

Ultrafine FePt Nanoparticles Prepared by the Chemical Reduction Method

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ABSTRACT

Monodisperse FePt nanoparticles with particle size of about 2 nm have been prepared by 1,2-hexadecanediol reduction of iron acetylacetonate and platinum acetylacetonate in dioctyl ether. The as-synthesized particles have a chemically disordered fcc structure and can be transformed into chemically ordered fct structure after thermal processing at temperatures above 500 °C. The ordered fct FePt phase has high magnetic anisotropy and thus large coercivity up to 1.8 T.

Chemically synthesized magnetic nanoparticles have drawn much attention^{1–3} due to the unique magnetic properties derived from small particle sizes and uniform size distribution. FePt hard magnetic nanoparticles are of special interest as they may be used for future ultrahigh-density magnetic recording media⁴ and high performance permanent magnetic nanocomposites.⁵ Previous work on the synthesis of FePt nanoparticles involved the reduction of Pt(acac)₂ and the decomposition of Fe(CO)₅.⁶ Other works included addition of Ag, Co to the FePt nanoparticles to improve their physical and magnetic properties.^{2,7} Recently, the formation of FePt nanoparticles via the simultaneous reduction of FeCl₂ and Pt(acac)₂ as well as Fe and Pt acetylacetonate has also been reported.^{8,9} Particle size produced by the above-mentioned methods is generally around 3–4 nm.

In this letter we report an alternative approach for synthesizing FePt nanoparticles with size of only about 2 nm in diameter. The process involves simultaneous chemical reduction of Pt(acac)₂ and Fe(acac)₃ by 1,2-hexadecanediol at high temperature in solution phase. The as-synthesized FePt particles have chemically disordered fcc structure and can be transformed into the chemically ordered fct structure after proper thermal treatment. The fct structured FePt nanoparticle assemblies exhibit hard magnetic properties with coercivity reaching as high as 1.8 T.

The synthesis was handled under standard airless techniques in an argon atmosphere. The reagents were obtained

from commercial sources and used without further purification. A mixture of 0.5 mmol of Pt(acac)₂, 0.5 mmol to 2 mmol of Fe(acac)₃, and a corresponding amount of 1,2-hexadecanediol was added to a 125 mL European flask containing a PTFE coated magnetic stir bar. Dioctyl ether (30 mL) was then transferred into the flask and the contents stirred while purging with Ar for 20 min at room temperature. The flask was then heated to 100 °C and held at 100 °C for 20 min. During this hold, 0.05 mmol (0.17 mL) of oleylamine and 0.05 mmol (0.16 mL) of oleic acid were injected into the flask while continuing the Ar purge. After the 20 min hold, the mixture was maintained under an Ar blanket and heated to 295 °C at a rate of approximately 7 °C per minute. The flask was maintained at the refluxing temperature of 295 °C for 30 min before cooling down to room temperature under the Ar blanket. Afterward, all handling was performed open to the atmosphere.

Purification of the nanoparticles was accomplished as follows: 5 mL of the dispersion taken from the flask was added to 20 mL of ethyl alcohol (EtOH) and the mixture centrifuged (6000 rpm for 15 min). The supernatant was discarded and the precipitate redispersed in 10 mL of hexane and 5 mL of EtOH. Additional small amount of oleylamine and oleic acid might be added to aid in redispersing the nanoparticles. This dispersion was centrifuged for 15 min at 6000 rpm. The supernatant was transferred to a new centrifuge tube, discarding any precipitate that separated. An additional 15 mL of EtOH was added to this dispersion and centrifuged again. The supernatant was discarded and the remaining dark brown precipitate redispersed in hexane and stored under refrigeration.

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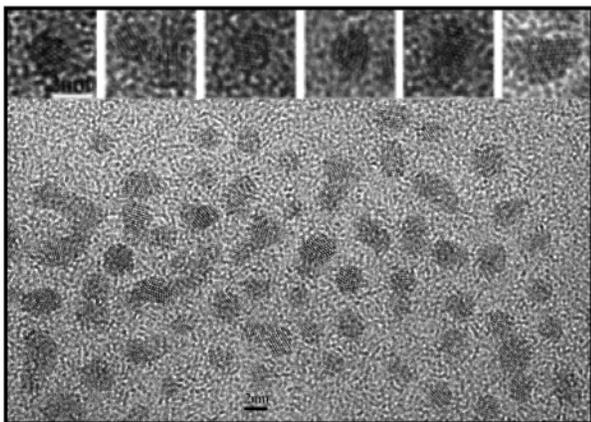


Figure 1. TEM image of the as-synthesized FePt particles. The HRTEM images of individual particles selected at random are shown at the top. The scale of these images is 2 nm and it is shown in the first image on the top left corner.

