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Surface Modification of SiO_2-Coated FePt Nanoparticles with Amino Groups*

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Magnetic nanoparticles (NPs) with modified surface are important materials for applications in biological systems. In this paper, FePt NPs have been prepared by electrodeposition method. After annealing at 700°C for 1 h under a mixture of 5% H_2 and 95% Ar atmosphere the FePt NPs exhibit the coercivity of 11.5 kOe. The FePt NPs are then coated with a layer of silica SiO_2 by using the Stober method assisted by mechanical waves originated from a sonicator. The FePt/SiO_2 NPs were easily bound with 3-aminopropyl-triethoxy-silance to have an amino surface. Analysis of transmission electron microscope reveales the core-shell structure of the NPs.

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Keywords: Nanoparticles; Electrodeposition; FePt; Amino groups; Core-shell structure

I. INTRODUCTION

Surface modification of nanoparticles (NPs) is important for modern biotechnology and life science. The controlled, optimized attachment of biomolecules to solid surfaces plays a crucial role in their ultimate utility [1]. Surface modification with organosilanes is an attractive approach as it is compatible with many of the materials used in a biological context, i.e., silica gel, glass slides, or silicon wafers [2].

FePt NPs are an excellent magnetic material for ultrahigh-density magnetic recording media because of their superior magnetic properties such as high magnetocrystalline anisotropy energy, high saturation magnetization and high chemical stability [3, 4]. Meanwhile, FePt NPs are also expected to be a high-performance nanomagnet for magnetic medicine, such as magnetic hyperthermia [5], immunomagnetic cell separation [6], and excellent contrast agents for magnetic resonance imaging [7].

In this paper, we report the use of the electrodeposition method for the preparation of FePt NPs and surface modification with amino groups of silica-coated FePt NPs.

II. EXPERIMENTAL

The electrolytes were prepared by using a grade chemical reagent and were composed of 1 M $FeSO_4 \cdot 7H_2O$, 0.01 M H_2PtCl_6, and 0.525 M Na_2SO_4, contained in an 100 mL three-neck flash. The pH of 3 of the electrolyte was adjusted by H_2SO_4. Poly(vinyl-pyrrolidone) (PVP) with a molecule weight of 30,000 as a surfactant that was added with a concentration of 4.25 mg/mL. Before starting electrodeposition, nitrogen gas was bubbled in the electrolyte for 20 min to remove the amount of dissolved oxygen. Electrodeposition was conducted ganvanostatically in a two-electrode home-made cell at room temperature. A platinum plate with a cross-section of 1 cm^2 was used as a counter electrode. Current pulse J was 15 mA/cm^2. The duration of the current pulse, ton, was 0.5 s then the current was turned off for a fixed duration toff of 0.3 s. The electrodeposition was carried out under nitrogen atmosphere. After 1 h deposition, a black solution was obtained and as-prepared NP powder was collected by using centrifuging at 9000 rpm for 30 min. The powder was annealed at 700°C for 1 h under a mixture of 5% H_2 and 95% Ar atmosphere. The increasing rate of temperature was 6°C/min and then the furnace was naturally cooled. Then coating of the FePt NPs with silica has been achieved easily using a versatile modified Stober process by the aid of the sonication. Typically, 0.10 g of as-obtained FePt was added to 50 mL of ethanol and the mixture sonicated for 15 min. Then 5 mL of 26% $NH_3 \cdot H_2O$ and a certain amount of tetraethylorthosilicat (TEOS) were added subsequently. The reaction lasted for 1.5 h under sonication without any cooling. The products were obtained by centrifugation, washed several times, and then vacuum-dried. Surface modification with amino was peformed by using 3-aminopropyl-triethoxy-silance (APTES). For surface activation, 0.10 g of NPs was added to a freshly prepared solution of APTES (2% w/v) in the desired solvent. The final volume was adjusted to 10 mL. The mixture was stirred vigorously on a magnetic stirrer at the 60°C while reacting and washed five times with fresh solvent. The structure of the nanostructure was analyzed by using a Bruker D5005 X-ray diffractometer (XRD). Magnetic measurement was conducted by using a DMS-880 vibrating sample magnetometer (VSM) with maximum magnetic field of 13.5 kOe at room temperature. The nanostructure morphology was studied by a transmission electron microscopy (TEM JEM1010-JEOL). The chemical composition of the FePt NPs was studied by using an energy dispersion spectroscopy (EDS OXFORD-ISIS 300). FTIR measurements have also been performed.

