



Original Article

CTAB-assisted Synthesis and Characterization of FePd Nanoparticles

Nguyen Hoang Nam^{1,2}, Nguyen Thi Bich Ngoc¹, Truong Thanh Trung¹,
Tran Thi Hong¹, Phi Thi Huong¹, Nguyen Hoang Luong^{1,2,*}

¹VNU University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam

²VNU Vietnam - Japan University, Luu Huu Phuoc, Nam Tu Liem, Hanoi, Vietnam

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Abstract: In this study, Fe₅₀Pd₅₀ nanoparticles with small size of around 5-9 nm were prepared by sonoelectrodeposition in the presence of cetyltrimethylammonium bromide (CTAB) surfactant. The as-prepared nanoparticles were annealed at 550°C for a series of times from 1 h to 6 h. After annealing, a transformation from a disordered face-centered-cubic structure to the ordered L1₀ structure occurred. It was revealed that the coercivity of the nanoparticles was larger compared to that of the samples prepared by the same method in the absence of CTAB. The structural and magnetic properties of the samples were studied in dependence of annealing time. The results indicate a similar behavior of the evolution of tetragonality ratio and coercivity with annealing time in the nanoparticles.

Keywords: FePd, sonoelectrodeposition, coercivity, magnetic nanoparticles.

1. Introduction

FePt, FePd and CoPt nanoparticles with large magnetocrystalline anisotropy of the L1₀ ordered structure have attracted much interest because of their potential applications in ultrahigh-density magnetic storage [1,2]. As for FePt and CoPt nanoparticles, the as-prepared FePd nanoparticles have a disordered face-centered cubic (fcc) structure, and a thermal annealing is necessary to transform them into the desired ordered face-centered tetragonal (fct) L1₀ phase.

*Corresponding author.

Email address: luongnh@hus.edu.vn

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Various methods of synthesis of the FePd nanoparticles were employed, including the epitaxial growth by electron beam deposition [3-6], the modified chemical synthesis [7-9], the modified polyol process [10,11], or microwave irradiation [12]. Van et al. [13] have studied hard magnetic properties of the FePd nanoparticles prepared by sonochemistry. Recently, sonoelectrodeposition was used to synthesize the FePd nanoparticles [14,15]. The obtained results so far indicate that properties of FePd nanoparticles vary according to the synthesis methods. Luong et al. [16] studied structure and magnetic properties of the FePd nanoparticles synthesized by sonoelectrodeposition without using a surfactant. It is known that use of surfactant (or some other technological conditions) has strong effect on the various physical and chemical properties of prepared nanoparticles. Only few reports are available about the influence of cetyltrimethylammonium bromide (CTAB) surfactant on the magnetic properties of the L1₀ nanoparticles. Goswami et al. [17] reported on the magnetic properties of the FePt nanoparticles using wet chemical synthesis in the presence of CTAB aiming to use them in hyperthermia therapy. In this work, we report on structural and magnetic properties of the FePd nanoparticles prepared by sonoelectrodeposition with added CTAB. The influence of annealing time on the properties of the prepared FePd nanoparticles is discussed.

2. Experimental

The mixture of iron(II) acetate [Fe(C₂H₃O₂)₂], palladium(II) acetate [Pd(C₂H₃O₂)₂], Na₂SO₄ and CTAB were mixed under (Ar + 5% H₂) atmosphere in the electrolysis cell of 100 ml volume. The mixture was then sonoelectrodeposited for 2 h by using Sonics VCX 750 ultrasound emitter with power density of 100 W/cm², on/off current pulse of 500 ms/800 ms to form FePd nanoparticles. The nanoparticles were washed, collected by using a Hettich Universal 320 centrifuge at 9000 rpm for 30 min and then dried in air at 70°C for 30 min. The annealing under (Ar + 5% H₂) atmosphere was carried out on the as-prepared samples at 550°C for 1, 2, 4 and 6 h. The annealing temperature of 550°C was chosen because it gave a maximum coercivity of the samples compared to other annealing temperatures [16].