Samples for magnetic characterization were prepared by depositing a few drops of the final dispersion onto a 3×3 mm silicon substrate and evaporating the solvent at room temperature, which led to the formation of the FePt nanoparticle assemblies on the substrate. The samples were then dried in a vacuum to remove volatile organics from the assemblies. The samples were annealed either in N_2 or $Ar+H_2$ (7%) atmosphere for 30 min at temperatures between 500 and 600 °C. Magnetic hysteresis loops of the samples were measured by a magnetic properties measurement system (MPMS). X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to identify the crystal structures and the particle sizes. An inductively coupled plasma–optical emission spectroscopy (ICP) technique was performed on the samples to determine their chemical composition.

Figure 1 shows a typical TEM image of the as-synthesized FePt nanoparticles. The particle sizes are approximately 2 nm. The row of images at the top represents the HRTEM of individual particles. Careful examination of the HRTEM images reveals that the particles show good crystallinity with many being single crystals and some possessing multiple twin boundaries within the particle. The crystal structure of the particles is chemically disordered fcc and the (100) lattice spacing is about 3.8 Å, which is consistent with the known fcc FePt structure.^{10,11}

XRD patterns in Figure 2 show that the as-synthesized nanoparticles possess a chemically disordered fcc crystal structure. Such structure has low anisotropy and hence needs to be annealed in order to obtain the fct phase with high uniaxial magnetocrystalline anisotropy responsible for the high coercivity.¹² Figure 2 also shows the XRD pattern for the sample annealed in nitrogen at 600 °C for 30 min and the XRD pattern for the fct FePt sample produced by the method outlined in ref 6. It can be clearly seen from this figure that both the peak position and intensity for the annealed sample prepared by our new method match perfectly with those of the sample made from other known methods, indicating that fct FePt is indeed formed after thermal annealing.

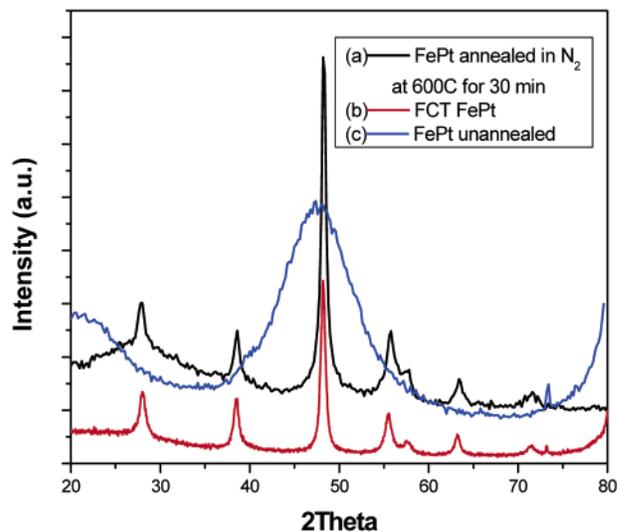


Figure 2. X-ray diffraction patterns of (a) the annealed FePt particle assemblies, (b) the standard fct FePt structure prepared using the procedure in ref 6, and (c) the as synthesized FePt nanoparticle assembly.

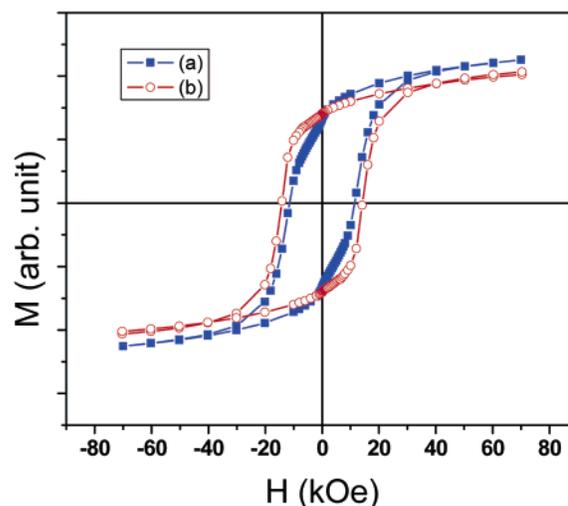


Figure 3. (a) Hysteresis loop of the sample annealed in N_2 at 600 C for 30 min, (b) hysteresis loop of the sample annealed in FG at 600 C for 30 min, with a coercivity of about 1.8 T. Both samples are from the 2:1 precursor mole ratio synthesis.

