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A Novel Approach to Synthesis of FePt Magnetic Nanoparticles

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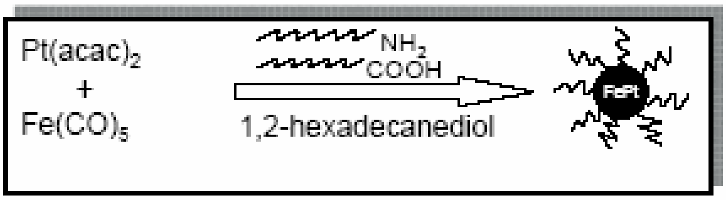
Abstract. Chemical reduction of ferric acetylacetonate (Fe(acac)$_3$) and platinum acetylacetonate (Pt(acac)$_2$) using polyol as a reducing agent as well as an effective surfactant, has successfully yielded monodisperse FePt nanoparticles with a size of approximately 2 nm. When annealed samples were compared to FePt nanoparticles synthesized using oleic acid and oleylamine as the surfactants under identical conditions, nearly 30% increase in coercivity (H$_c$) was achieved with the new, simple and economic method.

Introduction

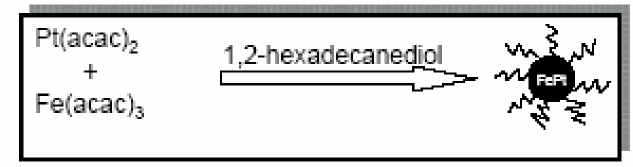
Chemically synthesized magnetic nanoparticles have drawn great attention because the magnetic particles have reduced dimensions down to few nanometers with well controlled size, size distribution and shape. Monodisperse magnetic nanoparticles have potential applications in high performance nanocomposite magnets [1], high-density magnetic storage media [2], magnetic resonance imaging contrast agents [3], biological sensors and directed drug therapy [4]. Polyol reduction methodology used by Fievet et al. [5] and modified by Sun et al. [2] has been developed by many researchers to provide a wide variety of nanoparticle systems for investigations in the mentioned applications. The polyol process requires at its basis, a diol as reducing agent, metal salt precursors, surfactants and a solvent. The surfactants are added to prevent particles from agglomeration and inhibit oxidation. In certain cases, surfactants can also induce geometric changes to the particles [6]. In a typical polyol synthesis route, as shown in Scheme 1, FePt particles are synthesized via decomposition of iron pentacarbonyl, Fe(CO)$_5$ and reduction of (Pt(acac)$_2$, in presence of 1,2-hexadecanediol (HDD). Oleic acid and oleyl amine are used as the surfactants in a proper solvent [7-17].



Scheme 1. Typical polyol synthesis route for FePt nanoparticles.

It is still a research focus to develop simple, efficient and cost effective methods to synthesize FePt nanoparticles with better control of morphological, structural and magnetic properties of the particles. In our previous studies, modified synthesis recipes have been used to produce FePt nanoparticles with alternative morphological and magnetic properties. By using iron acetylacetonate (Fe(acac)$_3$) to replace iron pentacarbonyl Fe(CO)$_5$, we obtained monodisperse FePt nanoparticles with particles size of 2 nm [18]. It was also found that the FePt nanoparticles can be synthesized without using any polyol reducing agent [19] in octyl ether. We also studied the effect of various synthesis parameters, especially the surfactant addition, on the particle size and shape and have obtained FePt nanoparticles with particle size from 2 to 9 nm with 1 nm accuracy [20].

Here we report a novel one-pot synthesis of FePt nanoparticles with controlled composition by the polyol reduction of Fe(acac)$_3$ and Pt(acac)$_2$ only in presence of 1,2-hexadecanediol in octyl ether, where the conventional surfactants such as oleic acid and oleylamine, are not used, as shown in Scheme 2. It is interesting to find out that monodisperse FePt nanoparticles can be prepared by using this simple recipe and the resulted nanoparticles show improved magnetic properties.