The structure of the samples was studied by X-ray diffractometer (XRD) D5005, Bruker. The chemical composition of our sample was Fe₅₀Pd₅₀ according to energy dispersive spectroscopy (EDS) included in scanning electron microscope (SEM) JSM-IT100, JEOL. The average crystallite size, d , was calculated using Scherrer's formula: $d = 0.9\lambda / (B \cos \theta)$, where λ is the wavelength of X-rays, B is the full width at half maximum of a XRD peak and θ is the angle of a XRD peak. The particle morphology was investigated by a transmission electron microscope (TEM) JEM1400, JEOL. Magnetic properties of the samples were studied using a vibrating sample magnetometer (VSM) at room temperature.

3. Results and Discussion

Figure 1 shows the TEM images of the as-prepared and annealed Fe₅₀Pd₅₀ nanoparticles for various times. Particle size of the as-prepared Fe₅₀Pd₅₀ sample is about 5-9 nm. The particle size increases with increasing annealing time, to about 7-30 nm for the sample annealed for 6 h due to the annealing effect. Compared to the results for as-prepared samples obtained by Luong et al. [16], the size of the nanoparticles prepared with CTAB is smaller than that of the nanoparticles synthesized without CTAB due to the steric interference properties of surfactant.

The XRD patterns of the as-prepared and annealed samples are shown in Figure 2. The XRD pattern of the as-prepared sample showed diffraction peaks at 40°, 46.5° and 68.5°, which can be assigned to (111), (200) and (220) reflections of the disordered fcc structure. From XRD results we obtained the

lattice parameter $a = 3.885 \pm 0.015 \text{ \AA}$. The average crystallite size deduced from Scherrer's formula was 8.4 nm, in good agreement with the particle size observed by TEM. The X-ray patterns of $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles annealed at 550°C for various times show that the diffraction peaks were shifted to a higher position compared to that in the as-prepared sample. The peak (200) is splitted into two peaks (200) and (002) due to the tetragonal symmetry of fct FePd ($a \neq c$) [18]. These results indicate a structural transition from fcc to fct. In addition, the patterns show another clear splitting of the peaks (220) into two peaks (220) and (202). The observed (001) and (110) peaks in the samples annealed for 4 h and 6 h are also a chemical order signature of the samples. α -Fe phase was also formed in the samples annealed for 1 h and 2 h. The average crystallite size determined using Scherrer's formula was 13.4, 14, 14.4 and 15.4 nm for the samples annealed at 550°C for 1, 2, 4 and 6 h, respectively, in agreement with the TEM observation. Comparing these results on particle size with those obtained for the as-prepared and $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles annealed at 550°C for 1 h reported in [16] shows that the particle size was smaller for CTAB added $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles. Similar effect on reduction of particle size in the presence of CTAB was reported by Goswami et al. [17] for the FePt nanoparticles. Probably, the reason for reduction of particle size in CTAB added $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles is that CTAB molecules act like barrier hindering some reactions from taking place [19].

