Hard magnetic FePt nanoparticles by salt-matrix annealing

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To transfer face-centered-cubic (fcc) FePt nanoparticles to the face-centered-tetragonal (fct) phase with high magnetic anisotropy, heat treatments are necessary. The heat treatments lead to agglomeration and sintering of the nanoparticles. To prevent the particles from sintering, salts as the separating media (matrix) have been used for annealing the nanoparticles in our experiments. The fcc nanoparticles produced by chemical synthesis were mixed with NaCl powders. The mixture was then annealed in forming gas (93% H_2+7% Ar) in different conditions to complete the fcc to fct phase transition. After the annealing, the salt was washed out by water and monodisperse fct FePt nanoparticles were obtained. Detailed studies on the effect of the NaCl-to-FePt weight ratios (from 1:1 to 400:1) have been performed. It was found that a suitable NaCl-to-FePt ratio is the key to obtain monodisperse fct FePt nanoparticles. A higher NaCl-to-FePt ratio is needed for larger particles when the annealing conditions are the same. Increased annealing temperature and time should be accompanied by a higher NaCl-to-FePt ratio. Magnetic measurements show very high coercivity (up to 30 kOe) of the monodispersed fct nanoparticles by the salt-matrix annealing.
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INTRODUCTION

In 2000, Sun *et al.*, reported the chemical synthesis of FePt nanoparticles.[1] The chemically synthesized FePt nanoparticles, however, are of face-centered-cubic (fcc) phase without magnetic anisotropy. To transfer FePt nanoparticles from fcc phase to face-centered-tetragonal (fct) phase, heat treatments above 600 °C are necessary, which undesirably lead to sintering of these nanoparticles.

Since 2000, great efforts have been made to produce monodisperse fct FePt nanoparticles[2–8] driven by potential applications of the magnetically anisotropic nanoparticles in high-density recording media and high-performance nanocomposite magnets. Recently, we obtained monodisperse fct FePt nanoparticles with retained size and shape by using salts as the annealing separating media.[9] The salts can be completely removed after the annealing just by washing the samples in water. High coercivity up to 30 kOe of the fct particles has been obtained. In this paper we report detailed results in controlling the particle morphology and properties by adjusting the salt-to-FePt particle ratio.

EXPERIMENT

The fcc FePt nanoparticles with size of 4, 8, and 15 nm were synthesized by chemical solution methods.[1,10–13] Sodium chloride (NaCl) was selected as a separating media in this investigation due to its chemical stability and high solubility in water. NaCl was first ball milled for 24 h to reduce the particle size. The ball-milled NaCl powder was then dispersed in hexane and mixed with hexane dispersion of as-synthesized fcc FePt nanoparticles. The mixture was stirred until all the solvent evaporates. Then the mixture was annealed in forming gas (93% H_2+7% Ar) in different conditions to complete the fcc to fct transition. The annealed powders were washed in de-ionized water and centrifuged for several times to remove all the NaCl.[9] Different NaCl-to-FePt weight ratios from 1:1 to 400:1 were tested and the annealing time was varied from 2 to 8 h at 700 °C in forming gas. The effect of salt-to-particle ratio on particle size was investigated with various annealing conditions. Morphology of FePt nanoparticles before and after annealing was observed by a transmission electron microscope (TEM). Phase

