Synthesis of Ferromagnetic Mn−Pt Nanoparticles from Organometallic Precursors

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We have synthesized Mn−Pt nanoparticles using a chemical preparation based on a liquid-phase reaction caused by decomposition of organometallic precursors. The synthesized monodisperse $Mn_{52.5}Pt_{47.5}$ nanoparticles show an fcc crystalline structure and ferromagnetic properties even at the room temperature. $Mn_{52.5}Pt_{47.5}$, which is not ferromagnetic in a bulk form, shows a completely different physical property in nanoparticles.

Nanoscale materials exhibit unique physical and chemical properties that are different from their bulk properties.[1] A magnetic property may also be changed in a nanoscale. This opens the way to the search for novel magnetic materials that could be applied to nano-spintronics and ultrahigh-density storage devices.[2] Here we present a realization of highly crystalline monodisperse ferromagnetic nanoparticles of Mn−Pt, which is antiferromagnetic in a bulk form, using a chemical synthesis. We adopted a chemical preparation for nanoparticles, which is based on a liquid-phase reaction caused by decomposition of organometallic precursors. This method is considered to be one of the most promising bottom-up techniques in nanotechnology, because of the high uniformity and controllability of synthesized nanoparticles.

Studies on magnetic properties of nanoparticles have been extensively performed on nanoparticles of a bulk ferromagnet, such as Co, Fe−Pt, ferrites, etc.[3] Ferromagnetic nanoparticles are considered to be the key materials from a viewpoint of the application for ultrahigh-density magnetic storage media. However, concerning nanoparticles of a bulk antiferromagnet, their fabrication and magnetic properties were not investigated at all. In this letter, we report on the preparation and realization of Mn−Pt nanoparticles that show room-temperature ferromagnetism and a large coercivity. Mn−Pt alloy is a typical metallic antiferromagnet, which is used for a spin-valve in a hard disk drive, whose crystalline structure is CuAu−I type, being face-centered-tetragonal (fct), and having a high Néel temperature (975 K) and also a high magnetic anisotropy.

A typical procedure for the preparation of Mn−Pt nanoparticles is as follows.[4] $Pt(acac)_2$ (159 mg; acac = acetylacetonato) was suspended in *n*-dioctyl ether (15 mL) containing 1,2-tetradecanediol (273 mg) at room temperature and heated to 100 °C in an oil bath under N_2 atmosphere. At around 90 °C, $Pt(acac)_2$ began to dissolve, and a clear yellow solution was obtained at 100 °C. Then $Mn_2(CO)_{10}$ (148 mg), oleic acid (50 μL), and oleylamine (50 μL) were added to the yellow solution at this temperature. The mixture was further heated to reflux in a salt bath. At around 250 °C the color of the solution began to change from yellow to black. Reflux was continued for 30 min at 300 °C, and the resultant black colloidal solution was cooled to room temperature. Mn−Pt nanoparticles were easily separated

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from this colloidal solution by centrifugation. Ethanol/hexane/oleic acid solution (ethanol: hexane = 2:1 and 1 mL of oleic acid per 1 mL) was used as a centrifugation solvent and added to this colloidal solution. Black precipitate and yellow-brown supernatant were obtained by centrifugation. Centrifugation was repeated 2 or 3 times. Black precipitate was redispersed in hexane and dropped on glass substrates, and then annealed under N_2 atmosphere at 300 °C for 2 h, 500 °C for 1 h, 500 °C for 5 h, and 550 °C for 1 h.

Mn−Pt alloy nanoparticles were synthesized by using organometallic precursors. Namely, polyol reduction of $Pt(acac)_2$ by an alcohol and thermal decomposition of $Mn_2(CO)_{10}$ were allowed to undergo in a high-boiling solvent, where the manipulation was conducted under an N_2 atmosphere to prevent oxidation of the nanoparticles. We chose *n*-dioctyl ether containing 1,2-tetradecanediol as a solvent, whose boiling point (287 °C) is suitable for these reactions. To stabilize Mn−Pt colloids, oleic acid and oleylamine were added to the solvent. The decomposition of the organometallic precursors started at around 250 °C, and the reactions were allowed to go completion by refluxing for 30 min. The Mn−Pt particles were uniformly dispersed in the resultant colloidal solution. The composition of Mn and Pt in the nanoparticles, which was determined by fluorescent X-ray analysis, can be controlled by changing the ratio of $Mn_2(CO)_{10}$ and $Pt(acac)_2$ used. In this experiment, use of $Mn_2(CO)_{10}$ and $Pt(acac)_2$ in the molar ratio of 1:1 produced the nanoparticles with the composition of $Mn_{52.5}Pt_{47.5}$. The nanoparticles could be separated from the solution, and were easily redispersed in hexane or other hydrocarbon solvents. By repeated cycles of centrifugation and redispersion, the nanoparticles were thoroughly purified.

The structure of the $Mn_{52.5}Pt_{47}$ nanoparticles was investigated by transmission electron microscopy (TEM) and transmission electron diffraction (TED) using JEOL JEM2010F operated at 200 kV and Cu Kα powder X-ray diffraction (XRD) using Rigaku RINT 2400 operated at 40 kV, 200 mA. Magnetic properties were measured by superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-XL).

