

Decoration of carbon nanotube with size-controlled L1₀-FePt nanoparticles for storage media

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Abstract In this work, first multi-wall carbon nanotubes (MWCNTs) with outer diameter about 20–30 nm are synthesized by a CVD method; they have been purified and functionalized with a two-step process. The approach consists of thermal oxidation and subsequent chemical oxidation. Then, monosize FePt nanoparticles along carbon nanotubes surface are synthesized by a Polyol process. The synthesized FePt nanoparticles are about 2.5 nm in size and they have superparamagnetic behavior with fcc structure. The CNTs surfaces as a substrate prevent the coalescence of particles during thermal annealing. Annealing at the temperature higher than 600 °C for 2 h under a reducing atmosphere (90 % Ar + 10 % H₂) leads to phase transition from fcc to fct-L1₀ structure. So, the magnetic behavior changes from the superparamagnetic to the ferromagnetic. Furthermore, after the phase transition, the FePt nanoparticles have finite size with an average of about 3.5 nm and the coercivity of particles reaches 5.1 kOe.

1 Introduction

In recent years, magnetic nanoparticles have attracted extensive attention because of their extremely diverse applications in magnetic recording media, permanent magnets, magnetic sensors and drug delivery in biomedical applications [1–4]. L1₀ FePt nanoparticles with face-centered tetragonal (fct) structure have very high magnetocrystalline anisotropy ($k_u = 7 \times 10^7$ erg/cm³) and also they have very high coercivity which makes them suitable candidates for using in ultrahigh density magnetic recording media [5]. Chemical methods are adequate to produce nanoparticles with uniform size distribution. But, the nanoparticles synthesized using the chemical method have disordered A1 phase with face-centered cubic (fcc) structure, they have small anisotropy and show superparamagnetic behavior at room temperature [6]. Therefore, an additional thermal treatment process is required to transform the nanoparticles from the disordered A1 phase to the ordered L1₀ phase. With respect to the aggregation of nanoparticles at high temperature, nanoparticle size increases and makes them inappropriate for using at data storage media [7].

Various methods have been suggested for preventing the aggregation of nanoparticles, such as decreasing of phase transition temperature with using the additive metals like Au, Ag and B₂O₃. The salt method (NaCl) able to prevent the sintering of nanoparticles, the direct synthesis method, rapid thermal annealing and core/shell structure are all interesting approaches to prevent coalescence of magnetic nanoparticles [8–15]. But the results after annealing show that in these methods the coercivity decreases significantly. To solve this problem, an appropriate substrate is required during the annealing process.

Carbon nanotubes (CNTs) have received great attention because of their electrical, optical and mechanical properties and high thermal stability [16]. In this paper, we suggest

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coating the FePt nanoparticles on the surface of CNTs and then annealing them at high temperature for transition from A1 to fct-L1₀ phase, with small changes in size.

It is necessary to mention that the so-synthesized nanotubes have no ability to absorb Fe or Pt atoms for nucleation and growth of FePt nanoparticles. Therefore, the nanotubes are functionalized with appropriate functional groups such as: carboxyl (–COOH), carbonyl (–C=O) and hydroxyl (–OH). To do this, first the nanotubes should be oxidated at high temperature and then oxidized in the mixture of various acids until the functional groups are placed on their surface [17].

FePt nanoparticles of small size are successfully prepared on a multi-wall carbon nanotube (MWCNT), which is used as an appropriate substrate to prevent the FePt nanoparticles from coalescing in the presence of Pt(acac)₂ and Fe(acac)₃ salts and 1,2-hexadecanediol as the reduction agent.

2 Experimental

2.1 Synthesis of MWCNTs

In this study, MWCNTs (with 20–30 nm outer diameter and 5–10 μm length) were prepared by the Catalyst Vapor Deposition (CVD) method in a tube furnace at the temperature of about 650 °C and by using acetylene (C₂H₂) as a carbon precursor and MgO nanoparticles as catalyst for CNTs growth. Therefore, MgO nanoparticles dispersed on a quartz glass were inserted into the tube furnace with the temperature of about 650 °C under the flow of acetylene (C₂H₂) and Ar gas with rates of about 10 sccm and 150 sccm, respectively. Then, we removed quartz glass from the furnace after 20 min with black powder on its surface.

The resulted products were a mixture of nanotubes, floris, amorphous carbon and graphite. To obtain nanotubes, they had to be purified and functionalized for growth of FePt nanoparticles on the surface of CNTs.