III. RESULTS AND DISCUSSION

The positive Pt^{4+} and Fe^{2+} ions went to the cathode surface and received electrons to make Pt and Fe NPs. If PVP surfactant was not present, Fe and Pt atoms would continously deposite on the plate and at the end, FePt film would be obtained. The presence of PVP around NPs created a steric force that limits the growth of NPs and we could obtained Fe and Pt NPs well dispersed in

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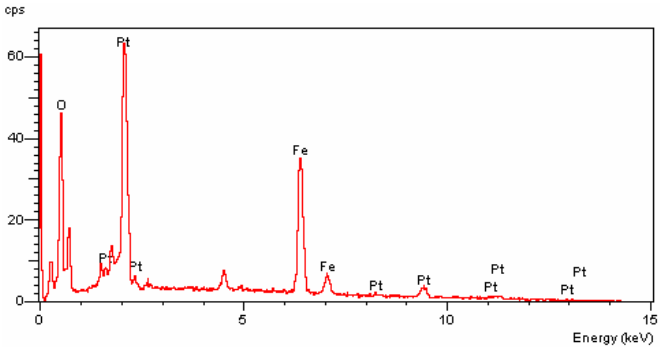

FIG. 1: EDS pattern of the as-prepared FePt nanoparticles.

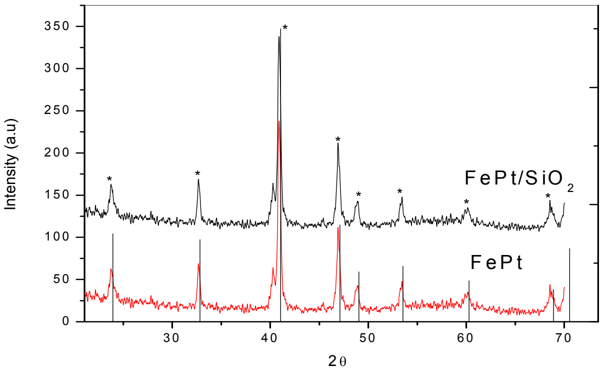

FIG. 2: XRD patterns of annealed FePt nanoparticles before and after coated by SiO_2.

the solution. Figure 1 shows EDS pattern of as-prepared FePt NPs. The concentration of Fe : Pt deduced from the EDS result is 60:40.

Figure 2 shows XRD patterns of FePt NPs before and after being coated by silica. The XRD results of the FePt before coated by silica showed the reflection of FePt face-centred tetragonal (fct) structure. The patterns of FePt nanostructure before and after silica-coating are the same, no reflection peak of SiO_2 is observed, but the value of background of FePt/SiO_2 is hight. There is a disturbance in reflections of FePt/SiO_2 demonstrating that the layer of silica is amorphous.

Magnetic measurements revealed low saturation magnetization ($M_{\rm s}$) and coercivity ($H_{\rm c}$) in as-prepared samples (data not shown). The low value of $M_{\rm s}$ of the as-prepared NPs may be explained by the oxidation or hydroxidation of Fe atoms in NPs which can result in the antiferromagnetic iron oxide and weak magnetic iron hydroxides. After annealing in H_2-Ar atmosphere the hard magnetic FePt phase formed. Figure 3 presents the hysteresis loops of the FePt and FePt/SiO_2. The curves show typical hard magnetic hysteresis loops with $H_{\rm c}$. Note that, because of the limit of maximum applied field of 13.5 kOe, the curves is a minor loop. Therefore, the real coercivity is expected to be higher than those obtained from the hysteresis loops. The loop shows a kink at low reversed magnetic field of 300 Oe, which indicates that there was a small amount of a soft magnetic phase. Classically, the coercivity is defined as the field for which the magnetization (M) vanishes ($H_{\rm c}'$). In a more physically meaningful definition, the coercivity $H_{\rm c}$ may be defined as the field where the largest number of moments reverses, i.e., the maximum of the susceptibility (dM/dH). In most cases, both definitions of the coercivity are almost equivalent. However in multiphase materials, two definitions are significantly different [8]. From Fig. 3 one can see that coercivity $H_{\rm c}$ is 11.5 kOe. When coating silica layer, the magnetization is lower compared to that before silica coating. The unchanged value in coercivity can be explained by the non-magnetic silica.

