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Reduced-temperature ordering of FePt nanoparticle assembled films by $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell structure*

He Shu-Li(贺淑莉)†, Peng Yin(彭 印), Liu Li-Li(刘丽丽),
Jiang Hong-Wei(姜宏伟), Liu Li-Feng(刘丽峰), Zheng Wu(郑 鹉), and Wang Ai-Ling(王艾玲)

Department of Physics, Capital Normal University, Beijing 100037*, China*

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In this paper, $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles were synthesized by chemical routine and the layered polyethylenimine (PEI)-$Fe_{30}Pt_{70}/Fe_3O_4$ structure was constructed by molecule-mediated self-assembly technique. The dimension of core/shell structured nanoparticles was that of 4nm core and 2 nm shell. After annealing under a flow of forming gas ($50\%Ar_2+30\%H_2$) for 1 h at or above 400°C, the iron oxide shell was reduced to Fe and diffused to Pt-rich core, which leaded to the formation of $L1_0$ phase FePt at low temperature. The x-ray diffraction results and magnetic properties measurement showed that the chemical ordering temperature of $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles assembly can be reduced to as low as 400°C. The sample annealed at 400°C showed the coercivity of 4 KOe with the applied field of 1.5T. The core/shell structure was suggested to be an effective way to reduce the ordering temperature obviously.

Keywords: FePt, core/shell structure, nanoparticles, magnetic properties
PACC: 7550, 8140

1. Introduction

FePt nanoparticles containing a near-equal atomic percentage of Fe and Pt are an important class of magnetic nanomaterials. They are known to have a chemically disordered face-centred cubic (fcc) structure or a chemically ordered face-centred tetragonal (fct) structure.[1] The fcc-structured FePt is magnetically soft whereas fct-structured FePt is magnetically hard. $L1_0$ ordered FePt film with fct-structure has been commonly regarded as a promising candidate for future ultrahigh density magnetic recording media due to its large magnetocrystalline anisotropy.[2−7] FePt films are usually constructed by physical vapour deposition method or chemically polymer-mediated self-assembly technique. The later becomes more and more attractive because of simple synthesis routine, narrow grain size distribution and separated nanoparticles.[8−12]

As chemically synthesized, the FePt nanoparticles have a fcc structure and is magnetically soft. Thermal annealing at high temperature is needed to transform the fcc structure into fct structure. However, the annealing also results in particle aggregation, leading to wide size distribution and strong intergrain exchange coupling.[13−15] Although many efforts have been made to prevent this uncontrolled agglomeration,[16−25] however, lowering ordering temperature is still challenging to the application of FePt films in high-density magnetic data storage.

Quite recent works[26,27] reported that FePt particle size was sensitive to the ordering process. The chemical ordering is more complete for FePt nanoparticles with larger size when the particles were annealed at the same condition. The chemical ordering of FePt was entirely inhibited when its size is smaller than a critical value around 2 nm. It is well known that FePt nanoparticles are commonly synthesized by decomposition and reduction or co-reduction methods. These methods can yield FePt nanoparticles with controlled composition and narrow size distribution but fail to produce particles larger than 4 nm. In this paper, $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell structure was synthesized followed by annealing under a reducing atmosphere. The iron was expected to be reduced from iron oxide shell and diffused to the Pt-rich core, which can lead to the formation of larger FePt nanoparticles during annealing process.

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†E-mail: hsl-phy@mail.cnu.edu.cn

2. Experimental details

The synthesis was carried out by using standard airless procedures and commercially available reagents. FePt nanoparticles were produced by reduction of $FeCl_2$ and $Pt(acac)_2$ at 200°C, followed by refluxing at 263°C. The particles growth is self-limited and about 4 nm FePt nanoparticles are readily separated.[15] This synthesis used $FeCl_2$ instead of thermally unstable $Fe(CO)_5$ and the composition of FePt nanoparticles was easily tuned. Then the as-synthesized $Fe_{30}Pt_{70}$ nanoparticles were used as seeds for iron oxide shell to be grown upon them through polyol process.[28] This polyol process, based on a heterogeneous seeded-growth mechanism, involves iron (III) acetylacetonate and 1,2-hexadecanediol. Experimental conditions should be controlled well so that all growth occurs upon the preformed seeds and little additional homogeneous nucleation of new particles takes place. The thickness of iron oxide shell was controlled 1nm by the relative amount of preformed particles and newly added iron salt.

A naturally oxidized silicon substrate was cleaned by using ethanol and dried under a flow of N_2. The substrate was functionalized by polyethylenimine (PEI), then was immersed into the hexane dispersion of FePt nanoparticles.[15] This yielded one layer of PEI and $Fe_{30}Pt_{70}/Fe_3O_4$ assembly. By repeating the coating of PEI and $Fe_{30}Pt_{70}/Fe_3O_4$, the multilayer of $Fe_{30}Pt_{70}/Fe_3O_4$ nanoparticle assembly was fabricated.