2.2 Purification and functionalization of CNTs

First, the synthesis products were heated under O₂ atmosphere with the rate of 10 °C/min to 400 °C and remained at this temperature for 30 min. Then, we increased the temperature to 500 °C with the rate of 5 °C/min and kept it constant for 1 hour. At the next step, the remaining thermal oxidation products were dispersed in the mixture of HCl and HNO₃ with the concentration of 3 M and the ratio 1:1, and ultrasound was applied for 10 min. Then, the mixture was stirred at 60 °C for 2 h.

At last, CNTs were immersed in a mixture of HNO₃ and H₂SO₄ (3 M) with the ratio 1:3 to functionalize of the side walls and the ends of CNTs with the carboxylic

functional group [18]. After the addition of nanotubes to the above mentioned acids, the resulted solution was stirred (1600 rpm) at 90 °C for 2–4 hours. Oxidized nanotubes have been washed with distilled water and dried under Ar atmosphere at 150 °C.

2.3 Synthesis of FePt/CNT nanocomposites

Polyol method was used to grow FePt nanoparticles on the surface of oxidized CNTs [5]. For that oxidized CNTs were dispersed in 40 mL phenyl-ether and ultrasound was applied for 10 min. Then, we mixed the above solution with Pt(acac)₂ (0.5 mmol) and Fe(acac)₃ (0.5 mmol) salts and also 1,2-hexadecanediol as a reducing agent in the reaction vessel. While stirring (1000 rpm), the solution temperature was increased to 100 °C during 20 min to start the reduction of Fe and Pt salts and nucleation. Withing 90 min, we raised the temperature of solution to 260 °C and kept at this temperature for 30 min. Then, we removed the heat source and let the solution cool down to room temperature.

Purification process was executed as follows: 40 ml ethanol was added to the mixture and the black product was precipitated and separated via centrifugation (8000 rpm, 10 min). The ethanol and impurities separated, and the discarded black was dispersed in hexane in the presence of oleic acid and oleyl-amine. Centrifugation (8000 rpm, 10 min) was applied again to remove any undispersed residue.

2.4 Characterization of nanocomposites

The morphology and diameter of nanotubes was studied using FE-SEM (HITACHI S-4160). To study the functionalization of nanotubes, FT-IR spectrum (Thermo Nicolet system) was used. The specification of size and shape of the nanoparticles and nanotubes was carried out by TEM analysis using a LEO system (9120AB, 120 kV). The Fe and Pt elemental analysis of samples was performed by EDX (Philips XL30, 17 kV). To determine the structure properties of nanoparticles, we performed the XRD measurement using an X'Pert MPD Philips system. The magnetization of FePt samples was measured using a VSM (Lake-Shore model 7400). The annealing of FePt/CNTs nanocomposite was carried in a tube furnace under reducing atmosphere (%90 Ar + %10 H₂) at 600 °C for 2 h.

3 Results and discussion

Figure 1 shows the FE-SEM images of CNTs at different steps. Figure 1(a) presents the CNTs synthesized by the CVD method. The CNTs have a diameter between 20–30 nm and also there are many impurities within CNTs. Figure 1(b) shows the CNTs after thermal oxidation at 500 °C,

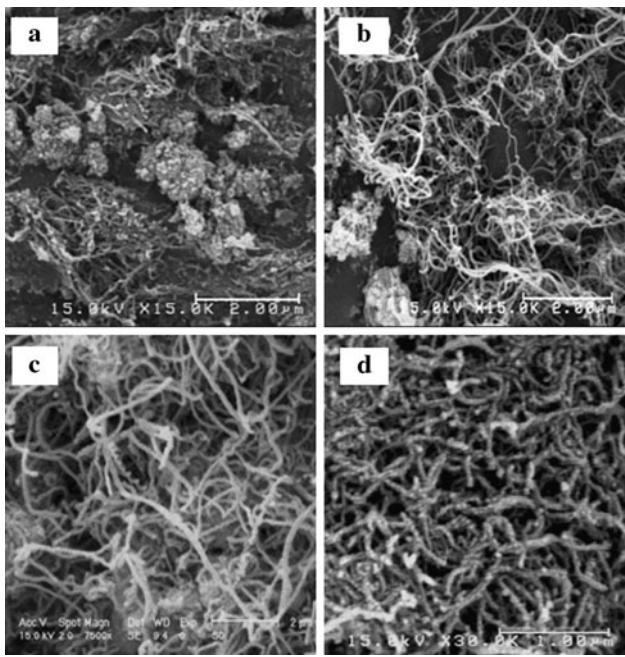


Fig. 1 FE-SEM images of carbon nanotubes and their purification steps: (a) as-synthesized, (b) after thermal oxidation, (c) after purification, and (d) after functionalization