Scheme 2. A simple synthesis route for FePt nanoparticles used in this investigation.

Experimental

The Fe(acac)$_3$, oleic acid, oleyl amine and 1,2-hexadecanediol were obtained from Aldrich, Pt(acac)$_2$ from Strem Chemicals, dioctyl ether from SAFC, ethanol from AAPER and hexane from EMD, which were used without further purification. Synthesis was carried out under standard airless techniques in an argon atmosphere. In a typical synthesis route, Pt(acac)$_2$ and Fe(acac)$_3$ in the molar ratio 1:1 were taken in a 125 mL European flask containing a PTFE coated magnetic stir bar at room temperature. 1, 2-hexadecanediol (5 times mole amount of Pt(acac)$_2$ and Fe(acac)$_3$) was added to the flask. 30 mL of dioctyl ether was then transferred into the flask and the contents were stirred while purging with Ar for 30 minutes at room temperature. The flask was then heated to 200^{o} C at 6^{o} C per minute by use of a Glas-Col hemispherical heating mantel connected to a programmable heat controller using a type J thermocouple. Once the temperature reached 200^{o} C, the flask was kept at this temperature for 30 minutes. After the 30 minute hold, the flask was heated to 295^{o} C at a rate of approximately 5^{o} C per minute. The flask was maintained at a refluxing temperature of 295^{o} C for 30 minutes before cooling down to room temperature under the Ar purge. Afterwards, all handling was performed open to the atmosphere. For comparison purpose FePt of average 2 nm size having Pt(acac)$_2$ to Fe(acac)$_3$ molar ratio of 1, was prepared similar to the method as reported earlier [18].

Purification of the nanoparticles was accomplished as follows: 5 mL of the dispersion taken from the flask was added to 20-25 mL of ethyl alcohol (EtOH) and the mixture was centrifuged (6000 rpm for 15 minutes). The supernatant was discarded and the precipitate was redispersed in 10 mL of hexane. The dark brown dispersion was stored under refrigeration at approximately 10^{o} C.

Samples for magnetic characterization were prepared by depositing a few drops of the hexane dispersion of the sample onto a silicon substrate and allowing the solvent to evaporate at room temperature. In order to transfer the disordered face-centered cubic (fcc) structure of the as-synthesized FePt nanoparticles to L1$_0$ structure with high magnetocrystaline anisotropy, the deposited thin film samples were annealed either in a nitrogen or forming gas (Ar + 7% H$_2$) atmosphere for 1 h at temperatures between 550 and 900^{o} C. Magnetic hysteresis loops of the samples were measured by a superconducting quantum interference device (SQUID). Powder X-ray diffraction (XRD) patterns were measured using a Phillips MPD diffractometer with a CuK$_\alpha$ source (λ = 1.5405 Å) and transmission electron microscopy (TEM) measured by a JEOL 1200 EX electron microscope at an accelerating voltage of 120 kV.

Results and Discussion

Fig. 1 shows a TEM image of the as-synthesized FePt nanoparticles. It can be seen that the average particle size is 2 nm, which is typical for FePt nanoparticles reported earlier for recipes using Fe(acac)$_3$ [18]. It is clear that the particles have spherical shape and narrow size distribution.

