

# Magnetic hardening in ultrafine FePt nanoparticle assembled films

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## Abstract

Ultrafine FePt nanoparticles have been synthesized via a novel chemical solution synthesis route. Without using a reducing agent, the stoichiometric FePt nanoparticles were produced by the decomposition of iron acetylacetonate and platinum acetylacetonate in octyl ether in the presence of oleic acid and oleyl amine as the surfactants. The particle size was found to be around 2 nm with a narrow size distribution. The particles were then deposited on substrates and heat treated afterwards. Upon annealing, the nanoparticles sintered together to form continuous thin films and at the same time to transform from disordered face centred cubic (fcc) structure to the highly anisotropic ordered face centred tetragonal (fct) structure and therefore magnetic hardening was realized in the thin films. Coercivity up to 27 000 Oe at room temperature has been obtained in the annealed samples. The very high coercivity indicates a highly completed fcc–fct phase transition which may be related to the very fine original particle size.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The synthesis of uniform nanoparticles has been intensively pursued because of their technological and scientific importance [1, 2]. These nanoparticles often exhibit very interesting electrical, optical, magnetic and chemical properties which cannot be observed in their bulk counterparts [3–5]. Chemically synthesized magnetic nanoparticles [6–8] have drawn much attention due to their unique magnetic properties derived from small particle sizes and uniform size distribution. FePt nanoparticles are of special interest as they may be used for future ultrahigh density magnetic recording media [9] and high performance nanocomposite permanent magnets [7, 10]. With bottom-up approaches, nanostructured thin film and bulk magnets can be fabricated from self-assembled nanoparticle arrays [10].

Previous work on the chemical synthesis of FePt nanoparticles involved the reduction of  $\text{Pt}(\text{acac})_2$  and the decomposition of  $\text{Fe}(\text{CO})_5$  [6, 7, 11], in which a reducing agent was used. Later, the formation of FePt nanoparticles via the simultaneous reduction of  $\text{FeCl}_2$  and  $\text{Pt}(\text{acac})_2$  as well as Fe and Pt acetylacetonate has also been reported [12, 13].

The particle size produced by the above-mentioned methods is generally around 3.5–4 nm.

In this study, we report an alternative approach for synthesizing FePt nanoparticles with mean size of only about 2 nm by the decomposition of  $\text{Pt}(\text{acac})_2$  and  $\text{Fe}(\text{acac})_3$  without any reducing agent. The composition of as-synthesized FePt particles can be easily tuned by adjusting the ratio of precursors as both are solid powders. These as-synthesized particles have chemically disordered fcc structure and can be transformed into the chemically ordered fct structure by an appropriate thermal treatment. The fct-structured FePt nanoparticle assembled thin films exhibit hard magnetic properties with room-temperature coercivity as high as 27 000 Oe.

## 2. Experimental procedure

The synthesis experiments were carried out using a standard airless technique in an argon atmosphere. In a typical procedure, 0.5 mmol each of platinum acetylacetonate ( $\text{Pt}(\text{CH}_3\text{CHOCH}_2\text{OCHCH}_3)_2$ ) and iron acetylacetonate ( $\text{Fe}(\text{CH}_3\text{CHOCH}_2\text{OCHCH}_3)_3$ ) were added to a 125 ml flask containing a magnetic stir bar and mixed with 20 ml of

octyl ether in the presence of 0.5 mmol each of oleic acid ( $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ ) and oleyl amine ( $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{NH}_2$ ). Argon gas was flowed throughout the whole experiment. After purging with argon for 30 min at room temperature, the flask was heated up to 200 °C for 30 min and then up to 295 °C for 30 min before it was cooled to room temperature under the argon blanket. The heating rate of 7 °C  $\text{min}^{-1}$  was maintained during the experiment.