some impurities that include amorphous carbon and black are removed. In this process, since amorphous carbons have free bonds from all sides, they are oxidized quickly and change into CO and CO₂. But CNTs have free bonds only at their two ends, so the oxidation rate is slower and they remain. Figure 1(c) relates to the CNTs that are purified by HCl and HNO₃ (3 M) acids. As shown in the figure, HNO₃ oxidized carbonic impurities and HCl made the MgO nanoparticles dissolve. Figure 1(d) shows the CNTs after functionalization by HNO₃ and H₂SO₄ (3 M), the surface defects are oxidized by acid, CNTs are broken and their length has become shorter.

Figure 2 shows the FT-IR of CNTs used to investigate their functionalization. Figure 2(a) highlights the CNTs that are not functionalized. This is because there's no peak relating to carboxylic functional groups. Figures 2(b) and 2(c) show the spectra of CNTs that are functionalized for 2 and 4 hours, respectively. The broad peak at 3423 cm⁻¹ relates to O–H bonds and the one at about 1630 cm⁻¹ relates to C = O bonds that shows the carboxylic functional group on CNTs.

Therefore, a lot of active sites on CNTs' surface are made during functionalization processes that are useful for nucleation and FePt nanoparticle growth. Also, increasing the functionalization time, the peak intensity relating to carboxylic group increases; this shows a great number of active sites on the surface of CNTs.

Figure 3(A) shows TEM images of synthesized FePt nanoparticles on the CNTs' surface that are functionalized for 2 and 4 hours, respectively. It is observed that CNTs have

the external diameter of about 20–30 nm. Also, the black spots on CNTs' surface are matched to FePt nanoparticles that grow on the surface of CNTs. By comparing panels (a) and (b) in Fig. 3(A), we find that the coating of CNTs surfaces improves with increasing functionalization time. The average size of nanoparticles is the same, about 2.5 nm, and their size distribution is very narrow even without surfactant; and their relative standard deviation ($\sigma/\langle d \rangle$) is 0.16 and 0.1, respectively.

The histograms related to nanoparticles size are shown in panels (a) and (b) of Fig. 3(B), and the average size of FePt nanoparticles for them equals to 2.47 and 2.59 nm, respectively. The uniform coating of FePt nanoparticles in panel (b) of Fig. 3(A) is a result of increasing and uniformity of functionalized sites on the surface of CNTs. Furthermore, the elemental composition of the FePt nanoparticles was confirmed by the EDX measurement as shown in Fig. 3(C). It shows that the composition of the FePt alloy was Fe₅₁Pt₄₉. This composition transforms into L1₀-ordered phase after annealing.

X-ray diffraction patterns of as-synthesized FePt/CNT nanocomposites which were annealed at 700 °C for 2 h have been shown in Fig. 4. The as-synthesized FePt/CNTs have chemically disordered fcc structure; and the annealed nanocomposites have the chemically ordered fct-L1₀ structure. According to Fig. 4(a), the as-synthesized nanocomposites have (1 1 1), (2 0 0), and (2 2 0) broad peaks that shows the chemically disordered fcc structure of FePt nanoparticles. The average size of FePt particles by Scherrer' equation ($D = \frac{k\lambda}{\beta \cos \theta}$) was calculated to be about 3.1 nm. In addition, the (0 0 2) peak related to graphite structure of CNTs. Figure 4(b) shows the XRD pattern of FePt/CNTs that were annealed at 700 °C for 2 h.

The transportation of (1 1 1) peak position to larger angles, the existence of (1 1 0), (0 0 1), and (1 1 2) peaks and the separation of (2 0 0) and (0 0 2) peaks together show a phase transition to the chemically ordered fct-L1₀ structure. The separation of (2 0 0) and (0 0 2) peaks results from a difference in lattice constants in the direction of *a* and *c* axes that was observed at the fct structure. Due to separation of Fe and Pt crystal planes and the difference in electron density in these two planes, the intensity of diffracted beams is different and the (1 1 0), (0 0 1), (2 0 1), and (1 1 2) peaks appear. To calculate *a* (*a* is a lattice constant) at the fcc structure, the (1 1 1) peak is used and *a* = 3.87 Å is calculated. But to calculate *a* and *c* at the fct-L1₀ structure, the (1 1 0) and (0 0 1) peaks are used, respectively, and the lattice constants *a* = 3.845 Å and *c* = 3.72 Å are attained.

