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Template-mediated assembly of FePt $L1_0$ clusters under external magnetic field

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FePt $L1_0$-structured clusters were synthesized by hydrogen reduction of $Fe(NO_3)_3 \cdot 9H_2O$ and $H_2PtCl_6 \cdot 6H_2O$ mixtures within the pores of alumina. They were released by dissolving the alumina matrix and capped with organic surfactants. After a series of chemical treatments, clusters with an average diameter of about 11 nm were precipitated. The clusters were drop casted onto ordered nanoporous arrays. Clusters reaching the bottom of the pores formed an ordered magnetic array. The corresponding magnetic film exhibits distinct anisotropic behavior caused by the external magnetic field. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1846592]

I. INTRODUCTION

Face-centered-tetragonal (fct)-structured FePt clusters have large magnetocrystalline anisotropy, high magnetization, and chemical stability. They are promising as building blocks for the fabrication of future high-density recording media and nanocomposite permanent magnets.[1–5] Self-assembled face-centered-cubic (fcc)-structured FePt clusters will produce highly ordered arrays.[1,4] Annealing in a protective atmosphere is necessary to transform the cluster from fcc to fct structure for achieving high magnetocrystalline anisotropy. The combination of self-assembly and subsequent annealing leaves the cluster array magnetically isotropic due to a random easy axis distribution, which is a potential drawback for practical applications. Thus the fabrication of $L1_0$ ordered clusters with narrow size distribution, the control of cluster location, magnetic orientation, and their interactions are important research issues. In this study, a scheme is used to assemble FePt $L1_0$-ordered clusters through the use of ordered nanopore templates and an external magnetic field. The fabrication of the $L1_0$-ordered clusters, location of the clusters after assembly, and the magnetic properties were studied.

II. EXPERIMENTAL METHODS

The $L1_0$-ordered FePt clusters were produced following a procedure modified from our earlier work,[3] and it is summarized as follows: commercially available porous alumina disks (13-mm diameter, 50-μm thickness, and average pore diameter of 200 nm) from Whatman Co. were loaded with 0.3 M alcohol solution of $Fe(NO_3)_3 \cdot 9H_2O$ and $H_2PtCl_6 \cdot 6H_2O$ (Fe:Pt=1:1) mixtures. FePt clusters will be formed inside the pores of the disks by simply heating the loaded disks in flowing hydrogen at 650 °C for 5 min. The disks carrying FePt clusters were soaked in 0.1 M ether solution of octadecanethiol for half an hour. Then they were dried in air and the alumina matrix was dissolved in an aqueous solution of sodium hydroxide. The black precipitate collected by centrifugation was cleaned thoroughly using pure water, and it was then dispersed in 0.1 M ether solution of oleic acid. After proper chemical processings, the FePt clusters with an average diameter of about 11 nm precipitated out and they were dispersed in hexane for further assembly. The alumina templates with an ordered pore distribution were made by two-step anodization of aluminum foils in 0.3 M oxalic acid under a bias of 40 V[6,7] The pore depth is about 600 nm and the pore diameter is about 60 nm. The templates were fixed between two poles of an electromagnet with pores parallel to the applied magnetic field. An assembly of FePt clusters onto alumina templates was accomplished by drop casting. X-ray diffraction (XRD) analysis was carried out with Cu K_α radiation. Magnetic properties were measured by a Quantum Design superconducting quantum interference device (SQUID). Magnetic images and the topographies of the films were obtained using magnetic force microscopy (MFM) with Co/Cr coated tips having coercivity ~400 Oe, as well as by atomic force microscopy (AFM).

III. RESULTS AND DISCUSSION

A. Preparation of FePt $L1_0$ clusters

When a porous alumina disk was loaded with 0.3 M iron and platinum salts solution and heated to 650 °C in hydrogen for 5 min, FePt $L1_0$-ordered clusters were formed inside the disk. Figure 1 is the x-ray diffraction pattern of the corresponding sample. No characteristic peaks can be indexed to the alumina matrix, suggesting that the porous disks are amorphous after heating at 650 °C. Compared with related publications on the synthesis of FePt clusters by hydrogen reduction within a porous alumina matrix,[2,3] it is also found that the cluster formation does not depend on the type of metal salts. For example, either iron chloride, sulfate, or nitrate, when mixed with platinum chloride at concentrations of 1 or 0.3 M and heated in hydrogen at certain temperatures, will lead to the formation of FePt $L1_0$-ordered clusters. This phenomenon demonstrates that the hydrogen reduction method is an efficient and convenient way for producing FePt clusters with high coercivity.