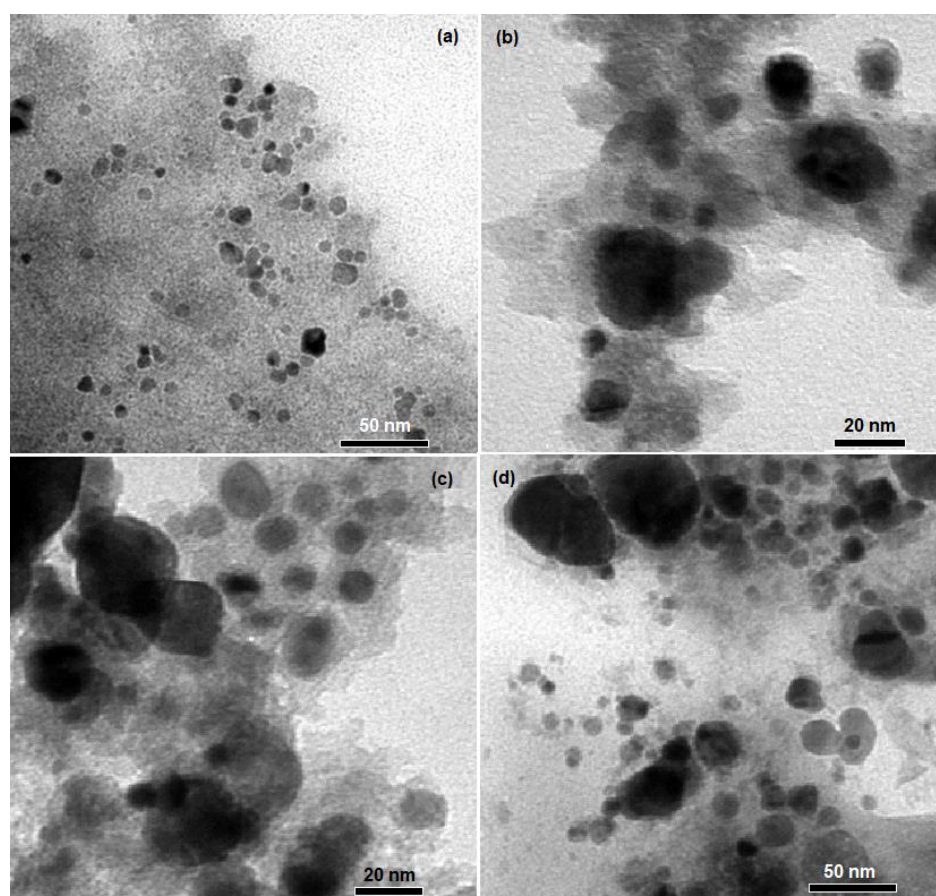


Figure 1. TEM images of $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles. (a) as-prepared; annealed at 550°C for (b) 2 h, (c) 4 h, (d) 6 h.

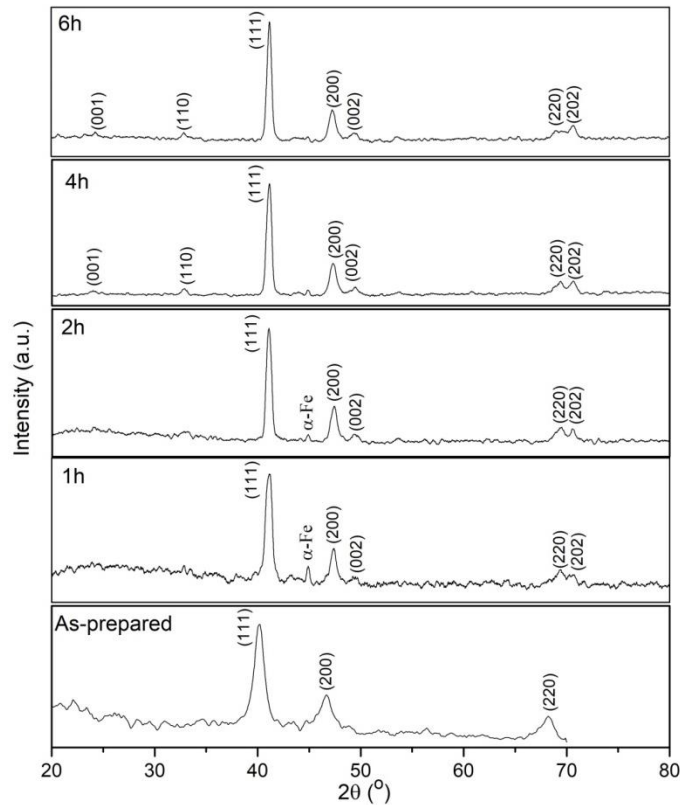


Figure 2. X-ray patterns of as-prepared and annealed $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles.