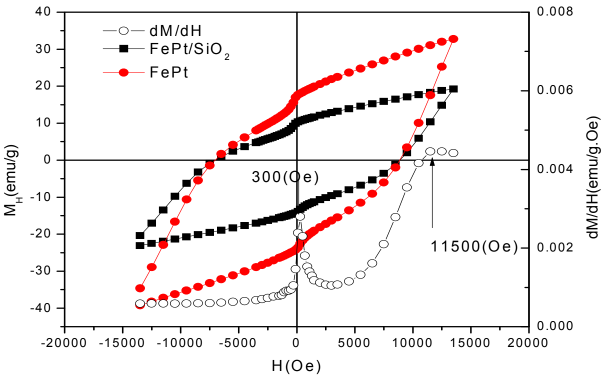

FIG. 3: Magnetic curves of FePt and FePt/SiO_2 samples.

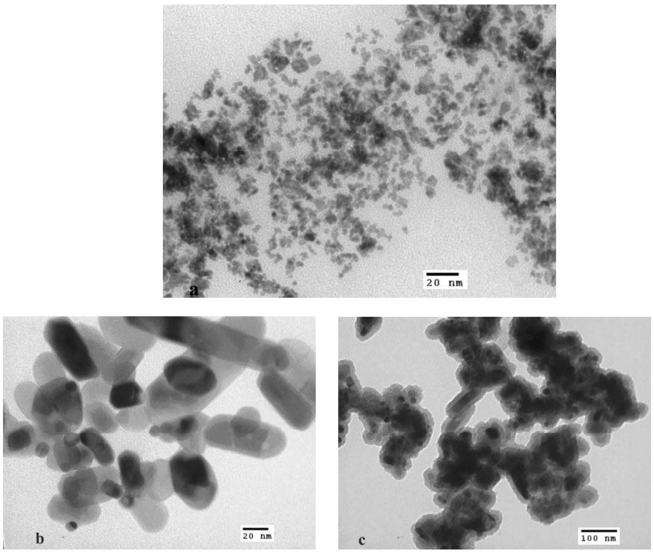

FIG. 4: TEM images of (a) as-prepared FePt, (b) annealed FePt and (c) FePt/SiO_2 samples.

Figure 4 illustrates the TEM images of typical (a) as-prepared FePt, (b) annealed FePt and (c) FePt/SiO_2. Particle size of the as-prepared FePt is estimated to be few nanometers. After annealing the particle size increases due to the diffusion and aggregation between particles to form fct FePt phase. At hight temperature, atoms on the surface of the particles are energetically less stable than the ones that were already well ordered and packed in the interior. As the system tries to lower its overall energy, atoms on the surface of a small (energetically unfavorable) particle will tend to diffuse to the surface of larger particles [9]. Therefore, the smaller particles continue to shrink, while larger particles continue to grow. As the re-