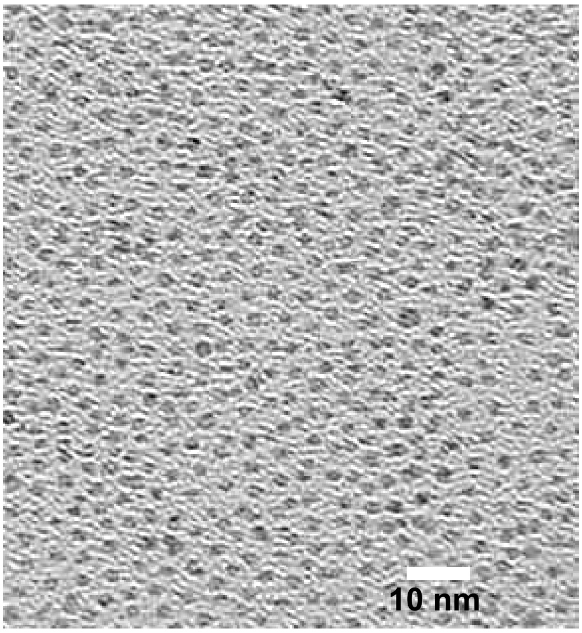


Fig. 1. TEM image of the as-synthesized FePt particles using HDD as the surfactant and reductant.

Fig. 2 shows XRD patterns of as-synthesize FePt nanoparticles. From the position of the peaks, it is clear that the as-synthesized FePt nanoparticles have a chemically disordered fcc structure. An average particle diameter of 1.6 nm was calculated from the peak width of the XRD pattern using Scherer formula, which is consistent with the diameter calculated by statistical analysis of TEM images, and is similar to the particle size reported in Ref. 18. Energy dispersive x-ray analysis of the formed FePt particles show the initial feed ratio of Fe and Pt metal precursors are maintained in the fcc FePt nanoparticles.

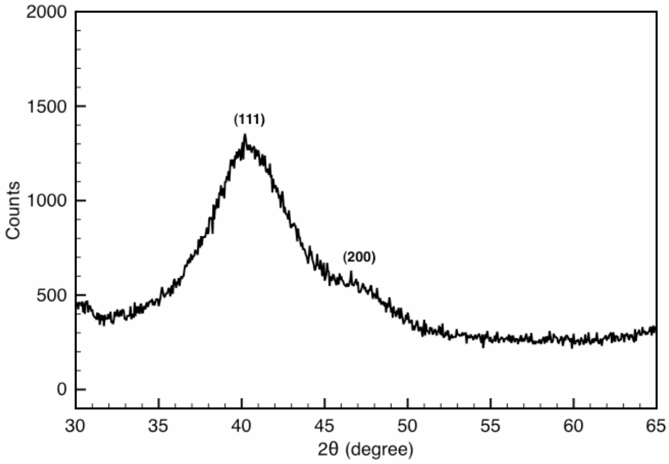


Fig. 2. Powder XRD scan of the as-synthesized FePt particles using HDD as the surfactant and reductant.

The above structural characterizations show clearly that fcc FePt nanoparticles with composition of equal atomic Fe:Pt ratio were synthesized by co-reduction of $Fe(acac)_3$ and $Pt(acac)_2$ in presence of 1, 2-hecadecanediol in octyl ether. More interestingly, the HDD also played role as an effective surfactant. Based on the structure and functionality, using HDD as a surfactant for dispersing the formed nanoparticles is not unreasonable, while also providing the reductive species needed to form the fcc FePt nanoparticles. In addition, it is possible that the oxidized HDD molecules are also used as capping ligands to protect the particles from oxidation and facilitate dispersion of particles in nonpolar solvents, unlike traditional methods where capping ligands such as oleic acid and oleylamine are used [7-17].

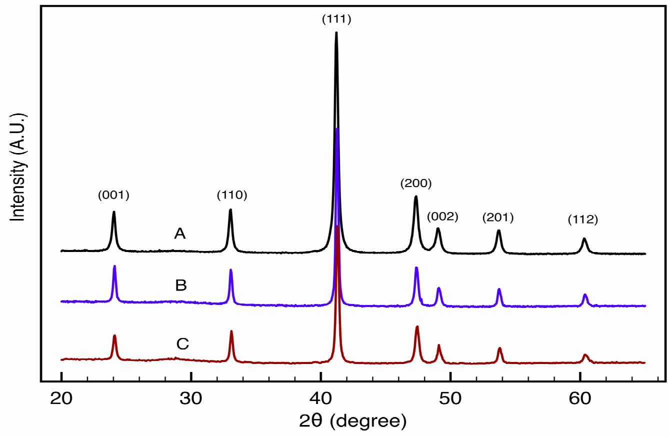


Fig. 3. XRD scans of the samples annealed at 700° C in A) nitrogen, B) forming gas (Ar + 7% H_2), and C) particles from the reference 18 method annealed at 700° C in forming gas.