Figure 3 presents magnetic hysteresis $M(H)$ loops of the $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles prepared with CTAB and without CTAB annealed at 550°C for 1 h. $M(H)$ loops of the $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles prepared without CTAB were obtained by Luong et al. [16]. The loops exhibit hard magnetic characteristics. Comparison of the results obtained for $M(H)$ loop of the sample synthesized with CTAB with those of the sample prepared without CTAB shows a prominent effect of CTAB on magnetic properties. The coercivity (H_C) of the sample increases from 1.1 kOe for the sample prepared without CTAB to 1.58 kOe for the sample synthesized with CTAB. The higher value of coercivity may be due to the higher degree of ordering. On the other hand, magnetization decreases with addition of CTAB, probably due to the decrease of particle size.

Several groups have synthesized the FePd nanoparticles without using CTAB. Watanabe et al. [10] have synthesized the $\text{Fe}_{49.2}\text{Pd}_{50.8}$ nanoparticles by the modified polyol process. They reported the coercivity value of 2.04 kOe at 5 K for the $\text{Fe}_{49.2}\text{Pd}_{50.8}$ samples annealed at 600°C for 1 h. Gajbhiye et al. [11] used the modified polyol process to prepare $\text{Fe}_{43}\text{Pd}_{57}$ nanoparticles and obtained H_C values of 0.085 kOe, 1.18 kOe and 1.3 kOe at 300 K for these nanoparticles annealed at 450°C , 550°C and 600°C for 1 h, respectively. Hou et al. [8] prepared the $\text{Fe}_{48}\text{Pd}_{52}$ nanoparticles using a chemical method with subsequent annealing at 550°C , 600°C , and 700°C for 30 min. These authors observed that the room-temperature coercivity of the samples increased with increasing annealing temperature and attained a maximum value of ~ 2 kOe at 600°C . When annealing temperature further increases, the coercivity decreases, probably because a soft phase is formed at higher temperatures.

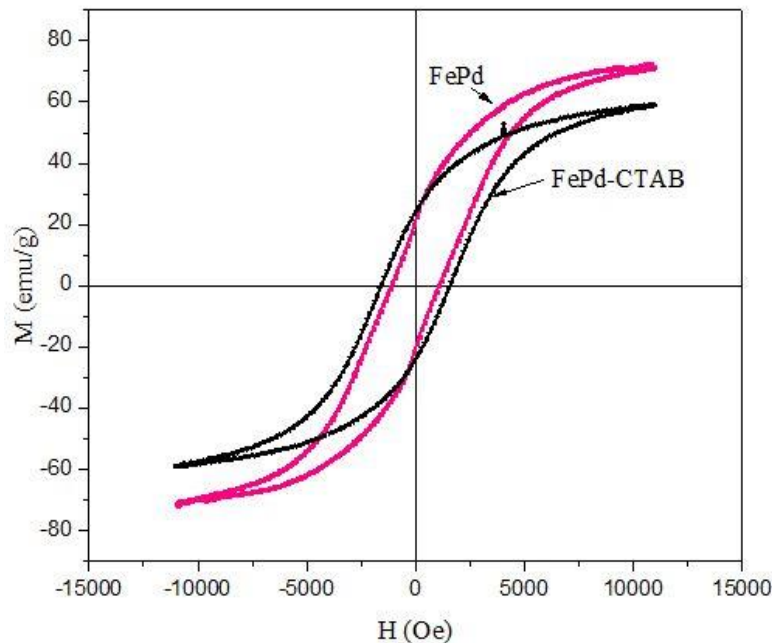


Figure 3. Magnetic hysteresis $M(H)$ loops of $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles prepared with CTAB and without CTAB (annealed at $550^\circ\text{C}/1\text{ h}$).

