

The stability of monodisperse FePt Nanoparticles

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High coercivity in FePt magnetic nanoparticles after annealing is the priority of these systems for application in ultrahigh-density magnetic recording media. Monodisperse FePt nanoparticles were synthesized by superhydride reduction of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Pt}(\text{acac})_2$ at 263 °C under N_2 atmosphere. TEM images show monosized FePt nanoparticles with a diameter of 3.5 nm and a standard deviation of about 10%. The average distance between monodisperse particles is nearly 3nm, which oleic acid and oleylamine surround the FePt nanoparticles as surfactants. Stability of FePt nanoparticles colloidal solution was investigated via spectrophotometer analysis in fabrication and purification stage. The results for FePt nanoparticles dispersed in hexane indicate that by increasing the oleic acid surfactant in centrifugation stage, the concentration and stability of FePt nanoparticles solution increased and by increasing the oleylamine surfactant in fabrication stage, the number and concentration of colloidal nanoparticles increased due to decreasing the size of particles.

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1. Introduction

FePt magnetic nanoparticles are an excellent candidate for ultrahigh-density magnetic recording. L1₀-FePt nanoparticles have the ability to form a chemical order fct phase after heat treatment [1,2] so that, coercivity increase up to Tesla order of magnitude [3,4]. Fabrication of FePt nanoparticles by chemical method makes it possible to produce a self-organized long-ordered superlattice on the substrate [5]. These eliminate two major limitations: exchange coupling and superparamagnetism [6].

In physical fabrication method, the nanolayers of Fe and Pt are sputtered on carbon as thin films and then by annealing, the FePt nanoparticles are diffused into carbon matrix. In this approach, the particles have wide distributions of size and distance [7]. One of the FePt nanoparticle fabrication chemical methods is high-temperature decomposition of $\text{Fe}(\text{Co})_5$ and reduction of platinum acetylacetonate ($\text{Pt}(\text{acac})_2$), in which the particle size depends both on the heat treatment condition and the molar ratio of oleic acid and oleylamine surfactants [8]. In addition, by changing the solvent type, the shape of FePt nanoparticles is varied [9]. By thermal decomposition of Iron (III) ethoxide ($\text{Fe}(\text{OEt})_3$) and $\text{Pt}(\text{acac})_2$ in octylether in the presence of oleic acid and oleylamine, it is realized that the molar ratio of these surfactants affects on the size of FePt nanoparticles [10]. In this condition, by increasing the oleic acid, the particle size is decreased and when molar ratios of two surfactants are the same, the standard deviation becomes minimum. Generally, Fe and Pt are attracted by oleic acid and oleylamine, respectively [8,10]. In addition, the effect of ligands on nucleation and growth of CdSe nanocrystals in reaction step show that diameter

of CdSe nanoparticles as a function of ligands concentration has a minimum behavior [11].

In superhydride method, by Applying an intense reducer such as superhydride (LiBEt_3H) on the compositions of $\text{Pt}(\text{acac})_2$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, in temperature reaction above 200°C in the presence of oleic acid and oleylamine, stable dispersion of monosized-FePt nanoparticles will be achieved after purification stage [12]. The stable colloidal system of FePt nanoparticles solution prepared by polymeric stabilizers also can make ordered arrays of FePt nanoparticles on a single crystal substrate [3, 13, and 14].

Concerning the magnetic moment of FePt nanoparticles, the agglomeration of the particles is important. To prevent agglomeration, one should cover the particles by surfactants to stabilize the system and therefore, eliminating the exchange coupling between them [9]. When the FePt stable colloidal system is dried on a substrate, an equal space between FePt nanoparticles are achieved in result of equilibrium condition [15].

For stabilizing of the magnetic single domain particles in a non-polar solvent, a type of polymer molecule with polar head and apolar tail should be used [16-18]. Nevertheless, studying the role of oleic acid and oleylamin in nucleation and growth of these FePt nanoparticles is necessary. In present work, the FePt nanoparticles with a 3.5 nm diameter have been fabricated by superhydride method and then FePt nanoparticles are dispersed in hexane with different amounts of oleic acid and oleylamine stabilizers. The amounts of oleic acid and oleylamine ligands have been varied in both reaction and purification stages and the stability have been studied by TEM and spectrophotometer analysis.