The in-plane hysteresis loops for the samples synthesized using a 2:1 precursor mole ratio ($Fe(acac)_3/Pt(acac)_2$) and annealed in nitrogen and forming gas are shown in Figure 3. The coercivity of the sample annealed in forming gas is about 1.8 T, indicating the high magnetocrystalline anisotropy of the fct FePt phase. The ICP analysis of these samples revealed their final particle composition to be $Fe_{44}Pt_{56}$. The coercivity of the samples annealed in nitrogen is less than the coercivity of the samples annealed in forming gas with all other variables being the same. This observation is in agreement with ref 13. Forming gas being a reducing atmosphere reduces any iron in the oxidized state present in the nanoparticles, thereby improving the chemical ordering in the fct crystal structure and hence the coercivity. Nitrogen is an inert atmosphere, unlike forming gas, and it cannot change the chemical composition of the particles during

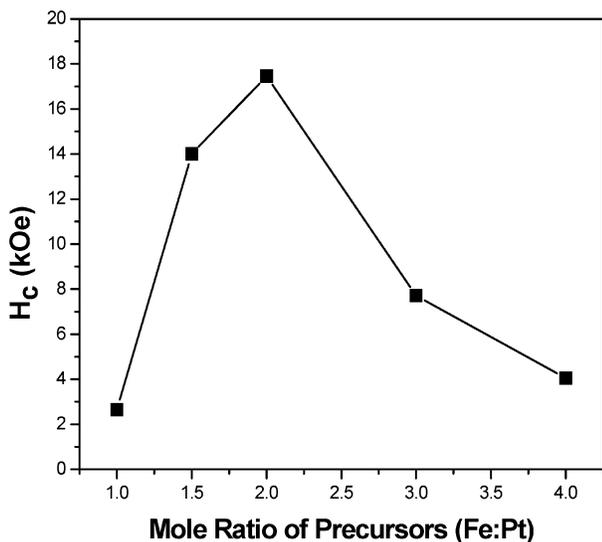


Figure 4. Coercivity as a function of initial mole ratio of the precursors $\text{Fe}(\text{acac})_3/\text{Pt}(\text{acac})_2$ for the samples annealed in FG at 600 °C for 30 min. The maximum coercivity is about 1.8 T for the 2:1 mole ratio sample.

annealing. From both XRD patterns and little difference between the in-plane and out-of-plane hysteresis loops, we concluded that as with the previous FePt nanoparticle assemblies, our FePt particle assemblies also show random orientation in magnetic easy axis.

The final particle composition was changed by changing the initial mole ratio of the precursors. However, the initial mole ratio of the precursors was not carried over to the final product. Figure 4 shows the coercivity dependence on the composition of the FePt samples annealed in forming gas at 600°C for 30 min. The coercivity of the annealed nanoparticles was found to increase rapidly to 1.8 T with increasing mole ratio of the precursors for ratios up to 2 and then decreased as the ratio is increased further to 4. We expect that the coercivity can be increased further if the synthesis and thermal processing are optimized.

In conclusion, FePt nanoparticles with particle size of 2 nm have been successfully synthesized by a polyol reduction

process. The chemicals used in this process have the advantages of nontoxicity, nonvolatility, and storage stability over the chemicals used in previous FePt synthesis. The as-synthesized FePt nanoparticles have chemically disordered fcc structure that can be transformed into chemically ordered fct structure through thermal annealing. Magnetic hardening is observed in the fct structured nanoparticles. The 2:1 mole ratio between $\text{Fe}(\text{acac})_3$ and $\text{Pt}(\text{acac})_2$ precursors resulted in FePt nanoparticles with high magnetic coercivity. These hard magnetic nanoparticles can be used as building blocks to fabricate nanostructures that may be useful for future high-density magnetic recording and nanocomposite permanent magnets.

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