4-layer of $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles self-assembled on a PEI-modified silicon oxide surface was constructed. The post annealing was performed at the temperatures from 350 to 650°C for 60 min under a flow of 50%Ar+50%H_2 atmosphere. The magnetic properties were measured at room temperature by using an vibrating sample magnetometer (ADE company). Film crystallographic structures were examined by Rikagu RB x-ray diffractometer using Cu Kα radiation. Microstructural observation of FePt nanoparticles and films were carried out on transmission electron microscope (TEM) (JOEL 100×). TEM samples were prepared by evaporating a drop of diluted particle solution deposited onto the carbon coated copper grid.

3. Results and discussion

Figures 1(a) and 1(b) show the x-ray diffraction (XRD) spectrum and TEM of $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles respectively. The XRD result suggests the coexistence of two phases in as-synthesized $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles: chemically disordered fcc FePt and iron oxide. TEM image shows $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles with 4nm core and 1nm shell, which was also observed by high resolution TEM (HRTEM) in the previous works.[16,20] The different contrast between the core and shell region is due to the different electron penetration efficiency on metallic FePt and iron oxide.

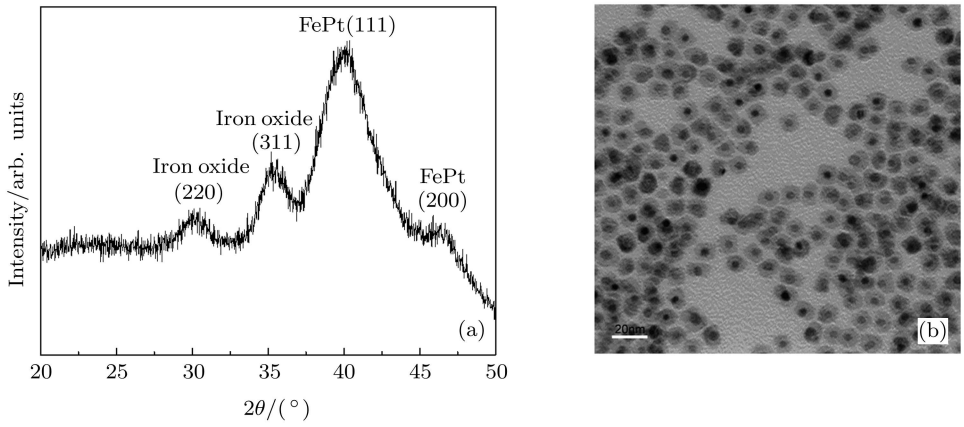


Fig.1. XRD spectra (a) and TEM image (b) of $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles.

Figure 2 shows the XRD patterns of 4-layer $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles assemblies annealed at different temperatures. The XRD spectra of the thin assembly annealed at 350°C indicate the coexistence of fcc FePt phase and iron phase. The relatively strong (111) peak of iron suggests a crystallographic alignment in iron shell. It is clear that the positions of the (111) peak shift to higher angle with

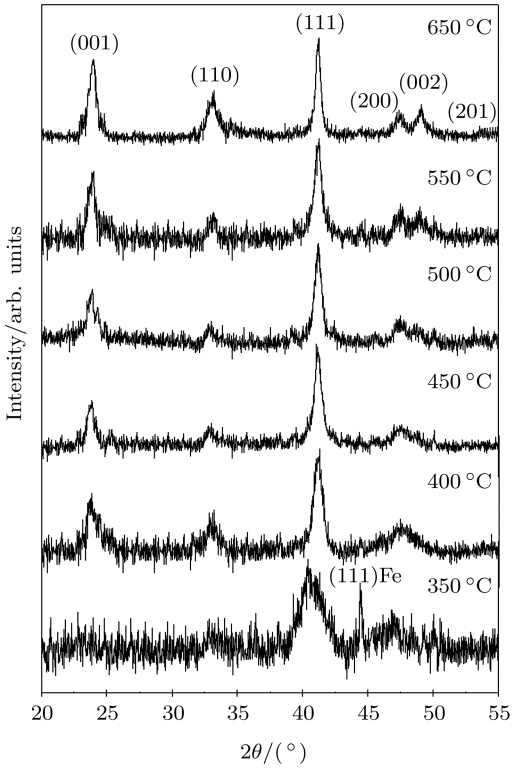


Fig.2. XRD patterns of 4-layer $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles assemblies annealed at different temperatures.