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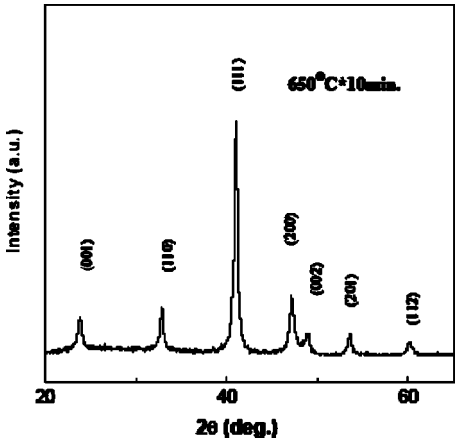

FIG. 1. XRD pattern of hydrogen-reduced iron nitrate and platinum chloride mixtures in porous alumina disks.

FePt clusters produced in this experiment have a size range of 3–45 nm. All of the clusters were capped with octadecanethiol and oleic acid through standard chemical treatments. Clusters with narrow size distribution were precipitated and dispersed in hexane. Figure 2 is a transmission electron microscopy (TEM) image of the FePt clusters assembled on a copper grid with a 10-nm carbon coating. It is estimated that the average diameter of the selected clusters is about 11 nm.

B. Assembly of FePt clusters into templates

Figure 3 is an AFM image of the topography of an alumina template made by two-step anodization in a 0.3 M aqueous solution of oxalic acid at a bias of 40 V. The pores were widened by immersing in a 5% H_3PO_4 aqueous solution for 30 min. An ordered array of pores with a pore diameter of about 60 nm was created. The films were placed with pores parallel to an external magnetic field up to 10 kOe. Several drops of FePt cluster suspension in hexane were spread onto the films and the cluster films were heated to 400 °C for 2 min in nitrogen. It is very interesting to note that no clusters stay on the surface of the templates and no magnetic signal was detected by MFM. These results indicate that all clusters entered the pores to a depth that they were not detectable by the scanning magnetic tip. The capture of clusters by nanopores is mainly induced by the capillary effect.

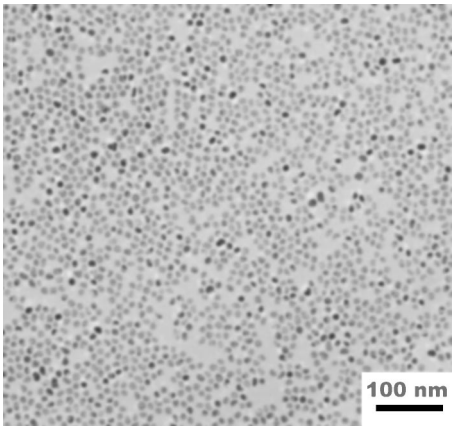

FIG. 2. TEM image of the FePt clusters assembly on a copper grid with a 10-nm carbon coating.

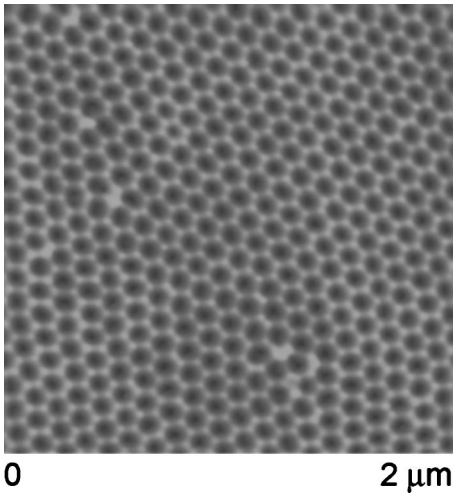

FIG. 3. AFM topography of an alumina template made by two-step anodization in a 0.3 M aqueous solution of oxalic acid.