The chemically disorder fcc FePt crystal has a low magnetocrystalline anisotropy, and hence is superparamagnetic at room temperature. To obtain high uniaxial magnetocrystalline anisotropy, which is required for many applications, the as-synthesized FePt nanoparticles typically have to be annealed at high temperature to transform to the chemically ordered $L1_0$ tetragonal FePt phase. Fig. 3 shows the XRD patterns for the samples annealed in nitrogen and Ar +H_2 (7%) at 700° C for 1 h, compared with the XRD pattern for the $L1_0$ FePt sample produced by the method reported in ref 18. It can be clearly seen from this figure that both the peak position and intensity for the annealed samples prepared by our new method match perfectly with those of the sample made from standard method, indicating that Ll_0 structure is indeed formed after thermal annealing. This double confirms that the particle composition is in the right rage for the formation of the equal atomic $L1_0$ phase. In addition, sample annealed in nitrogen do not show any oxide peaks in their XRD patterns which indicates that the HDD effectively protected the fcc FePt nanoparticles from oxidation when exposed to the open atmosphere.

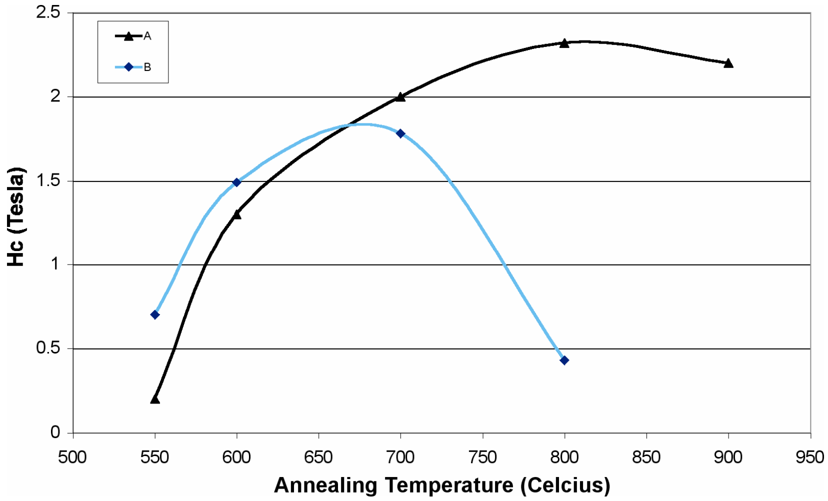


Fig. 4. Annealing temperature dependence of coercivity of annealed samples prepared by the current method (curve A) and the method reported in Ref. 18 (curve B). The samples were annealed in forming gas for 1 h.

Fig. 4 shows the coercivity change with annealing temperature of the annealed particles obtained from our new method, compared with the coercivity values of particles obtained by the method using oleic acid and oleylamine as surfactant. Particles were annealed on Si substrate under Ar + H_2 (7%) for 1 h. It was observed that for the traditional FePt sample maximum coercivity of 1.8 T was obtained at 700^o C and a sharp decrease in coercivity was observed above 700^o C. On the other hand, for the sample prepared by our new method, coercivity continues to increase above 700^o C, and a maximum coercivity of 2.3 T was obtained at 800^o C. It is interesting to find that there is an approximately 28% increase in coercivity of the particles obtained by our new method as compared to the particles prepared by the method in Ref. 18. This result shows that the magnetic hardening of the FePt nanoparticles prepared by our new method can be maintained up to 800^o C. Even when particles were annealed at 900^o C, only a slight decrease in coercivity of the FePt nanoparticles was observed. The exact nature of the observed coercivity enhancement by this method is not completely clear, however, it is possible that the nanoparticles derived from this new method did not sinter substantially during annealing, relative to the particles from the traditional method. This degree of isolation would be possible if the HDD is preferentially adsorbed to the particle surface during the synthesis, protecting the particles during annealing from sintering. The smaller particle size and high degree of chemical ordering within the particles would then result in higher coercivity at the higher annealing temperatures. This magnetic hardening behavior may also be related to the enhanced atomic diffusion during the heat treatment that expedited the $L1_0$ phase formation.