2. Experimental details

FePt nanoparticles were prepared via the following method reported by Sun et al [12]. The synthesis of these FePt nanoparticles involves the reduction of $\text{Pt}(\text{acac})_2$ (197 mg) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (139 mg) in phenyl ether solvent (25 mL) in the presence of 1,2-hexadecanediol (520 mg) under N_2 atmosphere. Oleic acid and oleylamine surfactants were added to the solvent at 100 °C. By adding superhydride (LiBEt_3H) under N_2 atmosphere at 200 °C, followed by refluxing at 245 °C, FePt nanoparticles were formed. The black reaction mixture was cooled to room temperature and then combined with ethanol to remove the impurity. Samples a_1 - a_3 were prepared with different values of oleic acid and oleylamine ligands in fabrication stage (according to Table 1).

Table1. The data achieved using spectrophotometer analysis of sample a, with different amounts of ligands in fabrication stage.

Samples	Oleic acid (μL)	Oleylamine (μL)	T	ΔT	$(\Delta T/T)\%$
Hexane	0	0	83.578	0	0
a_1	160	0	49.439	34.144	40.8
a_2	80	85	29.923	53.655	64.2
a_3	0	170	10.005	73.573	88.0

Afterwards, the product was precipitated and separated by centrifugation (8000 rpm, 10min). Then, FePt nanoparticles were dispersed in hexane in the presence of different values of renewed surfactant. Any undissolved material was removed by centrifuging. After the two stages of purification, 12 dispersion solutions of FePt nanoparticles, each one in 7 mL hexane were prepared with 4 different values of surfactant. Samples b_1 - b_4 were prepared with different values of oleic acid and oleylamine ligands in centrifuging stage (according to Table 2).

Table2. The data achieved using spectrophotometer analysis of samples b, with different surfactant concentrations in centrifuging stage.

Samples	Oleic acid (μL)	Oleylamine (μL)	T	ΔT	$(\Delta T/T)\%$
Hexane	4	2	82.615	0	0
b_1	0	0	73.834	8.781	10.9
b_2	0	2	66.264	16.351	19.8
b_3	4	2	27.532	55.083	66.7
b_4	8	4	25.463	57.152	69.2

We used a Varin-Cary 500 UV-Vis-NIR spectrophotometer system for comparing the concentration of colloidal solutions as a measure of the stability of FePt nanoparticles. For this purpose, the transmission was measured for colloidal solutions. The specification of size and shape of FePt nanoparticles, the distance between them, and their size distribution was carried out by TEM analysis using a Philips EM 208 TEM (100kV) with resolution 200kX. The sample b_3 was annealed in %90 Ar + %10 H atmosphere at 600°C for 4 hours. To determine the FePt nanoparticles structure before and after heat treatments, the X-ray diffraction measurement were performed using a Seifert system with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The magnetization of FePt samples in a variable magnetic field was measured using a PAR vibrating sample magnetometer (VSM).

3. Results and discussion

XRD patterns of as-made and annealed FePt nanoparticles are shown in Fig. 1. The peaks in pattern *a*, reveal *fcc* structure with lattice constant 3.871 \AA which is consistent with the report made on FePt structures analysis [4]. The average particle size for as-synthesis particles is 3.5 nm, which is estimated using Scherrer's formula on (111) peak and consistent with the observed TEM images. In pattern *b*, the FePt nanoparticles have the L1_0 structure after annealing process.

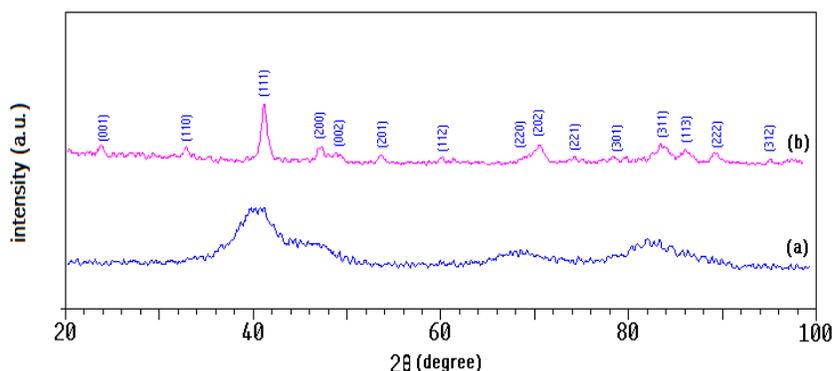


Fig.1. X-ray diffraction ($\lambda=1.54 \text{ \AA}$, $\text{Cu K}\alpha$ radiation) pattern of sample b_3 (a) as-prepared and (b) annealed FePt at 600 °C for 4 hours.