Figure 1 shows a TEM image of as-synthesized $Mn_{52.5}Pt_{47.5}$ nanoparticles. This TEM image shows that the average particle size is about 3 nm with uniformity in size. Our recipe brings uniform monodisperse Mn−Pt nanoparticles with good controllability in size and composition without a size-selection process. From the lattice fringe of high-resolution TEM image with
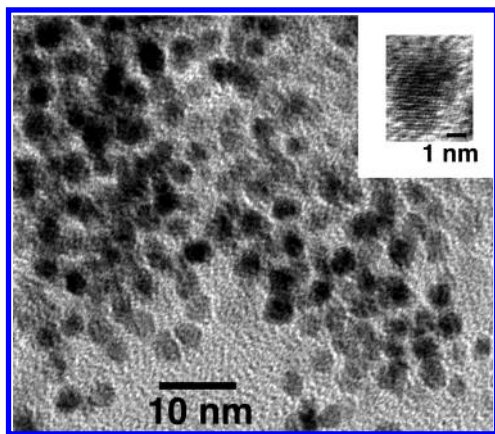
Figure 1. TEM images of as-synthesized $Mn_{52.5}Pt_{47.5}$ nanoparticles. The higher magnification image is shown in the inset. This TEM image shows that the average particle size is 3 nm with uniformity in size.
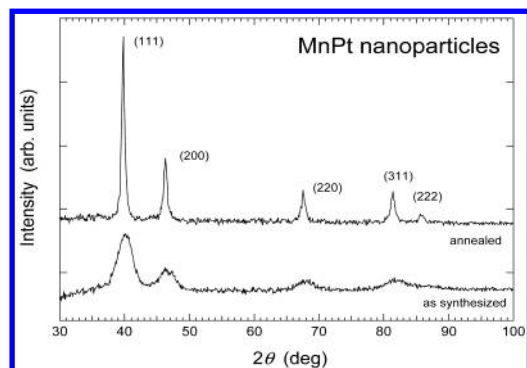

Figure 2. XRD patterns of as-synthesized and annealed $Mn_{52.5}Pt_{47.5}$ nanoparticles. The fcc structure of $Mn_{52.5}Pt_{47.5}$ nanoparticles is observed.

higher magnification in the inset in Figure 1, we confirmed that these nanoparticles are single crystalline.

The crystalline structure of $Mn_{52.5}Pt_{47.5}$ nanoparticles was determined by TED and XRD. TED pattern of as-synthesized $Mn_{52.5}Pt_{47.5}$ nanoparticles clearly exhibits an fcc structure which is similar to the results of Fe−Pt nanoparticles. The XRD patterns of as-synthesized and annealed $Mn_{52.5}Pt_{47.5}$ nanoparticles are shown in Figure 2. The fcc structure of $Mn_{52.5}Pt_{47.5}$ nanoparticles is also confirmed by XRD. It is observed that a peak width becomes narrower and peaks become sharper after annealing. This result indicates that the ordering of Mn−Pt alloy occurs after annealing. It is known that the annealing process is also essential for the high Néel temperature in a bulk Mn−Pt antiferromagnet. In the case of Fe−Pt nanoparticles, the structure changed from fcc to fct by annealing at 550 °C; however, in the case of $Mn_{52.5}Pt_{47.5}$ nanoparticles, the structure did not change and kept fcc even after annealing at 550 °C.

Magnetic hysteresis loops of $Mn_{52.5}Pt_{47.5}$ nanoparticles at 5 and 300 K are shown in Figure 3. Clear hysteresis loops are observed both at 5 and 300 K, indicating the $Mn_{52.5}Pt_{47.5}$ nanoparticles show ferromagnetic properties even at the room temperature. A surprising fact in this result is that the $Mn_{52.5}Pt_{47.5}$, which is not ferromagnetic in a bulk form, shows a completely different physical property in nanoparticles. On the other hand, as-synthesized nanoparticles exhibit only very weak ferromagnetism even at 5 K, and the annealing process,
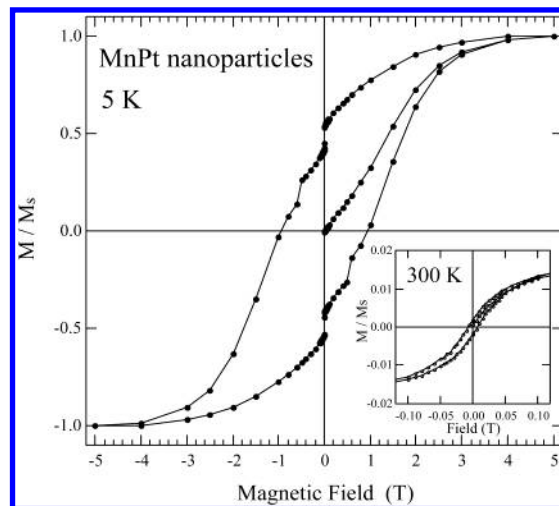

Figure 3. Magnetic hysteresis loops of annealed $Mn_{52.5}Pt_{47.5}$ nanoparticles at 5 and 300 K (inset) where the nonmagnetic background is subtracted. The magnetization (M) is normalized to the saturation magnetization (Ms) at 5 K.

which is an ordering of $Mn_{52.5}Pt_{47.5}$ alloy, is essential for a ferromagnetic ordering. The origin of the ferromagnetic ordering in $Mn_{52.5}Pt_{47.5}$ nanoparticles will be reported in detail elsewhere. It should be also noted that the $Mn_{52.5}Pt_{47.5}$ nanoparticles show a very large coercivity of 0.95 T at 5 K and 7 mT at 300 K.

In summary, we have synthesized Mn−Pt nanoparticles using a chemical preparation based on a liquid-phase reaction caused by decomposition of organometallic precursors. The synthesized monodisperse $Mn_{52.5}Pt_{47.5}$ nanoparticles show an fcc crystalline structure and ferromagnetic properties even at the room temperature.

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