ nanoparticles and (b) trilayer superlattice of $Fe_{53}Pt_{47}$ nanoparticles.

acid and oleylamine stabilizing groups.[14] Increasing the concentration of hexane solution containing FePt nanoparticles leads to the formation of self-assembled 3-D superlattices. Figure 2a shows the 3-D superlattice of 3.1-nm $Fe_{34}Pt_{66}$ nanoparticles. This 3-D superlattice consists of AB stacking of hcp 2-D superlattices of $Fe_{34}Pt_{66}$ nanoparticles forming the quasi-honeycomb structure, where the nanoparticles at the second layer occupy the three-fold hollow sites of the first layer. This structure formed on its self-assembling way is often observed in 3-D superlattices of magnetic nanoparticles,[15,16] and exclusively produced for small Au nanoparticles when using the interligand interaction.[10] When more concentrated solution was dropped on a TEM grid, the particles assembled to give a thick superlattice with an ABC close-packed (fcc type) structure,[16] as shown in Figure 2b.

Since the thermal annealing converts the internal particle structure from a chemically disordered face-centered cubic (fcc) phase to the chemically ordered face-centered tetragonal (fct or $L1_0$) phase and transforms the nanoparticle superlattices into ferromagnetic nanoparticle assemblies,[14] the annealing effect on the crystal structure and the magnetic property of the FePt nanoparticle superlattices were examined. After spreading the hexane solution of FePt nanoparticles on a quartz substrate followed by a slow evaporation of the solvent, the FePt nanoparticle assemblies were annealed at 600 °C for 30 min under vacuum (ca. 10^{-6} Torr). As-synthesized FePt nanoparticles are in the fcc phase independent of the Fe contents. For the FePt nanoparticles with Fe contents less than 34 atom %, the crystal structure of FePt nanoparticles remains unchanged to be an fcc structure in the XRD patterns. Also, the FePt nanoparticles having Fe contents larger than 67 atom % do not show the significant change in their crystal structure. To transform the crystal structure from fcc to $L1_0$ phase, Fe contents from 39 to 64 atom % are required. In this range, the FePt nanoparticle assemblies have $L1_0$ crystal structure, as indicated by the (111) peak shifts and clear evolution of both the (001) and (110) peaks in the XRD patterns.[14] The half-bandwidth of (111) peak became narrower by annealing the particles owing to the coalescence of particles to form the larger ones. A certain technique to transform the crystal structure from fcc to $L1_0$ without particle coalescence should be developed and is under investigation.

In general, 3-nm FePt nanoparticles with an fcc structure are superparamagnetic at room temperature, whereas the phase transformation to $L1_0$ endows the nanoparticles with ferromagnetic property. Figure 3 shows the coercivities of annealed FePt nanoparticle assemblies measured by a Vibrating Sample Magnetometer (VSM), as a function of Fe content. It was found that the FePt nanoparticles with $L1_0$ phase showed ferromagnetic nature and had the large coercivities. Especially, the coercivities of $Fe_{49}Pt_{51}$, $Fe_{55}Pt_{45}$, and $Fe_{64}Pt_{36}$ are quite large beyond our VSM limitation. The actual H_c values for these FePt nanoparticle assemblies would exceed VSM data, since only the hystereses with minor loops were observed.

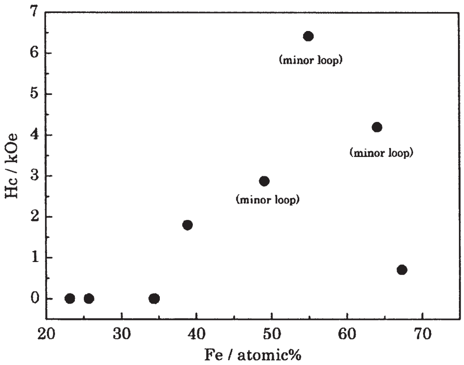

Figure 3. Composition-dependent coercivities of FePt nanoparticle assemblies annealed at 600 °C for 30 min under vacuum (ca. 10^{-6} Torr) (measured by VSM with maximum application field of 15 kOe).

In conclusion, we presented our novel synthetic procedure of FePt nanoparticles using the polyol reduction of $Fe(acac)_3$ and $Pt(acac)_2$, the formation of their 2-D and 3-D superlattices, and the heat-induced changes in their crystal structures and magnetic properties. Our technique is highly reproducible and practicable. The ferromagnetic FePt nanoparticle superlattices are the most promising candidates for future ultrahigh-density magnetic recording media in Tbit/in^2 region. For such application, a pile of problems, such as an arrangement of easy axes and the reduction of annealing temperature, should be overcome.[17]

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