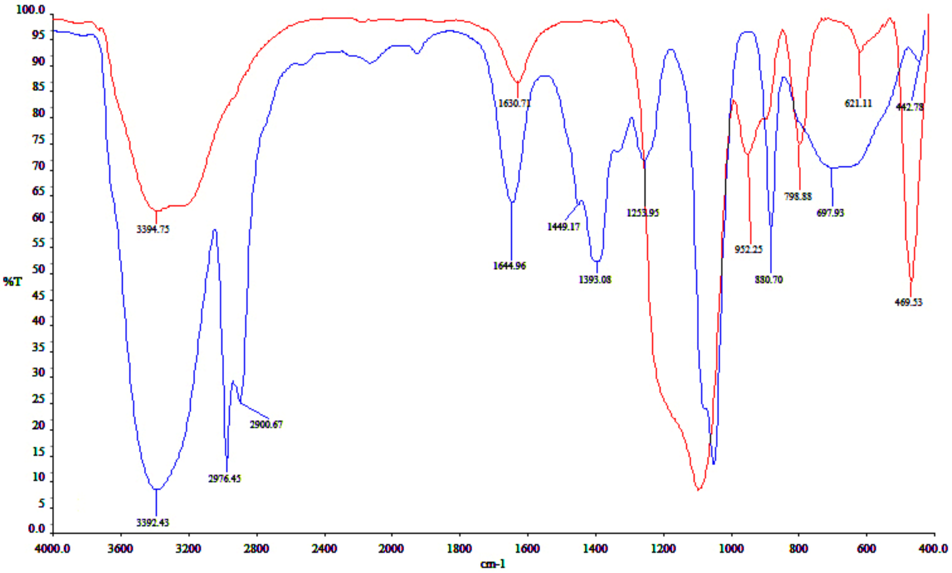

FIG. 5: FTIR spectra of the FePt/SiO_2 (above-red) and FePt/SiO_2 modified with amino groups (below-violet).

sults, the particles in annealed samples are of larger size than unannealed ones. The shape of FePt NPs after annealing is not sphere (Fig. 4(b)). This image shows the rods. After silica coating, silica layer is clearly visible in the TEM image (Fig. 4(c)). The core-shell structure of the NPs was observed.

Figure 5 shows FTIR spectra of samples. FTIR results confirmed the presence of silica and APTES in the samples. Absorption band at 3392 cm^{-1} corresponds to N–H stretching modes [10], the bands at 2976 and 2900 cm^{-1} correspond to C–H stretching modes, strong band at 1644 cm^{-1} corresponds to N–H bend modes of APTES and the bands at 880 and 1050 cm^{-1} correspond to Si–OH and Si–O–Si or Si–O–Fe stretching vibration of the silica shell, and three bands from 1449 to 1253 cm^{-1} are attributed to C–N stretching modes. The data strongly suggest that FePt/SiO_2 were really modified with amino groups.

IV. CONCLUSIONS

FePt NPs have been prepared by electrodeposition method. After annealing at700°C for 1 h these NPs exhibit the coercivity of 11.5 kOe. The FePt NPs are then coated with a layer of silica SiO_2. SiO_2-coated FePt NPs was modified with amino groups. The core-shell structure of the NPs was observed.

Acknowledgments

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[1] I. J. Bruce and T. Sen, Langmuir **21**, 7029 (2005).
[2] T. Coradin and P. J. Lopez, Chembiochem **4**, 251 (2003).
[3] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, Science **287**, 1989 (2000).
[4] S. Sun, Adv. Mater. **18**, 393 (2006).
[5] S. Maenosono and S. Saita, IEEE Trans. Magn. **42**, 1638 (2006).
[6] H. Gu, P.-L. Ho, K. W. T. Tsang, L. Wang, and B. Xu, J. Am. Chem. Soc. **125**, 15702 (2003).
[7] S. Maenosono, T. Suzuki, and S. Saita, J. Mag. Mag. Mat. **320**, L79 (2008).
[8] D. Givord and M. F. Rossignol, in *Rare-Earth Iron Permanent Magnets*, J. M. D. Coey (Ed.) (Clarendon Press, Oxford, 1996), p. 218.
[9] A. T. Hubbard, *Encyclopedia of Surface and Colloid Science* (CRC press, 2004), p. 4230.
[10] V. K. S. Hsiao, J. R. Waldeisen, Y. Zheng, P. F. Lloyd, T. J. Bunning, and T. J. Huang, J. Mater. Chem. **17**, 4896 (2007).