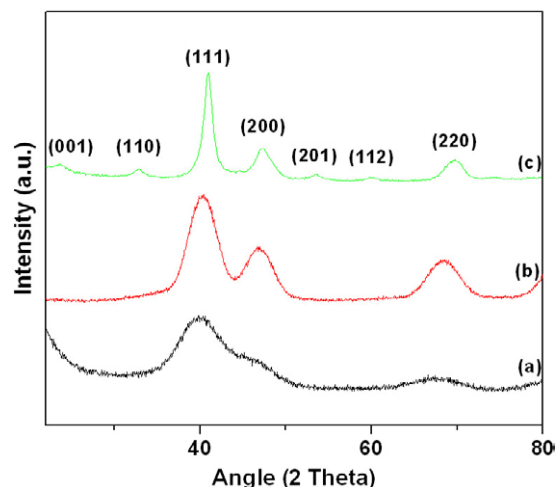
The black coarse particles (5 ml) were precipitated by adding ethanol and separated by centrifugation. After discarding the light brown supernatant, the precipitate was dispersed in hexane and a small amount of ethanol was added to separate large size particles from the dispersion while centrifuging. After discarding the precipitate, excess ethanol was then added to the supernatant to precipitate out fine and monodispersed particles after three rounds of centrifugation. These particles were re-dispersed in hexane and stored under refrigeration. Samples for magnetic characterization were prepared by depositing a drop of the final hexane dispersion on a 3 mm × 3 mm silicon substrate, evaporating the solvent at room temperature and further drying in vacuum, which led to the formation of FePt nanoparticle assembled thin films. The samples were then annealed at 650 °C for 1 h under a flow of forming gas (Ar + 7%  $\text{H}_2$ ) in a tube furnace.

The transmission electron microscopy (TEM) images were recorded on a JEOL 1200 EX electron microscope at an accelerating voltage of 120 kV. Powder x-ray diffraction (XRD) spectra were recorded on a Philips MPD diffractometer with a Cu  $K\alpha$  x-ray source ( $\lambda = 1.5405 \text{ \AA}$ ). The magnetic hysteresis measurements were carried out by using a superconducting quantum interference device (SQUID) magnetometer with the magnetic field up to 70 000 Oe.

### 3. Results and discussion

To make binary metallic nanoparticles by solution methods, care should be taken in choosing precursors, surfactants, solvents, reducing agents and reaction temperatures. In the synthesis of FePt nanoparticles, both the metal precursors  $\text{Fe}(\text{acac})_3$  and  $\text{Pt}(\text{acac})_2$  were first dissolved in octyl ether and then the nucleation started, which was followed by the growth of the nuclei. The colour transition of the solution was taken as the sign of decomposition of the precursors. To observe the decomposition temperatures of  $\text{Fe}(\text{acac})_3$  and  $\text{Pt}(\text{acac})_2$  individually, they were each heated in separate flasks with octyl ether under an argon blanket and it was found that they decomposed at approximately 180 and 140 °C, respectively. It is interesting to note that without a reducing agent, both of the precursors decompose completely. The use of a reducing agent (1,2 hexadecanediol) may facilitate the decomposition of  $\text{Pt}(\text{acac})_2$  at lower temperatures like 100 °C [6]. However in our reaction the intermediate reaction temperature was 200 °C; the reducing agent was therefore not necessary. This is an interesting finding as regards the mechanism of the FePt nanoparticle synthesis.

The surfactants were injected at 200 °C, on the basis of the fact that both the precursors completely dissolve in octyl ether at this temperature. Oleic acid and oleyl amine prove to provide a good ligand combination for FePt formation and stabilization. Oleic acid has long been used to stabilize varieties of colloids