increasing temperature. This shift is caused by the change of lattice parameters during the phase transition from fcc to fct. The typical superlattice peaks of (001) and (110), which are the characteristic of the ordered FePt compound phase, start to appear when the assembly was annealed at 400°C. With increasing annealing temperature, the fcc–fct phase transition was more complete, shown by the more pronounced (001) and (110) peaks. It should be noted that the diffraction peak of iron disappeared for the assemblies was annealed at 400°C or above, which indicates that the reduced iron in shell has already diffused to FePt core. Therefore, larger FePt particles can be obtained by annealing $Fe_{30}Pt_{70}/Fe_3O_4$ the core/shell structured nanoparticles under reductive atmosphere. Many efforts have been made to study the size effect on the ordering of $L1_0$ FePt nanoparticles. The previous work shows that the ordering temperature is very sensitive to the size of nanoparticles. Direct experimental evidence and calculation both showed that the long-range ordering parameter S decreased with reduced particle size and the ordering of $L1_0$ FePt is entirely inhibited when its size $d \leq 2\,\mathrm{nm}$.[26,27] Larger particle size not only results in lower ordering temperature but also withstands higher temperature annealing without noticeable particle sintering.

To evaluate the effect of chemical ordering of the $L1_0$ FePt in a quantitative way, the following equation was used to calculate the ordering parameter S

$$S \cong 0.85 \left[\frac{I_{001}}{I_{002}}\right]^{1/2}. \quad (1)$$

Where I is the integrated intensity of [001] and [002] peaks from XRD patterns respectively. The long-range S value of fct-FePt nanoparticles annealed at different temperatures was calculated according to Eq.(1). Figure 3 shows the relation between the annealing temperature and S. As expected, S increases with increasing temperature. As shown in Fig.3, S of the assembly annealed at 400°C almost reaches 0.8. In the case of the assembly annealed at 350°C, S vanishes because of no superlattice peaks. It was reported that fcc FePt is the only phase observed in XRD patterns at the annealing temperature of 400°C.[25] Liu *et al*[27,29] reported that the ordering parameter of 8nm FePt nanoparticles is less than 0.7 after annealing at 600°C for 2 hours. However, our results exhibit that chemical ordering can take place at the temperature as low as 400°C. The iron oxide shell is reduced to Fe and diffuses to Pt-rich core after $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles are annealed under reductive atmosphere, which can lead to larger size of FePt particle than that of core. The diffusion of iron in shell to core can promote the rearrangement of Fe atoms and Pt atoms during chemical ordering process. Therefore, the reduced ordering temperature results from not only larger particle size but also the concentration difference of iron atoms between shell and core.

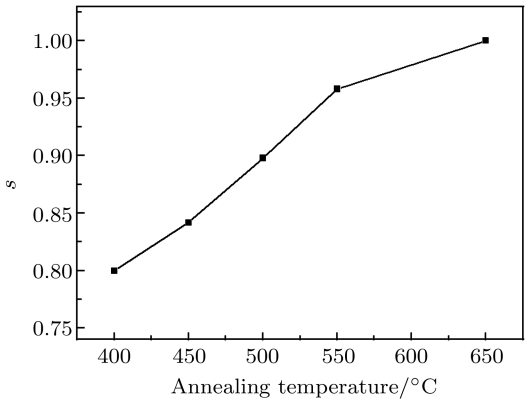


Fig.3. Dependence of long-range order parameters S on the annealing temperature.

Figure 4 shows the in-plane and out-plane hysteresis loops of 4-layer $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell

nanoparticles assemblies annealed at different temperatures. It is evident that the assembly annealed at 350°C is magnetically soft, which results from the phases of fcc FePt and iron as shown in Fig.2. The assembly annealed at or higher than 400°C is magnetically hard because of the appearance of superlattice structure in the annealed assembly. It is well known that ordered $L1_0$-FePt is magnetically hard and Fe_3O_4 is a much softer magnetic material. It should be noted that the hysteresis loops of the assemblies annealed at the temperatures from 400–650°C are magnetically hard and show single-phase behaviour. The magnetic measurement further confirms that Fe_3O_4 was reduced to Fe and Fe atoms diffused to FePt core in $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles assemblies annealed at the temperatures from 400–650°C. The diffusion of Fe atom to FePt core and fcc-fct phase transition can take place simultaneously in $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles assemblies during annealing process under reductive atmosphere.

