

## Easy axis alignment of chemically partially ordered FePt nanoparticles

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Partially ordered Fe<sub>53</sub>Pt<sub>47</sub> nanoparticles with size around 8 nm were prepared by the simultaneous decomposition of iron pentacarbonyl and platinum acetylacetonate. The high boiling point chemical, hexadecylamine, was used as a solvent, and 1-adamantanecarboxylic acid was used as a stabilizer. X-ray diffraction measurements reveal that as-made FePt particles were partially transformed into the ordered L1<sub>0</sub> phase with some weak superlattice peaks. The room-temperature hysteresis loop and remanence curve suggest a broad distribution of anisotropies in the partially ordered particles. By coating the partially ordered FePt nanoparticles with a polyvinylchloride polymer binder, the particles could be re-dispersed in cyclohexanone. Furthermore, the easy axis of the particles coated with the polyvinylchloride polymer binder could be aligned under an external field. Easy axis alignment was confirmed from both alternating gradient magnetometer and x-ray diffraction measurements. © 2005 American Institute of Physics. [DOI: 10.1063/1.1856698]

The synthesis and assembly of small hard magnetic nanoparticles have attracted much attention because of their potential applications in ultrahigh-density magnetic recording.<sup>1–7</sup> Nanoparticles of ferromagnetic materials with reduced sizes can support only single magnetic domains and potentially lead to dramatic increases in storage density. The ordered L1<sub>0</sub> phase of FePt systems possesses high magnetocrystalline anisotropy ( $K_u$ :  $\sim 7 \times 10^7$  erg/cc) and allows the use of thermally stable particles with 3–4 nm in diameter as the basic unit for recording. However, the as-synthesized particles are reported to be superparamagnetic, chemically disordered, and fcc in structure. To obtain the L1<sub>0</sub> structure, the particles need to undergo annealing at a temperature as high as 580 °C. The postannealing leads to poor control over the spatial arrangement of nanoparticles through extensive particle aggregation. Additionally, since the particles prepared with the conventional method are chemically disordered,<sup>1</sup> organizing them on a surface with their magnetic easy axes aligned is difficult, limiting their technological applications. Recently, Jeyadenvan *et al.* have tried to directly synthesize partially ordered FePt nanoparticles at 300 °C.<sup>8</sup> Also Reiss *et al.* have made partially ordered FePt nanoparticles using a biological route.<sup>9</sup> However, the nanoparticles prepared with these methods were significantly aggregated. In this letter, we report a simple route to directly synthesize and align partially ordered and re-dispersible FePt nanoparticles.

The synthesis of partially ordered Fe<sub>53</sub>Pt<sub>47</sub> nanoparticles involves the thermal decomposition of Fe(CO)<sub>5</sub> and Pt(acac)<sub>2</sub> in a high boiling point solvent. The experiments were carried out using standard airless procedures. A mixture of platinum acetylacetonate (120 mg), 1-adamantanecarboxylic acid (ACA 250 mg), and hexadecylamine (HDA 8 g) was heated to 100 °C in a three-necked round-bottom flask under a nitrogen atmosphere. After these chemicals were completely dissolved in HDA, the mixture was heated to 160 °C, and Fe(CO)<sub>5</sub> (0.05 mL) was added to this solution via syringe. Then the temperature was quickly increased to 350–360 °C and held there for 3 h. During syn-

thesis, a mechanical stirrer was used to avoid agglomeration of the partially ordered FePt nanoparticles. After cooling, the inert gas protected system could be opened to ambient environment. The black product was precipitated by adding 40 ml of ethanol (or hexane), and the mixture was centrifuged to isolate the particles from the brown supernatant. The dispersibility of the final black product, Fe<sub>53</sub>Pt<sub>47</sub>, was tested in several different hydrophobic solvents, such as hexane, toluene, and cyclohexanone.

The microstructure and morphology of the partially ordered FePt nanoparticles were observed using a Hitachi model H-8000 transmission electron microscope (TEM). In hexane and toluene solvents with a small amount of oleic acid and oleylamine as stabilizers, the partially ordered FePt particles tend to precipitate and aggregate. Figure 1(a) is a typical TEM image for the partially ordered FePt particles with hexane as the solvent. Clearly, the agglomeration was significant. In principle, only dispersed particles can be aligned; however, it is hard to separate and align aggregated particles. Therefore, appropriate surfactants and solvent need to be found in order to re-disperse the partially ordered FePt nanoparticles. Polyvinylchloride (PVC) is well known as a polymer binder for magnetic tape particles.<sup>10</sup> It can be dissolved in cyclohexanone. Before the ligands were exchanged, the FePt particles were cleaned with acetone. Then the particles and the PVC-cyclohexanone solution were mixed using an ultrasonic agitator for several hours. This procedure yielded a stable FePt dispersion. Figure 1(b) shows the TEM image of partially ordered FePt nanoparticles coated with the PVC polymer binder. Although there was a somewhat broad distribution of particle sizes, it is obvious that the particles were separated. There was no significant aggregation, which would make it easier for the particles to be aligned under an external magnetic field. The average particle size was about 8 nm.