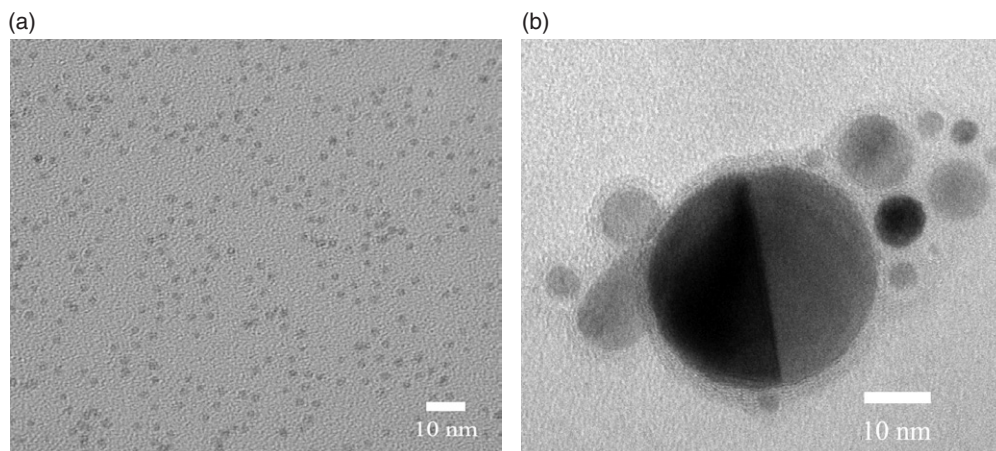
**Figure 1.** XRD patterns of (a) 2 nm and (b) 4 nm as-synthesized FePt nanoparticles and (c) the annealed FePt thin films.

including Fe nanoparticles [14]. Long carbon chain amines, on the other hand, are good stabilizing ligands for noble metal such as Pt. The structural similarity between oleic acid and oleyl amine provides a smooth ligand shell around each FePt nanoparticle, facilitating superlattice formation [15].

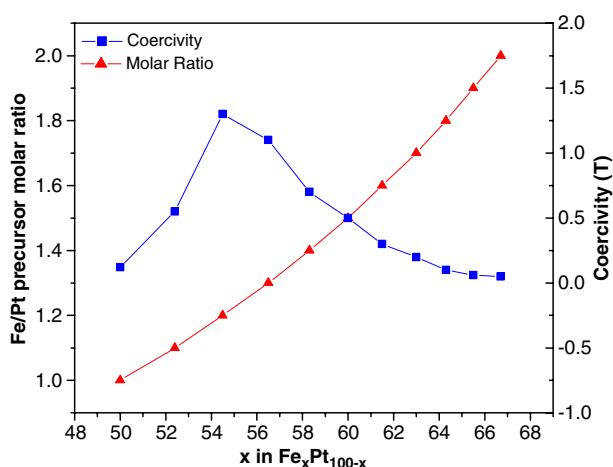
Figure 1 shows XRD patterns of the as-synthesized particles and the annealed FePt thin films (fcc structure); the annealing was done in forming gas at 650 °C for 1 h. The as-synthesized 2 nm particles exhibit a disordered fcc crystal structure with low magnetic anisotropy. Because of the small particle size, the peaks are very broad and hence overlap each other, which can be observed by comparing them with the XRD peaks of the as-synthesized 4 nm FePt particles. The average particle diameter estimated from Scherrer's formula [17] is consistent with that determined by statistical analysis of the TEM images (figure 2), indicating that each individual particle is a single crystal. The reason for such small size may be the sudden nucleation from precursor decomposition and precursor depletion. The nucleation rate dominates over the growth rate, and the abundance of nuclei with less growth causes particles of size about 2 nm.

Annealing induces the Fe and Pt atoms to rearrange into the chemically ordered fct structure, as indicated by the (111) peak shifts and evolution of (001) and (110) peaks (figure 1). After annealing in forming gas at 650 °C for 1 h, the particles sintered together to form continuous granular thin films. When the solution was much diluted, in some areas of the substrate separated particles can be found. These particles were sintered together to form large particles with size up to 30 nm as shown in figure 2(b).