Figure 4 presents the room-temperature magnetic hysteresis $M(H)$ loops of the $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles annealed at 550°C for different times. The annealed samples exhibit hard magnetic properties with good coercivity. Figure 5 shows the coercivity of the $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles as a function of annealing time. H_C decreases from the value of 1.58 kOe to the minimum value of 1.37 kOe with increasing annealing time from 1 h to 2 h. With further increasing annealing time from 2 h to 6 h, H_C increases, reaching a value of 1.64 kOe for the sample annealed for 6 h. Tournus et al. [20] performed the atomic structure study of CoPt and FePt nanoparticles with a diameter of 2 to 5 nm synthesized by low-energy cluster-beam deposition. These authors showed that, in addition to particles corresponding to a single $L1_0$ ordered domain, even small particles which can consist of several $L1_0$ ordered domains are evidenced. The coexistence of several domains having different c orientations will drastically reduce the magnetocrystalline anisotropy as compared to mono- $L1_0$ domain particles. The coercivity of our nanoparticles annealed for 2 h is reduced probably because diffusion of Fe and Pd atoms upon annealing creates several multi- $L1_0$ domain particles, leading to the reduction of magnetocrystalline anisotropy. With further increasing annealing time, the coercivity increases because $L1_0$ ordered region increases. We have studied the variation of the degree of ordering with annealing time in our samples. The tetragonal structure of the ordered FePd phase is of CuAu-I type. During the ordering transformation, dimensions decrease along the z -axis while increase along the x and y -axis, leading to tetragonality with the lattice parameter ratio $c/a < 1$. Degree of ordering (S) can be deduced from c/a ratio using the relation $S = [(1 - c/a)/(1 - (c/a)_{\text{eq}})]^{1/2}$ where c/a is the measured value for the nanoparticles under investigation and $(c/a)_{\text{eq}}$ is the equilibrium value for the tetragonality obtained from fully ordered sample [21]. The c/a ratio, or tetragonality ratio, for our $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles as a function of annealing time is shown in Figure 5. As can be seen from this figure, the c/a ratio has highest value for annealing time of 2 h, corresponding to lowest degree of ordering for this annealing time. This result indicates that the coercivity strongly depends on the degree of ordering in these nanoparticles.