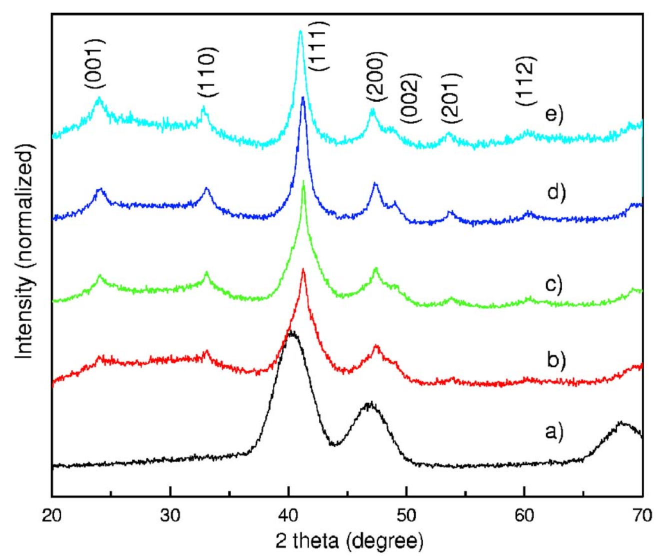

FIG. 1. (Color online) XRD patterns of 4 nm FePt nanoparticles (a) as synthesized, and (b) annealed at 600 °C for 2 h with NaCl:FePt ratio of 40:1, (c) at 700 °C for 2 h at a ratio of 40:1, (d) at 700 °C for 4 h with the ratio of 100:1, and (e) at 700 °C for 8 h with the ratio of 400:1.

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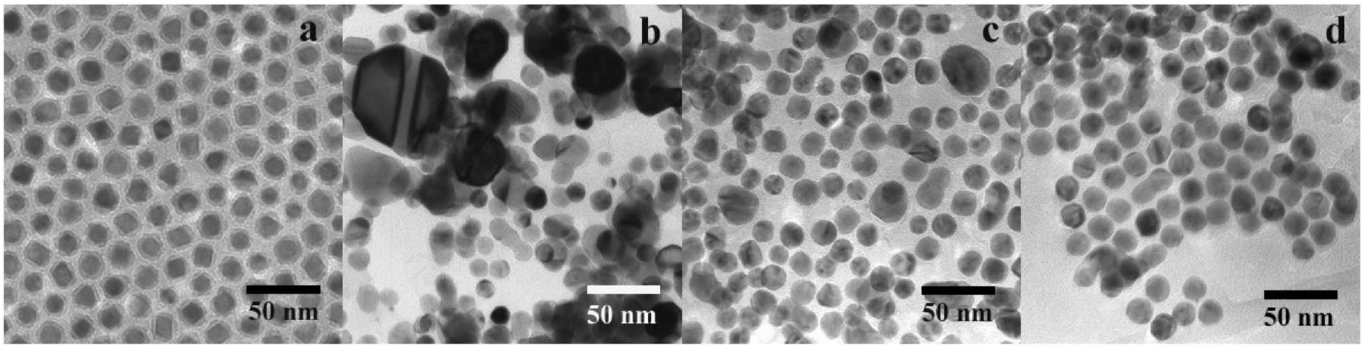

FIG. 2. TEM images of 15 nm FePt nanoparticles (a) as synthesized and annealed in NaCl matrix at 700 °C for 2 h with NaCl-to-FePt ratios of (b) 4:1, (c) 40:1, and (d) 100:1.

identification and composition were analyzed by an x-ray-diffraction (XRD) analyzer and inductively coupled plasma–optical emission spectroscopy (ICP–OES). Magnetic property measurements were carried out by the superconducting quantum interference device (SQUID) magnetometer. The nanoparticles were embedded in hardened epoxy (randomly) for the magnetization measurements.

RESULTS AND DISCUSSIONS

Figure 1 shows the XRD pattern of the recovered 4 nm FePt nanoparticles annealed at different annealing conditions. It was found that the (001) and (110) peaks characteristic for the fct FePt phase started to appear when the nanoparticles were annealed in NaCl matrix at 700 °C for 2 h. With increasing annealing time, the fcc-fct phase transition was more complete, shown by the more pronounced (001) and (110) peaks. From the XRD pattern, no peaks of NaCl were found, indicating that salt was not left after washing the mixture with water after annealing. The ICP–OES result also confirmed that the NaCl level is very low (only 0.099% in weight) and the average composition of the annealed particles is $Fe_{52}Pt_{48}$.