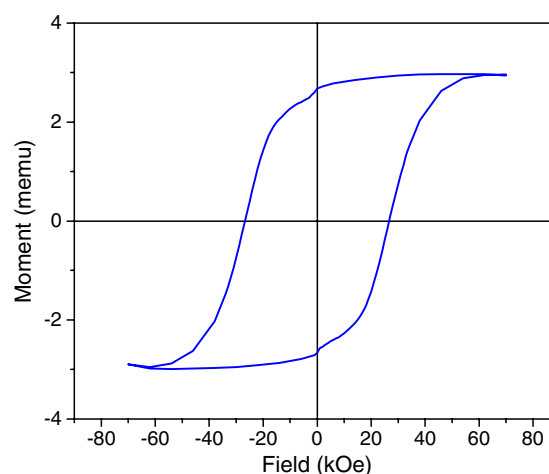
In the equiatomic FePt phase, the magnetic hardening shown by the coercivity is based on the fcc–fct phase transition [18]. The as-synthesized fcc particles have no coercivity. To convert the fcc particles to fct structure ones, the particles were deposited on Si substrate and annealed in forming gas at temperatures above 500 °C for 1 h. We tested several temperatures and 650 °C was found to give the highest coercivity. The composition of the FePt nanoparticles is tuned via the initial molar ratio of the  $\text{Fe}(\text{acac})_3$  and  $\text{Pt}(\text{acac})_2$  precursors in the reaction. On the basis of 1 mmol of



**Figure 2.** TEM images of (a) the as-synthesized 2 nm FePt nanoparticles and (b) the annealed FePt nanoparticles.



**Figure 3.** Composition dependence of the coercivity.



**Figure 4.** Magnetic hysteresis loop of the annealed assembly.

$\text{Pt}(\text{acac})_2$  and 0.5 mmol each of oleic acid and oleyl amine and 20 ml of octyl ether, the molar amount of  $\text{Fe}(\text{acac})_3$  and the resulting FePt particle compositions are shown in figure 3. The resultant compositions of Fe and Pt are average compositions determined by EDX analysis. It was observed that the precursor molar ratio of 1:1 yielded  $\text{Fe}_{50}\text{Pt}_{50}$  particles while the ratio 2:1 led to  $\text{Fe}_{67}\text{Pt}_{33}$  nanoparticles which leads us to conclude that, unlike in the cases where  $\text{Fe}(\text{CO})_5$  was used [11], all the  $\text{Fe}(\text{acac})_3$  contributes to the FePt formation because of the low precursor volatility at the reaction temperature of 295 °C. In the same figure, the coercivity dependence of the annealed FePt nanoparticle thin films with different percentages of Fe is also shown. The highest coercivity achieved was 19 000 Oe at  $\text{Fe}_{55}\text{Pt}_{45}$ , similar to the previous results [11]. However, if the reflux time during the reaction was increased from 30 min to 4 h, the particle assembly gave a huge coercivity of 27 000 Oe after annealing at similar conditions, as shown in figure 4. As can be understood, when the refluxing time was increased, the chemical composition of particles became very homogeneous, which leads to a high degree of chemical ordering in the nanoparticles and the assemblies. The very high coercivity

may also be originated from the fact that the very small particle size (2 nm) leads to high degree of homogeneity in the film assembled by the particles. It is known that the composition distribution of the nanoparticle dispersion has a significant influence on the phase transformation from disordered fcc to ordered fct [16]. In other words, although the particles sinter together after annealing, the homogeneity of the composition before annealing plays a very important role for achieving high coercivity. Moreover, a higher percentage of atoms on the surface will lead to a higher chemical potential of the whole system, which will facilitate the diffusion of the atoms. We have also worked with the same method in processing thin films by using FePt nanoparticles with the size of 4 nm or larger and coercivity lower than 20 kOe was obtained.

It is interesting to note that there are small kinks on the loop shown in figure 4 at  $H = 0$  which might be related to the existence of a trace amount of magnetically soft fcc phase in the film. We have found recently that the fcc–fct transition is particle size dependent [18]. The details need to be investigated further.

#### 4. Conclusions

We have presented an alternating chemical synthesis route for producing monodisperse 2 nm fcc FePt nanoparticles by decomposition of ferric acetylacetonate and platinum acetylacetonate in octyl ether in the presence of surfactants without reducing agents. This approach proves to be useful in decreasing the particle size and enhancing the magnetic hardening in the annealed assemblies. Coercivity up to 27 000 Oe at room temperature has been obtained with Fe<sub>55</sub>Pt<sub>45</sub> nanoparticles refluxed at 295 °C for 4 h after an appropriate heat treatment. These hard magnetic nanoparticles can be used as building blocks of nanostructured thin film and bulk magnets with high performance.

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