Tailoring FePt-Fe_3O_4 exchange spring coupling magnet in silica

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ABSTRACT

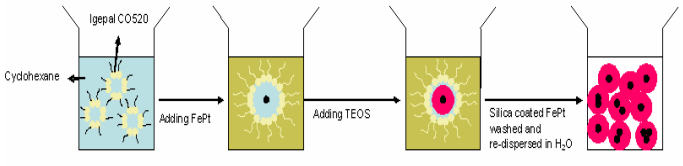
The synthesis of magnetic nanoparticles has been intensively investigated not only for their electrical, optical and magnetic properties but also for their various new technological applications, such as in the areas of biology and medicine. Exchange-spring magnets are nanocomposites that are composed of magnetically hard and soft phases that interact by magnetic exchange coupling. Such systems give a major advantage of combining the permanent magnetic field with magnetization hence rendering the mixture with many unique magnetic properties compared to traditional single-phase nano-magnets. However, one major current problem encountered is to generate the stable homogeneous mixed phase nano-composites with a narrow particle distribution. Thus, the new nanocomposites can give an optimum exchange coupling for applications. Here, we report the synthesis of exchange spring coupling of FePt/Fe_3Pt nanocomposites by modified polyol process. The nanocomposite is deliberately placed in silica such that the treatment could offer advantages of further stabilizing and isolating the nano-magnets from interferences by their embedment in silica during annealing. As a result, tailoring of the silica encapsulated FePt-Fe_3O_4 in its $L1_0$ phase can be, *for the first time*, demonstrated.

Keywords: exchange coupling, magnetic nanoparticles, silica encapsulated iron-platinum, energy storage

1 INTRODUCTION

Magnetic FePt nano-alloy particles with a face-centered tetragonal (fct) structure (also known as $L1_0$ phase) is one important candidate for future generation of ultrahigh density magnetic recording media, due to its large uniaxial magnetocrystalline anisotropy, high coercivity and good chemical stability [1]. However, control synthesis of these nanoparticles with tailored size, morphology and chemical composition still remains a major challenge. As a result, a large effort has recently been devoted to exploring a wide variety of methods in order to prepare stable alloy nanoparticles of tailored size and composition. Chemical routes using high-temperature solution-phase conditions are the most practical and widely chosen fabrication method for such preparation [2]. Typically, FePt nanoparticles can be synthesized by co-reduction of platinum and iron precursors, in the presence of polyol reducing agents, as so called the 'polyol' process [2,3]. It is noted that the size and composition of the nanoparticles prepared from this polyol method can be extremely well-controlled with standard deviations usually within 10%.[3] It is believed that Pt plays a critical role in accelerating the co-reduction of Fe species which is considered difficult to be reduced on its own through the polyol process. However, most as-synthesized FePt nanoparticles reported are to have a chemically disordered face centered cubic (fcc) structure and are superparamagnetic in nature. They will therefore not be suitable for use as magnetic recording media. In order to obtain the desirable fct structure the as-synthesized nanoparticles are usually annealed at temperatures of above 500°C for the phase transition to take place. But, at such high annealing temperatures, a severe sintering of the nanoparticles is commonly encountered. On the other hand, it has recently been reported that using excess Fe precursor in the ployol process will result in the formation of nanoparticle with a FePt core in Fe_3O_4 shell [4]. This core-shell particle appears to offer a kind of thermal stability to the FePt against sintering. Also, the antiferromagnetic Fe_3O_4 could increase the anisotropy of the composite material by magnetic exchange coupling between the core-shell components [4]. Nevertheless, there are concerns on the chemical and thermal stabilizations of this composite nanoparticle especially its size is very small. Also, too close packing of these nano-magnets on a surface could cause undesirable magnetic interference to each others.

By using sequential nano-chemistry preparation techniques, we have first fabricated FePt-Fe_3O_4 nanocrystallite and then encapsulated it in a silica particle. The silica coating offers the composite nanoparticle a further physical barrier against sintering by modifying its diffusion rate and surface energy during high temperature annealing required for the fct phase transition. Also, the larger separation of the coated nano-magnets may avoid magnetic interference from each others in a close packed surface.



2 EXPERIMENTAL

2.1 Synthesis

Chemicals: Platinum acetylacetonate, $Pt(acac)_2$, was obtained from Johnson Matthey, Iron(0) pentacarbonyl(Aldrich, 99.999%), octyl ether (99%), oleyl amine (70%), oleic acid, tetraethyl orthosilicate (TEOS, 98%) and Igepal CO-520 were purchased from Aldrich. 1,2-hexadecanediol (90%). Ammonia solution (35% w/w), and n-cyclohexane (95%) were obtained from Fischer

Synthesis of FePt-Fe_3O_4 nanoparticles:

Synthesis of monodisperse iron-platinum nanoparticles by reduction of platinum acetylacetonate and decomposition of iron pentacarbonyl in the presence of oleic acid and oleylamine stabilizers has been reported by Sun *et al* [5,6]. From this literature method, the composition of FePt nanoparticle can be controlled, and the size can also be tunable. FePt-Fe_3O_4 is carried out in a similar manner but in an excess of the Fe precursor and with air exposure after preparation [7]. As a result, 394 mg of 1.0 mmol $Pt(acac)_2$, 391 mg, 2.0 mmol $Fe(CO)_5$, 1.040 g of 4 mmol 1,2-hexadecanediol and 50 mL of octyl ether were added to a round bottom flask under a nitrogen atmosphere, stoppered with a nitrogen in/outlet, a condenser and a thermometer. 0.32 mL of 1.0 mmol oleic acid and 0.34 mL of 1.0 mmol oleylamine were then added into the same flask. The mixture was first heated to 100°C for carrying out the pre-decomposition of the iron precursor. At the meanwhile, the black colour product was gradually observed. The mixture was continued to heat to 286°C for 1h with a short air exposure. After cooling the mixture to room temperature, the black sample was precipitated and washed with ethanol followed by centrifugation (1200rpm,1h). The FePt/Fe_3O_4 was dried at 150 °C in air for 1h.

Synthesis of silica encapsulated FePt-Fe_3O_4:

The re-dispersed as-synthesized FePt-Fe_3O_4 in cyclohexane (1mg/mL) was prepared prior to the post silica encapsulation treatment according to a modified method by Ying *et al* [8] which demonstrated the ability to tune the thickness of silica over-layer. As a result, 1 mmol Igepal CO-520 (Polyoxyethylene(5)nonylphenyl ether) was pre-dispersed in 9 mL cyclohexane by sonication for 20 min. Following this step 1.0 mL the FePt-Fe_3O_4 solution together with 80μL of ammonia solution (35%) were added upon. Finally, 60 μL tetraethyl orthosilicate was added and the mixture was allowed to age for 48 h in order to complete the hydrolysis and condensation reactions of the precursors to silica. The resulting SiO_2 encapsulated FePt-Fe_3O_4 nanoparticles were finally collected by centrifugation, washed and dried. Scheme 1 graphically summaries the preparative procedure.

Scheme 1 Synthetic procedure for making silica encapsulated iron-platinum/iron oxide nanoparticle

2.2 Characterization

Figure 1 shows a typical X-ray diffraction (XRD) of iron-platinum/iron oxide in silica. the X-ray powder diffraction, XRD shows extremely broad peaks of 38-43° (2θ) and 45-50° (2θ) marked in black arrows, corresponding to fcc FePt <111> and <200> in the as-synthesized FePt-Fe_3O_4 nanoparticles from the polyol process. Assuming the FePt core is spherical in shape, the average particle diameter is calculated to be 2.6 nm according to the Scherrer equation. This core size also matches the observed size from the TEM (not shown). Characteristic three strong peaks of iron oxide of around 30° (2.95), 35.5° (2.51), and 62.5° (1.48) marked in blue are clearly identified. These peaks match with either the structures of Fe_3O_4 or γ-Fe_2O_3 as compared with an XRD database. The average particle size of 19.0 nm is obtained using the Scherrer equation from the full width at half maximum (FWHM) of the 35.5° peak. It is noted that the patterns match well with both crystalline magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) phases. However, assignment to one of this phase or to the mixture of them based entirely on XRD proofs very difficult since their closely related structures (with almost identical patterns) and nano-metric regime (peak broadening). However, regarding to the preparative procedure in the inert gas, it is believed that the iron oxide is likely to be in Fe_3O_4 phase (confirmation is required). Upon the heat treatment (500°C, 2h) of the FePt/Fe_3O_4, the sizes of FePt and Fe_3O_4 correspond to 4.5 nm and 16.7nm, respectively. Thus, these sizes are similar to those of the as-synthesized sample. However, it is clearly evident that the FePt peaks are slightly shifted to the right suggesting the fcc FePt has been converted to the fct FePt (the extra peaks are identified to be the fct superlattice peaks).

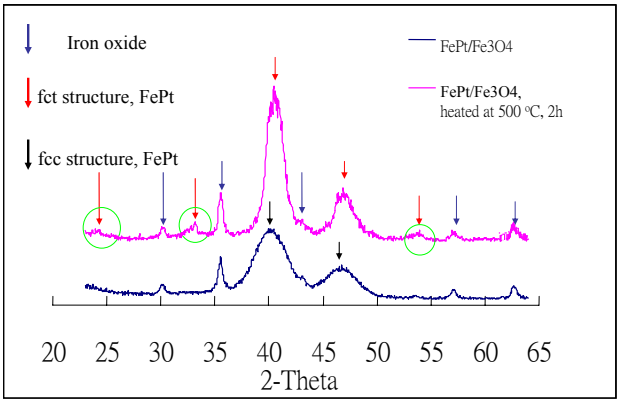


Figure 1: X-ray diffraction spectra of FePt-Fe_3O_4 before and after heat treatment.

Figure 2 shows the XRD spectra of the silica encapsulated FePt-Fe_3O_4 with and without the heat treatment. It is noted that the FePt peaks are extremely weak in a large background of amorphous silica however, the phase transition of FePt core from fcc FePt (3.0nm) to fct FePt (5.8nm) in silica is also evident (same peak shifts).