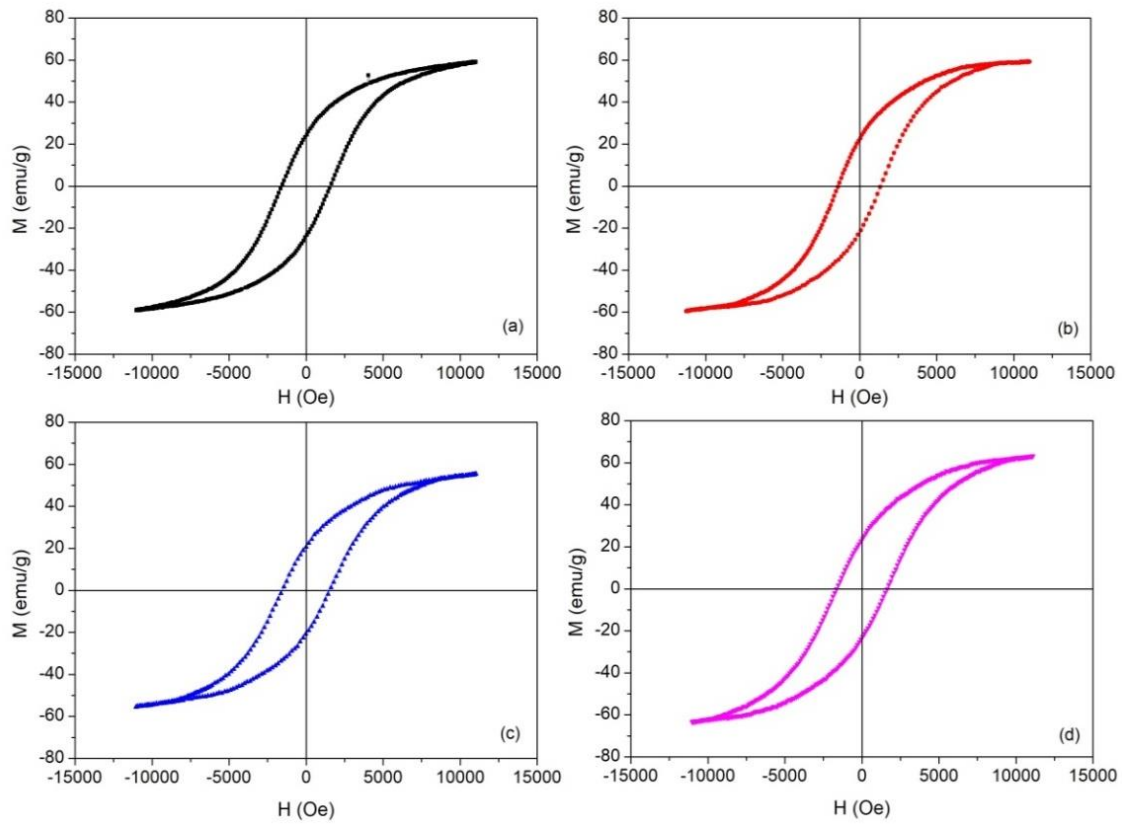


Figure 4. Magnetic hysteresis $M(H)$ loops of $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles annealed at 550°C for a) 1 h, (b) 2 h, (c) 4 h, (d) 6 h.

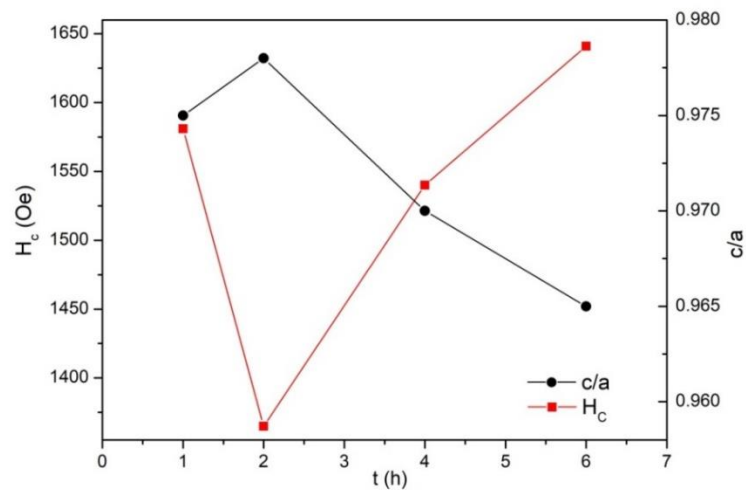


Figure 5. Coercivity and c/a ratio of $\text{Fe}_{50}\text{Pd}_{50}$ nanoparticles as a function of annealing time.

4. Conclusion

In this study, the Fe₅₀Pd₅₀ nanoparticles were prepared by sonoelectrodeposition in the presence of CTAB surfactant. After annealing at 550°C for a series of times from 1 h to 6 h, a transformation from disordered fcc structure to the ordered L1₀ structure occurred. It was revealed that the coercivity of the nanoparticles was larger compared to that of the samples prepared by the same method in the absence of CTAB. The coercivity decreases with increasing annealing time from 1 h to 2 h, then increases with further increasing annealing time, reaching a value of 1.64 kOe for the sample annealed for 6 h. The evolution of the tetragonality ratio as a function of annealing time shows similar tendency, indicating that the coercivity strongly depends on the degree of ordering in the Fe₅₀Pd₅₀ nanoparticles.

Acknowledgments

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