In-plane magnetic hysteresis loops and remanence curves were measured on a Princeton Micromag 2900 alternating gradient magnetometer using a 19 kOe saturating field. Shown in Fig. 2(a) are the room-temperature hysteresis loop and remanence curve of the as-made FePt nanoparticles. The value of  $M_s$  was not determined because of the unknown

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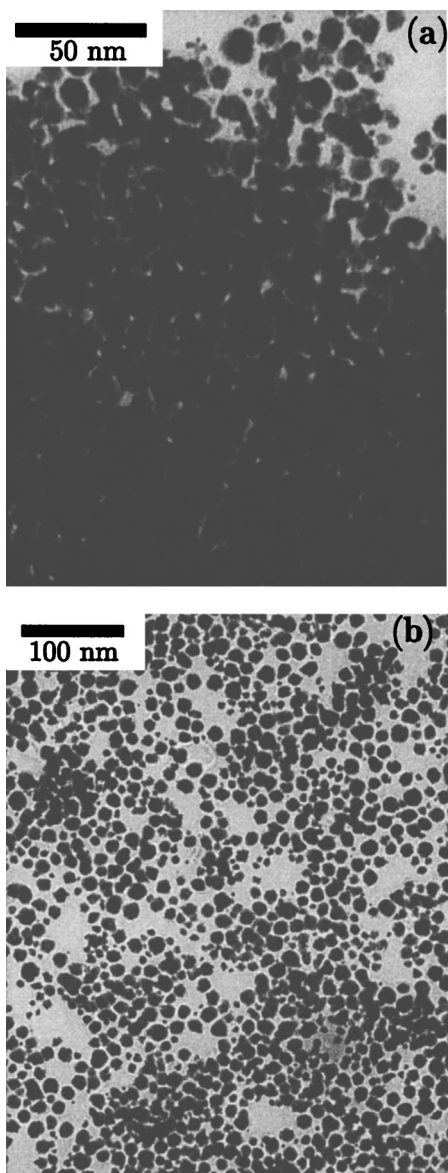


FIG. 1. TEM images of partially ordered FePt nanoparticles in different solvents: (a) hexane and (b) cyclohexanone with PVC coating.

amount of surfactants in the films. The hysteresis loop shows that the partially ordered FePt particles have a sufficient anisotropy to be ferromagnetic at room temperature. The hysteresis loop coercivity is about 600 Oe; however, the loop is wide open and hard to saturate. The remanence coercivity obtained from the remanence curve is about 2.5 kOe, which is four times larger than the hysteresis coercivity. The large remanent to hysteresis coercivity ratio and the shapes of the hysteresis loop and remanence curve suggest a broad distribution of anisotropies in the partially ordered particles.<sup>11</sup> The squareness of the hysteresis loop is about 0.5 due to the three-dimensional random distribution of easy axes. Delta-M measurements show a small negative peak and indicate a weak magnetostatic interaction between these particles. In order to align the easy axes of particles, the particle dispersion was first dropped onto a Si substrate. A magnetic field was then applied in a direction parallel to the surface of the substrate while the solvent was allowed to slowly evaporate. For a small field of a few hundred oersted, there was only a slight difference in the squareness and coercivity for the directions parallel and perpendicular to the field direction.

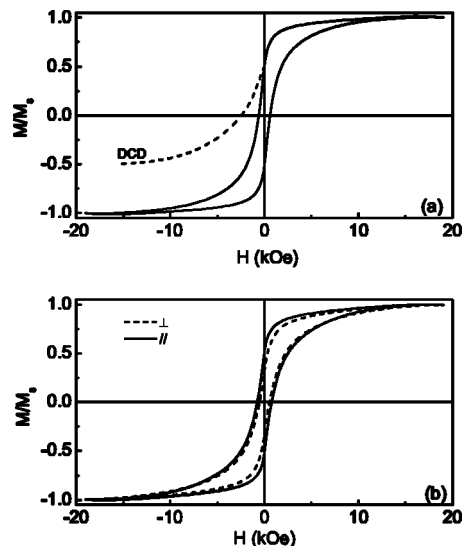


FIG. 2. (a) In-plane hysteresis loop and remanence curve for partially ordered FePt nanoparticles. (b) In-plane hysteresis loops for applied field parallel (solid line) and perpendicular (dashed line) to the aligning direction. All measurements are done at room temperature.