We have also investigated the effect of HDD amount on the nanoparticle formation. During the FePt synthesis, the mole amount of HDD was varied from 5, 10 and 15 times of $Fe(acac)_3$ and $Pt(acac)_2$. It was observed that increased HDD mole amount during FePt synthesis does not lead to changes in the annealed FePt samples. There is essentially no change in coercivity of the samples with different HDD amount.

Conclusions

A simplified and cost effective synthetic route has been found that provides a straightforward synthesis of FePt nanoparticles. HDD alone can be used as reducing agent as well as an effective surfactant to protect the particle from agglomeration and oxidation. The as-synthesized particles have uniformity in size with particle diameters of approximately 2 nm. Detailed structural and magnetic characterization show that FePt nanoparticles synthesized through this simplified method can provide magnetically hard $L1_0$ FePt nanoparticles with coercivity reaching up to 2.3 Tesla in thin films, representing an increase in H_c of nearly 30% over the traditional method using oleic acid and oleyl amine as the surfactants processed under the similar conditions. These ultrafine magnetic nanoparticles can serve as building blocks for nanostructured high performance thin film and bulk magnets.

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References

[1] H. Zeng, J. Li, Z. L. Wang, J.P. Liu, S. Sun, Exchange-coupled nanocomposite magnets by nanoparticle self-assembly, Nature 420 (2002) 395-398.

[2] S. Sun, C.B. Murray, D. Weller, L. Folks, A. Moser, Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices, Science 287 (2000) 1989-1992.

[3] (a) W.S. Seo, J.H. Lee, X. Sun, Y. Suzuki, D. Mann, Z. Liu, M. Terashima, P.C. Yang, M.V. McConnell, D.G. Nishimura, H. Dai, FeCo/graphitic-shell nanocrystals as advanced magnetic-resonance-imaging and near-infrared agents, Nat. Mater. 5 (2006) 971-976. (b) Y.J. Wang, S.M. Hussain, G.P. Krestin, Superparamagnetic iron oxide contrast agents: physicochemical characteristics and applications in MR imaging, Eur. Radiol. 11 (2001) 2319-2331.

[4] S.H. Chung, A. Hoffmann, S.D. Bader, C. Liu, B. Kay, L. Makowski, L. Chen, Biological sensors based on Brownian relaxation of magnetic nanoparticles, Appl. Phys. Lett. 85 (2004) 2971-2973.

[5] (a) F. Fievet, J. P. Lagier, B. Blin, B. Beaudon, M. Figlarz, Homogeneous and heterogeneous nucleations in the polyol process for the preparation of micron and submicron size metal particles, Solid State Ionics 32/33 (1989) 198-205. (b) G. Viau, F. Fievet-Vincent, F. Fievet, Nucleation and growth of bimetallic CoNi and FeNi monodisperse particles prepared in polyols, Solid State Ionics 84 (1996) 259-270. (c) P. Toneguzzo, G. Viau, O. Acher, F. Guillet, E. Bruneton, F. Fievet-Vincent, F. Fievet, CoNi and FeCoNi fine particles prepared by the polyol process: Physico-chemical characterization and dynamic magnetic properties, J. Mater. Sci. 35 (2000) 3767-3784.