Additional MFM measurements were conducted on the opposite side of the template, which is the bottom of the pore array. Figure 4 shows the AFM topography (a) and the cor-

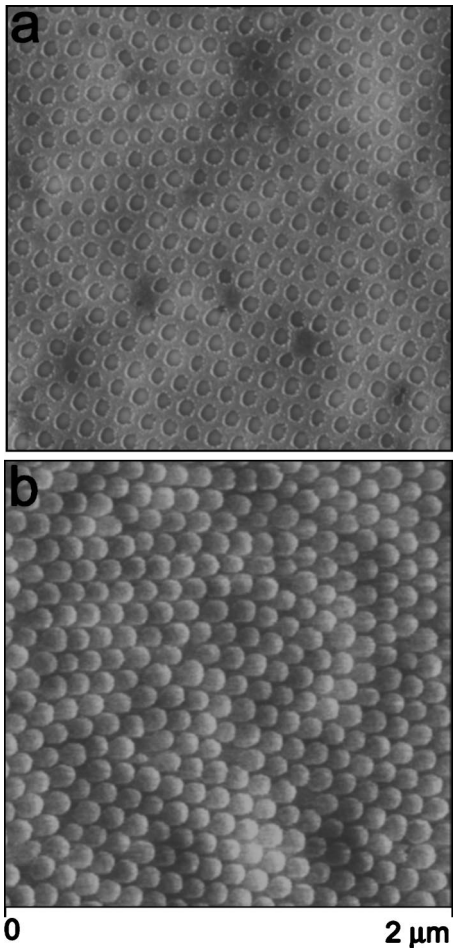

FIG. 4. AFM topography (a) and MFM image (b) on the bottom of the pores after removing the aluminum matrix.

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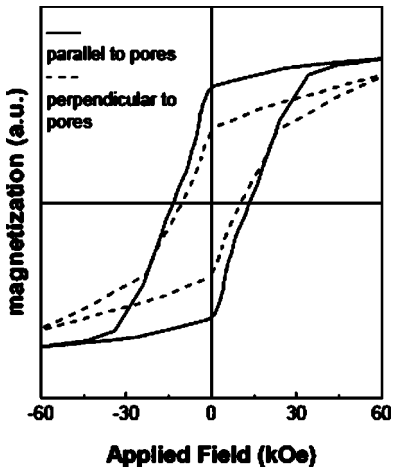

FIG. 5. Hysteresis loops of template-mediated assembly of FePt clusters under an external magnetic field of 10 kOe.

responding MFM image (b) obtained at the ends of the pores after removing the aluminum matrix. The bottom of the template consists of a regular hexagonal array of hemispherical cells, as shown in Fig. 4(a). There is a pore beneath each cell and the cells are the extreme ends that the cluster can reach. This AFM/MFM pair demonstrates clearly that the clusters reached the bottom parts of the pores and formed an ordered magnetic pattern. In other words, the cluster assembly is effectively controlled by the highly ordered array of pores.

C. Magnetic properties

Figure 5 shows two hysteresis loops of the cluster film measured perpendicular and parallel to the pores. The coercivities measured parallel and perpendicular to the pores are 13.4 and 10.2 kOe, respectively. The remanence measured along the pores is also higher than that measured perpendicular to the pores. Partial alignment of the *c* axis to external field is responsible for this anisotropic behavior.

Template-mediated assembly of FePt clusters under a magnetic field is a complex process. Besides the capillary effect from the pores to cluster suspension and the cluster alignment driven by magnetic field, the magnetic dipolar interaction among clusters, interactions of the FePt clusters with alumina and surfactants will all contribute to the assembly process. Further optimization of this process is in progress.

IV. SUMMARY

Hydrogen reduction is a very efficient way to produce FePt $L1_0$-ordered nanoparticles with high coercivity. When the selected FePt clusters were assembled onto highly ordered porous alumina templates, the presence of an external magnetic field aligned their easy axis, which produced magnetic films with anisotropic behavior. The coercivities measured along and perpendicular to the pores were 13.4 and 10.2 kOe, respectively. It is interesting to note that essentially all of the clusters enter the pores after assembly, which means that an ordered pore array will create an ordered array of clusters. The combination of template with magnetic field and cluster assembly is a novel and simple approach to tailor the location of clusters and their magnetic orientation, which may find applications in high-density magnetic recording media, nanodevices, and other related nanotechnology.

ACKNOWLEDGMENTS

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