The ordering parameter *S*, which is a measure of the volume fraction of the fct structure, is given by [19]:

$$S^2 = \frac{1 - (\frac{c}{a})}{1 - (\frac{c}{a})^*} \quad (1)$$

Fig. 2 FT-IR spectrum of CNTs: (a) before functionalization, (b) after functionalization for 2 h, and (c) after functionalization for 4 h

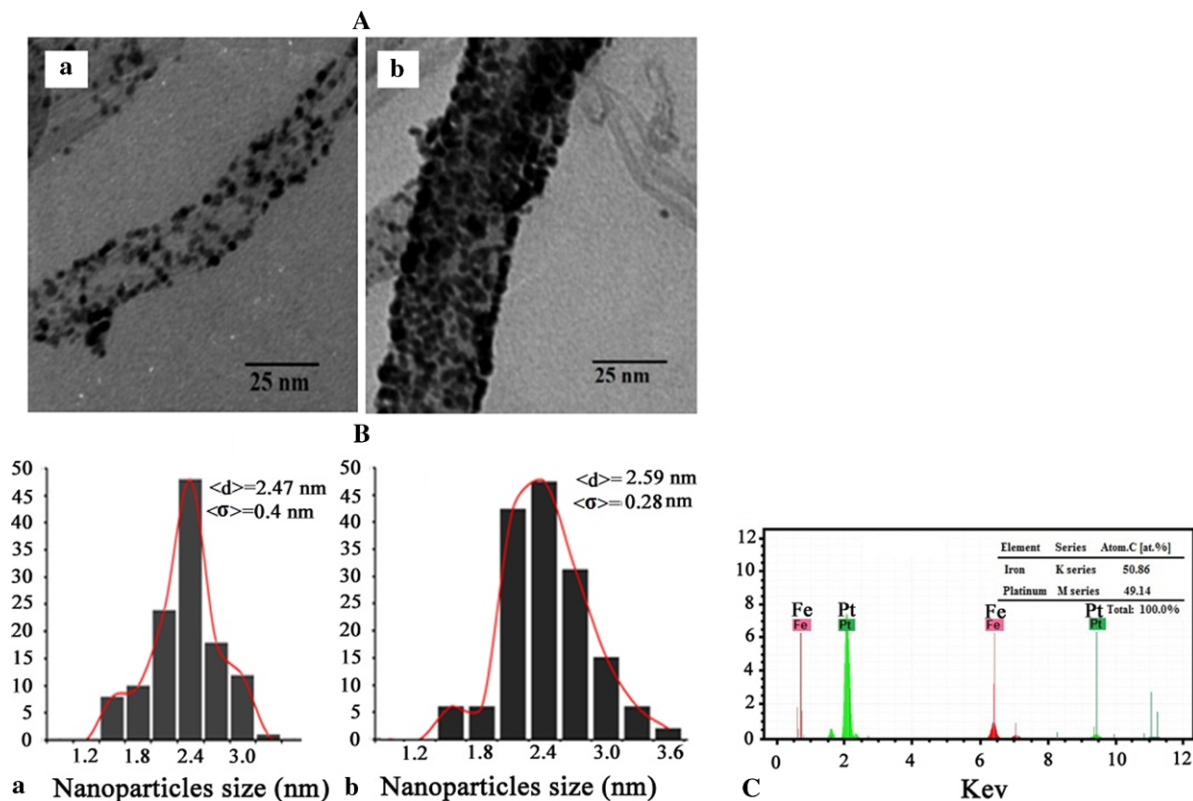
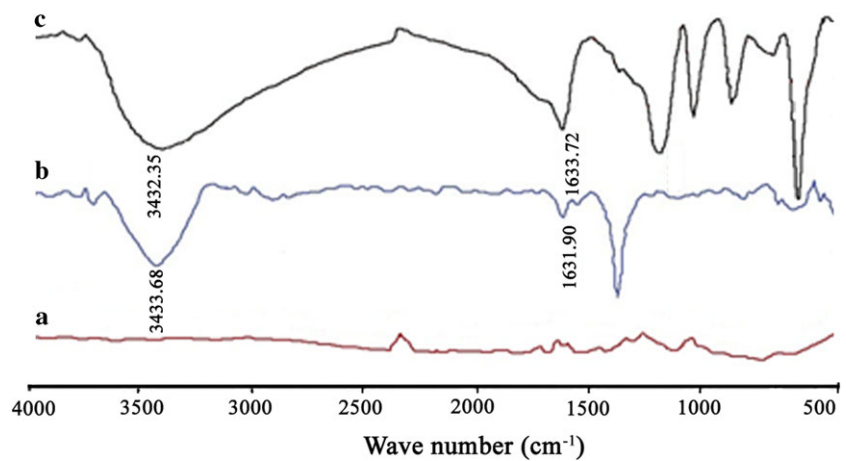