Fig. 2 show the TEM images of the as-synthesized fcc FePt particles. Figures 2a and 2b show samples b_2 and b_4 , respectively, which have two different stability conditions. In figure 2a, the FePt nanoparticles were prepared without oleic acid surfactant in the centrifugation stage. It can be seen that some FePt grains are connected to each other and form chains in result of interactions. On the contrary, in Fig. 2b, the particles have an average diameter of about 3.5 nm and narrow size distribution with standard deviation of about 10%. In fact, oleic acid and oleylamin molecules are attached to the FePt nanoparticles and establish a layer around each particle to prevent FePt nanoparticles to approach each other, assisting the monodispersity formation of particles. Our results show that the growth of metal particles using sodium borohydride (NaBH_4) in room temperature gives larger particle size in the range of order 100 nm [20].

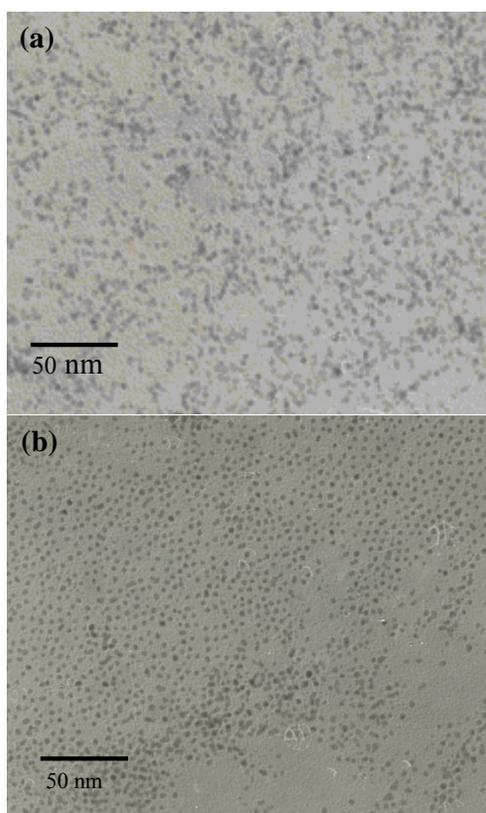


Fig.2. Magnetic hysteresis loops of sample b_3 (a) as-synthesized and (b) annealed FePt nanoparticles.

The results of magnetic measurements before and after heat treatments (Fig.3) indicate that as-made FePt nanoparticles is first superparamagnetism at room temperature and after annealing under Ar atmosphere at 600°C for 4 hours, the saturation magnetization increases to 45 emu/g. These results confirm the suitable magnetic property of particles.

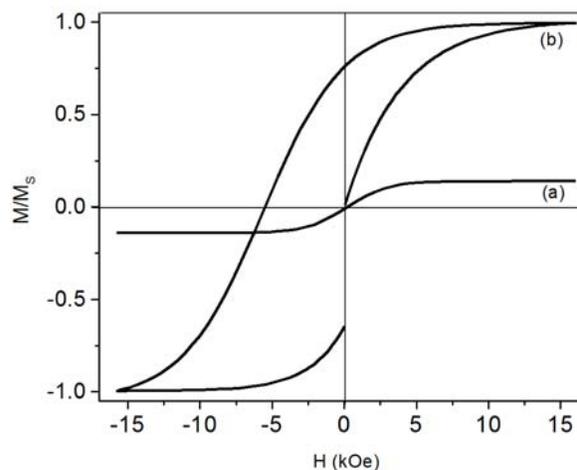


Fig.3. TEM images of the FePt nanoparticles after evaporation of hexane for samples (a) sample b_2 and (b) sample b_4 , annealing under Ar atmosphere at 600°C for 4 hours.

During formation of FePt nanoparticles first, 1,2-hexadecanediol leads to the reduction of $\text{Pt}(\text{acac})_2$ before adding superhydride and nucleation of particles is started with Pt atoms. Oleylamine molecules slow down the growth of particles by establishing a layer around the cores [11], which leads to increase the number of them. Then, after adding superhydride at 200°C , Fe atoms are released quickly and oleylamine molecules are separated from Pt atoms [10, 18 and 19]. Therefore, a layer of Fe atoms, as FePt nanoparticles shell, is formed around the core. In this step, the oleic acid molecules control the growth of FePt nanoparticles. In Fig. 4 and Table 1, the spectrophotometer results for colloidal solutions a_1 - a_3 dispersed in hexane have been compared in fabrication stage. The transmittance coefficient is measured as a function of wavelength. In Table 1, T is the transmittance percent for wavelength 1572 nm, ΔT is the difference between transmittance of hexane and colloidal solution, and $\Delta T/T$ is proportional to the concentration of FePt colloidal samples. The higher concentration of sample a_3 towards a_1 indicates that by increasing the amount of oleylamine during the reaction, the number of grown FePt nanoparticles increased [21]. In fact, this ligand halts the growth of the nanoparticle by establishing a layer around Pt core and therefore and the probability of nucleating new particles are decreased, while oleic acid controls the growth of FePt nanoparticles shell after adding superhydride.