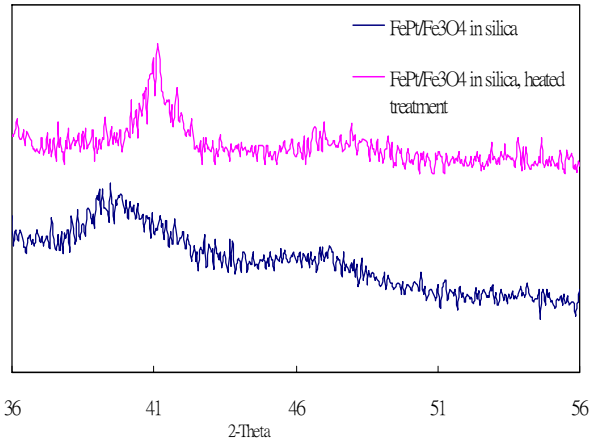


Figure 2: X-ray diffraction spectra of silica encapsulated FePt-Fe_3O_4 before and after heat treatment (500°C, 2h).

Figures 3a and 3b display the elemental mapping of the isolated particles of the FePt-Fe_3O_4 with and without silica coating before the heat treatment. After taking the correction of the response factor for each element into account, the atomic ratios of the particle before the application of the silica coating are Fe: Pt: O= 6.33: 2.03: 26.4 and with the silica coating are Fe :Pt: O : Si =0.34: 0.11: 63.05: 22.0 with a standard deviation of ± 0.2 %. (excluding carbon analysis because the use of carbon filmed holder which also affects the oxygen analysis). Thus, it is clearly demonstrated that the exchange nano-magnet is successful placed in a large silica matrix.

It is noted from Fig. 4 that the heat-treated, silica-encapsulated FePt-Fe_3O_4 displays a wider magnetic hysteresis (a higher coercivity) with the formation of fct structure in the FePt core, although for magnetic storage applications it is necessary to further increase the coercivity of this material.

Thus, the technique presented in this paper is capable of preparing silica embedded exchange-coupled nanomagnets for magnetic application.

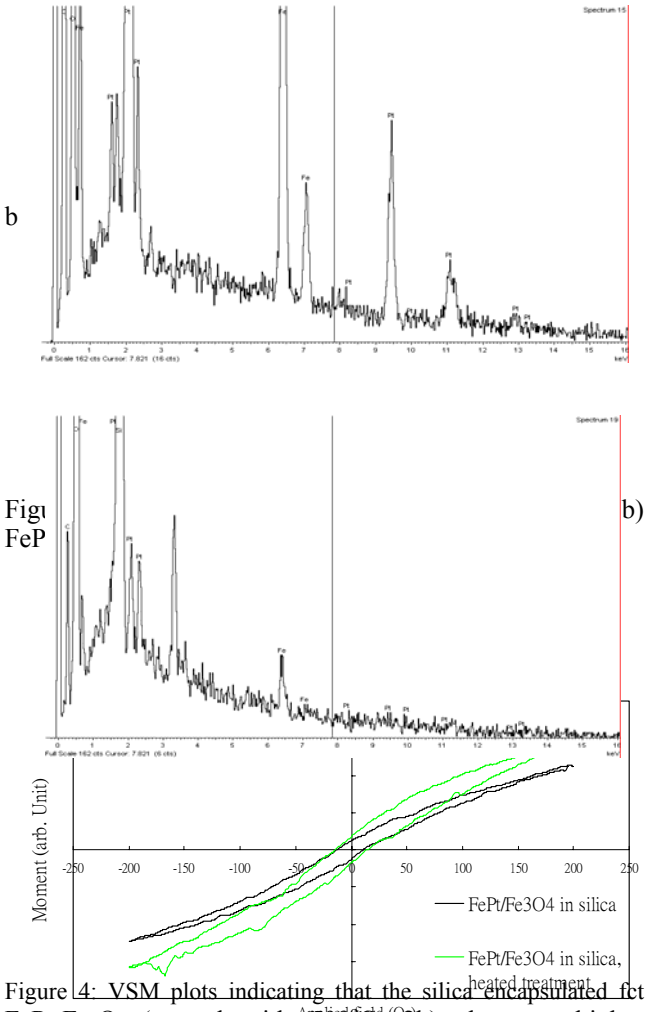


Figure 4: VSM plots indicating that the silica encapsulated fct FePt-Fe_3O_4 (treated with 500°C, 2h) shows a higher coercivity value than silica encapsulated fcc FePt-Fe_3O_4 (rt)

3 CONCLUSION

This report presents the first study of incorporating exchange coupled nanomagnets, the FePt-Fe_3O_4 in silica for potential magnetic recording applications. Material characterization clearly demonstrates the presence of silica embedding the magnetic nanoparticles, which could offer further stabilization to the particles and isolating them from undesirable magnetic interferences. The coated magnetic

nanocomposites characterized with a larger store energy, which may find application as a new data storage material.

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