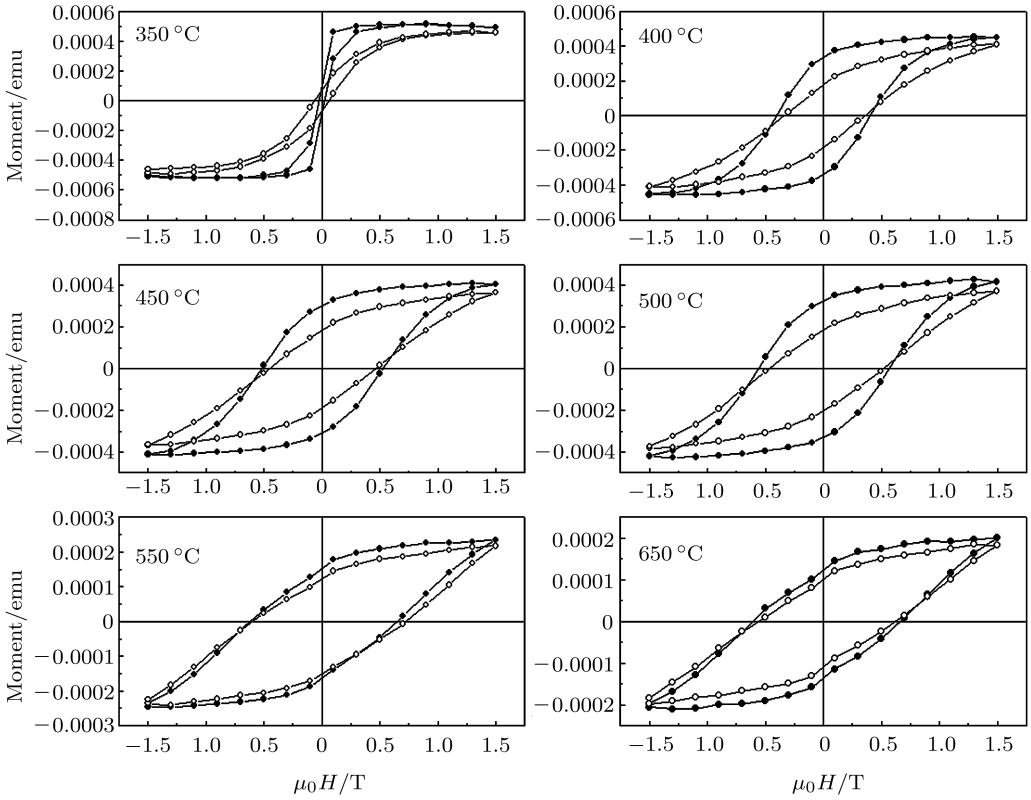


Fig.4. In-plane (solid symbols) and out-plane (open symbols) hysteresis loops of 4-layer $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles assemblies annealed at different temperatures.

Detectable difference between the loops measured in different directions can be found in Fig.4. According to the Stoner–Wohlfarth model, the ensemble of non-interaction particles should exhibit the same magnetization behaviour in different directions. Figure 4 shows that the films is easy to be magnetized in plane and difficult to be magnetized out of plane, which seems to result from the dipolar interaction between the nanoparticles. If the magnetic poles of the particles are parallel and lie in the plane of film, the magnetic line can connect each other and the stray field energy of the system is low. Otherwise, the stray field energy is high in the case of the magnetic pole of the particle perpendicular to the plane of film. The competition between the magnetocrystalline anisotropy and dipolar interaction determines the magnetization behaviour of the films.[30−32] The assemblies annealed at low temperatures are composed of FePt with small magnetocrystalline anisotropy and their magnetization behaviours are determined by the dipolar interaction. Therefore, they are difficult to be magnetized out of plane. The magnetocrystalline anisotropy

of FePt nanoparticles increases rapidly with increasing temperature when the temperature is equal to or higher than 400°C. It is confirmed by XRD results that the obvious superlattice peak can be found for the assemblies annealed at or above 400°C. It means that the effect of magnetocrystalline anisotropy is dominant in comparison with that of dipolar interaction for the assemblies annealed at higher temperatures. So, the difference between magnetization curves measured in different directions decreases with increasing annealing temperature.

4. Conclusion

In summary, FePt nanoparticles were enlarged by the diffusion of Fe atoms from the reduced shell to core during annealing process. The $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles self-assembled on a PEI-modified silicon oxide surface were annealed at the temperature from 350°C to 650°C under a flow of $50\%Ar+50\%H_2$ atmosphere. Iron was reduced from shell iron oxide to and diffused to Pt-rich core when the annealing temperature was equal to or larger than 400°C. The larger FePt particles size was achieved after $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles were annealed under reductive atmosphere. The sample annealed at 400°C showed the coercivity of 4KOe ($3.08 \times 10^5 A/m$) with the applied field of 1.5 T. The reduced ordering temperature was resulted from both larger particles obtained by annealing $Fe_{30}Pt_{70}/Fe_3O_4$ core/shell nanoparticles under reductive atmosphere and diffusion of iron atoms in shell to Pt-rich core.

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