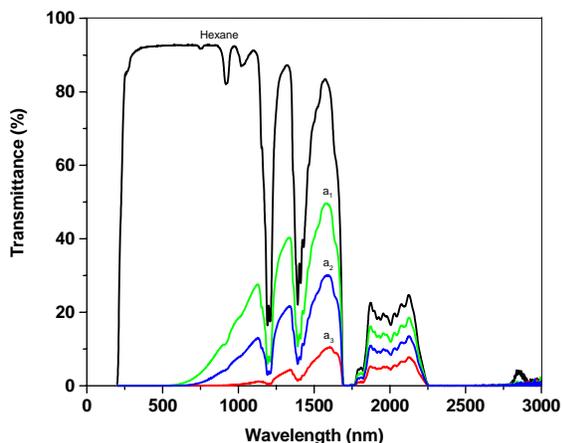


Fig.4. NIR spectrophotometer transmission of FePt colloidal solutions of samples a_1 - a_3 ; upper curve pertains to hexane solvent and is presented for comparison

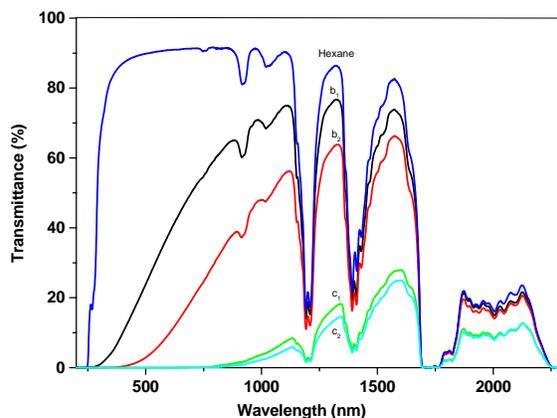


Fig.5. NIR spectrophotometer transmission of FePt colloidal solutions of samples b_1 - b_4 ; upper curve pertains to hexane solvent and is presented for comparison.

In order to stability of FePt nanoparticles, the polar head of the surfactant molecule is adsorbed by nanoparticle surface and its non-polar tail dissolved in hexane non-polar solvent. This solvating process leads to an apparent increase of entropy of the system, which prevents the agglomeration of FePt nanoparticles. Whenever two FePt particles are close to each other, as a result of the Vander Waals and magnetic dipole-dipole interactions, the compression of surfactant layers between them is intensified to prevent the increase of entropy. Therefore, steric repulsion interaction between particles appears and makes FePt nanoparticles system stable in their equal distances. In figure 5, transmittance coefficient is measured as a function of wavelength for different colloidal solutions of FePt nanoparticles by spectrophotometer analysis. In purification stage, another effect of surfactants, i.e. preventing the precipitation of metal FePt nanoparticles has been investigated for

colloidal solutions. Fig. 5 and Table 2, show the transmittance spectra of the samples b_1 - b_4 , which have different amounts of surfactant in their solutions. In spite of the fact that the volume of the solvent and initial amount of FePt nanoparticles are the same, the concentration of colloidal solutions b_3 and b_4 (2.14 g/L) is considerably more than that of solutions b_1 and b_2 .

4. Conclusions

Monosized-FePt nanocrystals with diameter of 3.5 nm were synthesized by superhydride method. The 1,2-Hexadecanediol reductant and oleylamine surfactant control the size of Pt cores and increase number of them. In this method, oleic acid surfactant controls the thickness of Fe shell and the final size of the FePt nanoparticles. Thus, in fabrication stage, oleylamine has more effect on the concentration of colloidal FePt solution than oleic acid surfactant. On the other hand, in purification stage, oleic acid has more effect on the stability of colloidal FePt nanoparticles than oleylamine surfactant because Fe atoms have higher contribution in FePt nanoparticles shell than Pt.

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