Figure 2 shows the TEM images of the as-synthesized 15 nm FePt nanoparticles and the particles after being annealed at 700 °C for 2 h with different NaCl-to-FePt ratios. For the ratio of 4:1, large particles as big as 50 nm can be found because of sintering between the particles and the particles have a very wide size distribution. When the ratio was increased to 40:1, the sintering was dramatically reduced but few large particles can still be observed, as seen in Fig. 2(c). Figure 2(d) shows that when the ratio of 100:1 was used the sintering was prevented completely and the particle size and shape were retained. It is found that the higher the salt-to-particle ratio, the lesser the sintering. In case of the 15 nm FePt particles, when the ratio is lower than 40:1, monodisperse fct nanoparticles cannot be obtained from the heat treatment at 700 °C for 2 h. Lower salt ratios give significant particle sintering and agglomeration. On the other hand, in salt-matrix annealing the degree of sintering of particles is also related to the particle size of the starting fcc FePt nanoparticles. Figure 3 shows the TEM images of 4 nm FePt nanoparticles annealed in different conditions with different salt-to-particle ratios. At the same annealing condition, a 40:1 ratio was sufficient to prevent sintering for 4 nm particles [Fig. 3(a)] while sintering still occurred for the 15 nm particles. This may be related to the fact that particles with a larger size have more chance to contact each other in the NaCl matrix during the heat treatments.

It was also found that smaller particles need more time to complete the phase transition. In our experiments, after being annealed for 2 h at 700 °C, the fcc particles with 4 and 8 nm sizes were not transformed to fct completely. Longer annealing time was required to complete the transformation from fcc to fct phase for these particles compared with the 15 nm particles. When the annealing time was increased, a higher NaCl-to-FePt ratio was required to prevent the particles from sintering. For example, when the ratio was increased to 100:1 and the annealing time was extended to 4 h, monodisperse 4 nm FePt particles were obtained, as seen in Fig. 3(b). However, the 100:1 salt-to-particle ratio was not

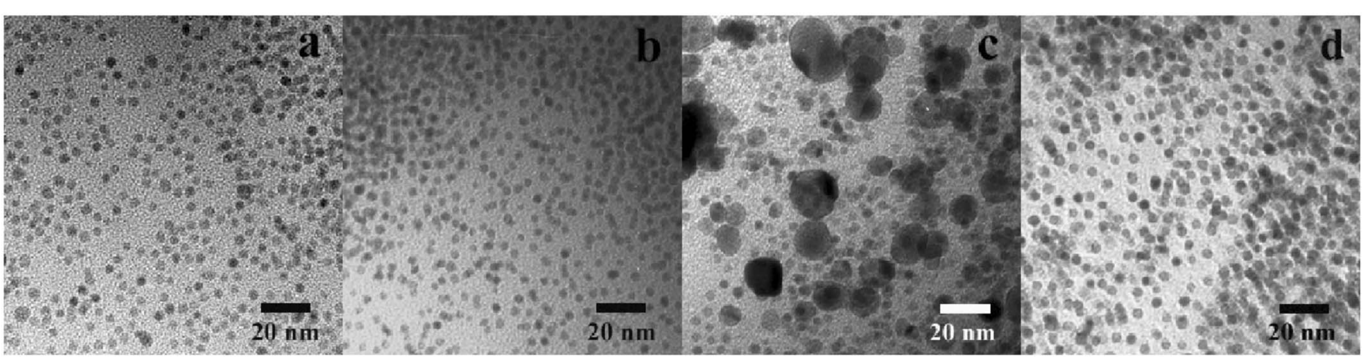

FIG. 3. TEM images of 4 nm FePt nanoparticles annealed in NaCl matrix at (a) 700 °C for 2 h with a NaCl: FePt ratio of 40:1, (b) 700 °C for 4 h with the ratio of 100:1, (c) 700 °C for 8 h with the ratio of 100:1, and (d) 700 °C for 8 h with the ratio of 400:1.