When a large magnetic field was applied, these differences were obvious. Figure 2(b) shows the hysteresis loops for partially ordered FePt nanoparticles under a 10 kOe external magnetic field. The squareness values are now  $\sim 0.35$  measured perpendicular to the aligning field direction and  $\sim 0.60$  measured parallel to the aligning field direction, while the coercivities in the perpendicular and parallel directions are  $\sim 500$  and  $\sim 800$  Oe, respectively. The angular dependence of squareness and coercivity obtained from in-plane hysteresis loops are plotted in Fig. 3. It is clear that the easy axes were preferentially aligned for the partially ordered FePt nanoparticles. X-ray diffraction (XRD) measurements noted in the following further confirmed this result.

The crystal structure and size of the FePt nanoparticles were determined on a Rigaku model D/MAX-2BX thin film diffractometer using  $\theta-2\theta$  scans. Figure 4(a) shows the XRD spectrum of as-made FePt nanoparticles before align-

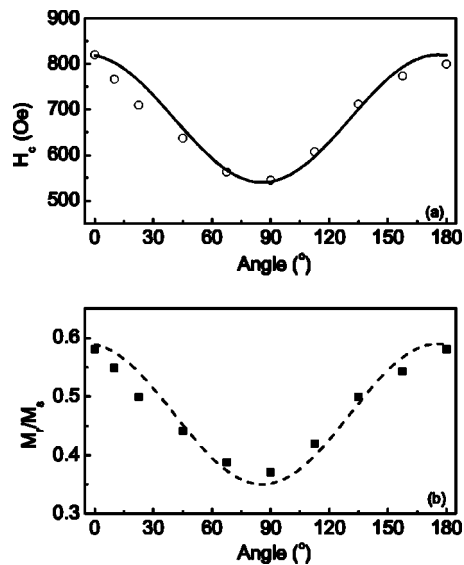


FIG. 3. The angular dependence of (a) coercivity and (b) squareness for partially ordered FePt particles aligned under a 10 kOe field. The lines are drawn as a guide for the eye.

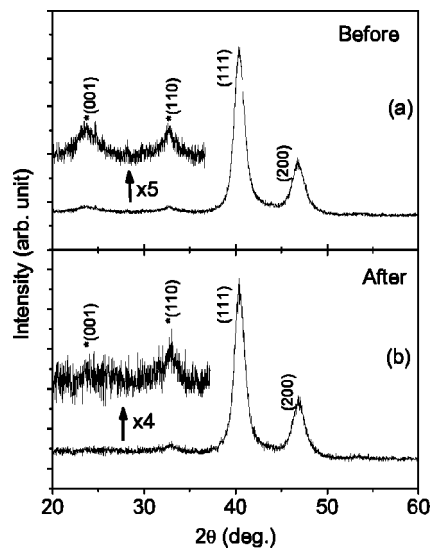


FIG. 4. XRD patterns for FePt nanoparticles: (a) before and (b) after aligning.

ment. From a Scherrer analysis of the linewidth, the average particle size was estimated to be  $\sim 8$  nm, which is close to that shown in the TEM image above. Careful examination of the curve in Fig. 4(a) shows that very weak (001) and (110) peaks for the tetragonal FePt phase appeared for as-made nanoparticles, which indicates that FePt nanoparticles were partially transformed to the fct structure, Figure 4(b) shows the XRD patterns for the partially ordered FePt nanoparticles aligned under a 10 kOe external magnetic field. In this spectrum, the (001) superlattice peak is nearly absent. This clearly confirms that the  $c$  axes of the partially ordered nanoparticles are preferentially aligned in the plane of the film.

In order to determine the anisotropy field,  $H_k$ , and thermal stability factor,  $K_u V/kT$ , of the partially ordered particles, the remanent coercivity was measured as a function of time.<sup>12</sup> A fit to the Sharrock formula gave  $K_u V/k_B T = 80$  and an intrinsic (short time) remanent coercivity of 4.5 kOe. This gives  $H_k \sim 2H_0 = 9$  kOe and  $K_u \sim H_0 M_s \sim 5 \times 10^6$  erg/cc. By comparison, the values for fully ordered bulk  $L1_0$  are  $H_k \sim 120$  kOe and  $K_u \sim 7.7 \times 10^7$  erg/cc.<sup>13</sup> In principle, it should be possible to enhance the anisotropy of the aligned nanoparticle array by postannealing in a magnetic field. This

would require a different binder that would survive the high annealing temperatures while inhibiting particle sintering.

In summary, we have reported the direct synthesis of partially ordered 8 nm FePt nanoparticles by the thermal decomposition of  $\text{Fe}(\text{CO})_5$  and  $\text{Pt}(\text{acac})_2$  in the high boiling point solvent, HDA. After the particles were coated a PVC polymer binder, they could be re-dispersed in cyclohexanone and the dispersion was stable for more than one month without precipitation. The hysteresis loop and remanence curves reveal a broad distribution of anisotropies in the partially ordered particles, which could result from a distribution of chemical ordering and/or particle sizes. The PCV polymer coated FePt nanoparticles could be aligned in a magnetic field. Further investigations are under way to improve the size and anisotropy distributions of the particles and the quality of the dispersion in order to increase the orientation.

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