[6] S. Lee, Y. Jun, S. Cho, J. Cheon, Single-crystalline star-shaped nanocrystals and their evolution: Programming the geometry of nano-building blocks, J. Am. Chem. Soc. 124 (2002) 11244-11245.

[7] S. Sun, Recent advances in chemical synthesis, self-assembly, and applications of FePt nanoparticles, Adv. Mater. 18 (2006) 393-403.

[8] M. Chen, J.P. Liu, S. Sun, One-step synthesis of FePt nanoparticles with tunable size, J. Am. Chem. Soc. 126 (2004) 8394-8395.

[9] S. Sun, S. Anders, T. Thomson, J.E.E. Baglin, M.F. Toney, H.F. Hamann, C.B. Murray, B.D. Terris, Controlled synthesis and assembly of FePt nanoparticles, J. Phys. Chem. B 107 (2003) 5419-5425.

[10] M. Chen, J. Kim, J.P. Liu, H. Fan, S. Sun, Synthesis of FePt nanocubes and their oriented Self-assembly, J. Am. Chem. Soc 28 (2006) 7132-7133.

[11] T. Iwaki, Y. Kakihara, T. Toda, M. Abdullah, K. Okuyama, Preparation of high coercivity magnetic FePt nanoparticles by liquid process, J. Appl. Phys. 94 (2003) 6807-6811.

[12] S. Sun, E.E. Fullerton, D. Weller, C.B. Murray, IEEE Trans. Magn. 37 (2001) 1239-1243.

[13] A.K. Sra, T.D. Ewers, Q. Xu, H. Zandbergen, R.E. Schaak, One-pot synthesis of bi-disperse FePt nanoparticles and size-selective self-assembly into AB_2, AB_5, and AB_{13} superlattices, Chem. Commun. (2006) 750-752.

[14] Y. Sasaki, M. Mizuno, A.C.C. Yu, T. Miyauchi, D. Hasegawa, M. Takahashi, B. Jeyadevan, K. Tohji, K. Sato, S. Hisano, Chemically synthesized $L1_0$-type FePt nanoparticles and nanoparticle arrays via template-assisted self-assembly, IEEE Trans. Magn. 41 (2005) 660-664.

[15] H.M Song, J.H. Hong, Y.B Lee, W.S. Kim, Y. Kim, S.J. Kim, N.H. Hur, Growth of FePt nanocrystals by a single bimetallic precursor $[(CO)_3Fe(mu\text{-}dppm)(Mu\text{-}CO)PtCl_2]$, Chem. Commun. (2006) 1292-1294.

[16] C. Liu, X. Wu, T. Klemmer, N. Shukla, X. Yang, D. Weller, A.G. Roy, M. Tanase, D. Laughlin, Polyol process synthesis of monodispersed FePt nanoparticles, J. Phys. Chem. B 108 (2004) 6121-6123.

[17] (a) S. Momose, H. Kodama, T. Uzumaki, A. Tanaka, Fine tuning of the sizes of FePt nanoparticles Jap. J. Appl. Phys. 44 (2005) 1147-1149. (b) M. Nakaya, M. Kanehara, T. Teranishi, One-pot synthesis of large FePt nanoparticles from metal salts and their thermal stability, Langmuir 22 (2006) 3485-3487.

[18] K.E. Elkins, T.S. Vedantum, J.P. Liu, , H. Zeng, S. Sun, Y. Ding, Z.L. Wang, Ultrafine FePt nanoparticles prepared by the chemical reduction method, Nano Lett. 3 (2003) 1647-1649.

[19] V. Nandwana, K.E. Elkins, J.P. Liu, Magnetic hardening in ultrafine FePt nanoparticle assembled films, Nanotechnology 16 (2005) 2823-2826.

[20] V. Nandwana, K.E. Elkins, N. Poudyal, G.S. Chaubey, K. Yano, J.P. Liu, Size and shape control of monodispersed FePt nanoparticles, J. Phys. Chem. C 111 (2007*)* 4185-4189.