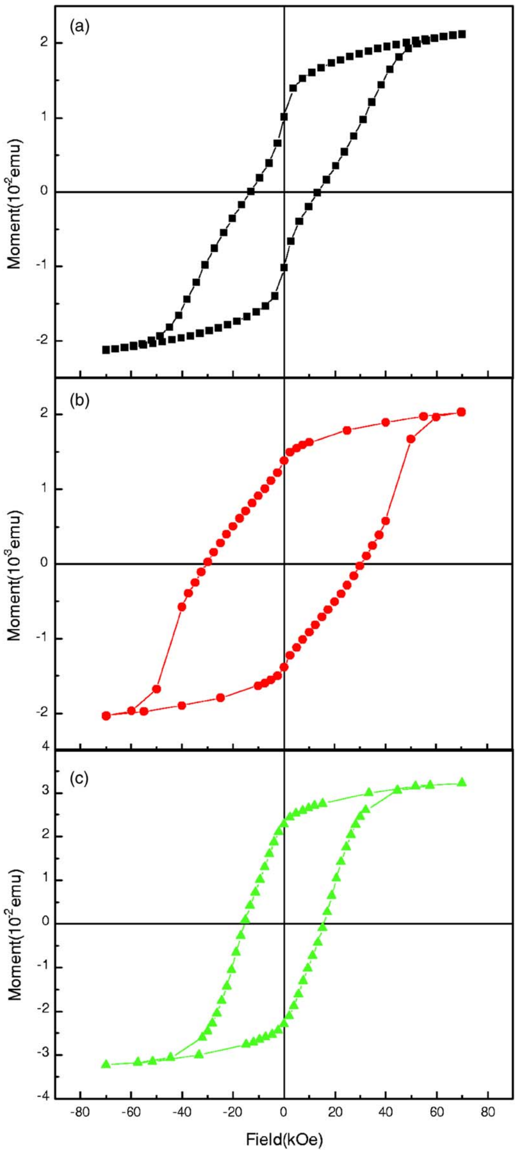

FIG. 4. (Color online) Hysteresis loops of (a) 4 nm FePt nanoparticles annealed at 700 °C for 4 h at a ratio of 100:1, (b) 8 nm FePt nanoparticles annealed at 700 °C for 8 h at a ratio of 400:1, and (c) 15 nm FePt nanoparticles annealed at 700 °C for 2 h at a ratio of 100:1.

sufficient to prevent sintering when the annealing time was increased to 8 h [see Fig. 3(c)]. It is found that the sintering was successfully prevented again [Fig. 3(d)] when the ratio was increased from 100:1 to 400:1. Annealing of larger particles at higher temperatures and extended time should be accompanied by a higher salt-to-FePt ratio in order to avoid sintering.

Figure 4 shows hysteresis loops of the 4, 8, and 15 nm particles annealed at 700 °C for different times with different NaCl-to-FePt ratios, measured by the SQUID magnetometer. Huge coercivity values (up to 30 kOe) have been obtained from the fct nanoparticles. The 8 nm fct particles have the highest coercivity, which may be related to their faceted shape.[9] It can be seen that the hysteresis curve of the 4 nm particles shows a kink even after annealing for 8 h. This may be attributed to the two-phase magnetization behavior and is related to the size-dependent phase-transition behavior, as we discussed above. In the case of the annealing at 700 °C for 4 h, even though the transition has been completed from the XRD pattern, a small amount of fcc phase may still exist. The particle-size-related phase transition and magnetic hysteresis are very interesting and worth to be further studied.

CONCLUSIONS

Salt (NaCl)-matrix annealing, an easy-handling method, has been developed to produce monodisperse fct FePt nanoparticles. Important parameters of this method, such as salt-to-particle ratio, have been carefully investigated. Annealing at higher temperatures and extended time should be accompanied by a higher salt-to-FePt ratio in order to avoid sintering. Larger particles need a higher salt-to-FePt ratio. Giant coercivity up to 30 kOe has been obtained which marked the availability of the smallest permanent magnets in the form of monodisperse nanoparticles free of nonmagnetic impurities. The nanoparticles with very high magnetic anisotropy can be used as building blocks for high-density recording media and high-energy product permanent magnet films or bulks, or can be directly applied in biomedical technology. This salt-matrix annealing technique can be also used for heat treatments of other nano- and microstructures where retained size and shape are required. Moreover, this technique is also significant for massive industrial production because of the low cost and the easy processing procedure.

ACKNOWLEDGMENT

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