Fig. 3 (A) TEM images of FePt nanoparticles on the surfaces of CNTs after functionalization: (a) for 2 h and (b) for 4 h. (B) Histogram of FePt nanoparticles on the surfaces of CNTs after functionalization:

(a) for 2 h and (b) for 4 h. Figure 3(C) shows EDX image of the as-synthesized fcc FePt nanoparticles

where $(\frac{c}{a})$ and $(\frac{c}{a})_*$ are the experimental and the theoretical axis ratios for the chemically ordered fct phase, respectively. $S = 1$ means that the FePt nanoparticles are fully in the ordered fct phase. Here $(\frac{c}{a})_*$ was determined to be 0.96 according to [20]. Accordingly, the value of S obtained by Eq. (1) is 0.91, very close to 1. It means that most of the FePt nanoparticles have transformed to the fct- $L1_0$ phase after 700 °C annealing.

TEM images of FePt nanoparticles and FePt/CNT nanocomposites that were annealed at 600 °C for 2 h have been shown in Fig. 5. From Fig. 5(a), we see that annealing at 600 °C causes coalescence and grate agglomeration. But as shown in Fig. 5(b), the nanoparticles on the surface of CNTs at the same annealing conditions have limited agglomeration and the size of coalesced particles with $L1_0$ phase is in the range of 2–6 nm.

Fig. 4 XRD patterns of FePt/CNT samples: (a) as-synthesized and (b) after annealing at 700 °C for 2 h

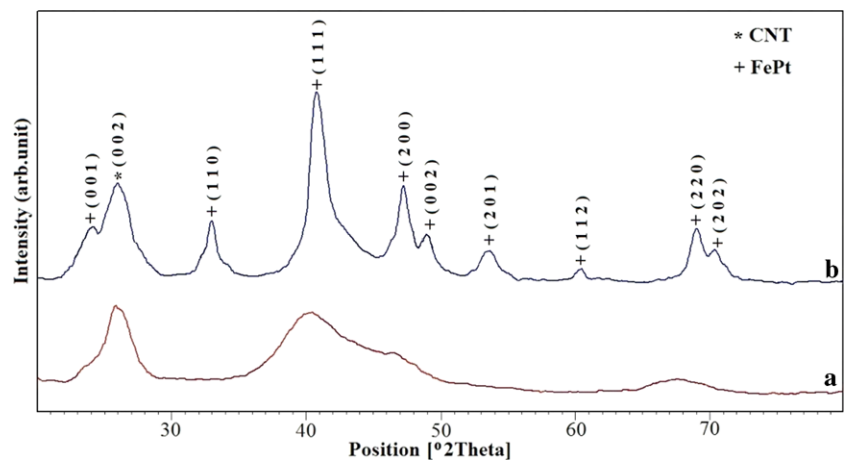
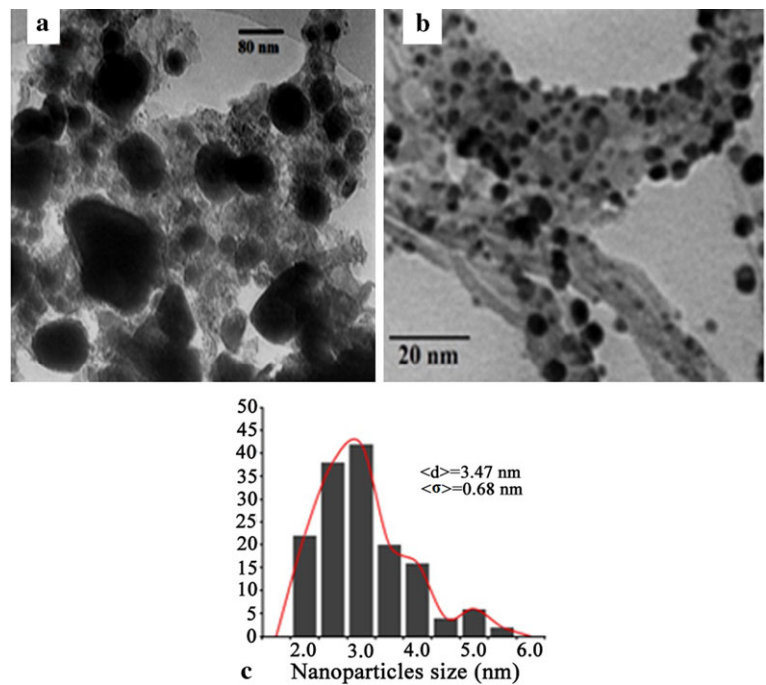


Fig. 5 (a) and (b) TEM images of FePt nanoparticles and FePt/CNT nanocomposite annealed at 600 °C for 2 h, respectively, and (c) histogram of FePt nanoparticles on the surface of CNTs



So, CNTs as an appropriate substrate prevent the nanoparticles from coalescence. A histogram of FePt nanoparticles on the surface of nanotubes has been presented in Fig. 5(c). The average size of particles is $\langle d \rangle = 3.47$ nm and their standard deviation is $\langle \sigma \rangle = 0.68$ nm that shows the uniform distribution of particle size.

Figure 6 shows the hysteresis loops of FePt/CNT nanocomposites at room temperature. As-synthesized FePt nanoparticles have a chemically disordered fcc structure, and they are superparamagnetic for their low magnetic anisotropy at room temperature (Fig. 6(a)). The CNTs are not magnetic at room temperature, so there's no interaction between FePt nanoparticles and CNTs.

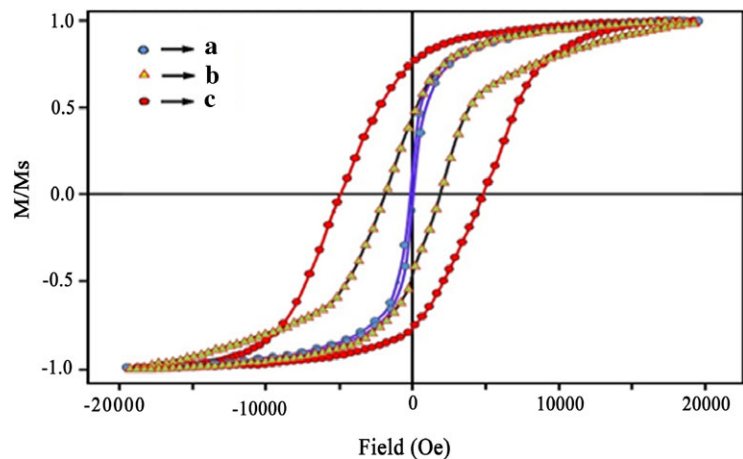
Figures 6(b) and 6(c) show nanocomposites annealed at 600 °C and 700 °C, respectively. As shown in the figure, the coercivity of FePt/CNTs at 600 °C and 700 °C is 2.2

and 5.1 kOe, respectively, even though they have the average size of about 3.47 nm. With an increase in annealing temperature, the coercivity of nanoparticles increases significantly and shows that the ordering of the L1₀ phase improves at a temperature higher than 600 °C.

4 Conclusions

In this paper, the even size FePt nanoparticles with an average size of 2.5 nm on the surfaces of CNTs were synthesized by a Polyol process, without any surfactant agent. The as-synthesized FePt nanoparticles have a chemically disordered fcc structure, and they have superparamagnetic behavior at room temperature due to their low magnetic anisotropy. Annealing at a temperature above 600 °C leads

Fig. 6 Hysteresis loops of FePt/CNT composites: (a) as-synthesized, (b) after annealing at 600 °C for 2 h, and (c) after annealing at 700 °C for 2 h



to a transition of the disordered A1 phase to the ordered L1₀ phase. The CNTs as a suitable substrate were prepared by a CVD method and used to prevent the agglomeration of FePt nanoparticles during the high thermal annealing. The reaction between nanoparticles' and the CNTs' surfaces results in finite size FePt nanoparticles with an average size of about 3.5 nm for annealing at 600 °C and their magnetic coercivity reaches 5.1 kOe at 700 °C.

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