Synthesis of Patterned Media by Self-Assembly of FePt Nanoparticles

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Abstract

Patterned media is one of the most promising candidates for ultrahigh magnetic storage. Commonly, electron beam lithography is used to synthesize a very high areal density media beyond 1 Tb/in\(^2\). However, such techniques require very high budgets and are time consuming. Self-assembly of magnetic nanoparticles, especially FePt nanoparticles, has been realized as another prominent technique. Nevertheless in order to successfully exploit FePt nanoparticle self-assembly in patterned media fabrication, FePt nanoparticles of proper composition with the desired size and shape as well as a technique to control the assembled behavior of the particles in long range order are required. This review is focused on the chemical synthesis of FePt nanoparticles and how the particles self-assemble into regular arrays.

Keywords: Patterned media, FePt nanoparticles, magnetic nanoparticles, magnetic recording media, magnetic storage, self-assembly

Introduction

Magnetic recording media play an important role in the development of non-volatile data storage technologies. Particularly, magnetic hard disk drives are important parts in many devices such as video cameras and computers. In 1956, the first magnetic hard disk with a recording density of 2 kb/in\(^2\) was successfully built by IBM [1]. Since then, the areal density (the number of bits/unit area on a disk surface) has successively increased [2]. Nowadays, products with an areal density of more than 700 Gb/in\(^2\) are commercially available [3]. The increase in the areal density needs to be continued due to the future demand for information storage. Areal density in a level of 1 Tb/in\(^2\) or more would be unavoidable.

Conventional magnetic recording media are thin granular films of Co, Cr and Pt, with additional elements such as B or Ta. They are deposited onto either a glass or NiP-coated aluminum substrate. With segregation by a non-magnetic element, each grain (around 10 nm) behaves as a single-domain particle with the easy axis usually parallel to the film plane [4]. It is necessary to average the contributions from several hundred grains in order to form a bit which can be read with a sufficient signal-to-noise ratio (SNR) [5]. The recording density can be increased with a decrease in the grain size. However, when the grain size is very small, thermal energy is sufficient to reverse their magnetization spontaneously. This consequent loss of the recorded signal is known as the "superparamagnetic effect". To overcome this obstacle, materials with high magnetic anisotropy have been employed to prevent the thermal effect but a drawback arises regarding the higher magnetic field required for the write head [6].

In pursuit of higher areal density, novel fabrications of magnetic recording media have been introduced [7,8]. Magnetic bit patterned media (or patterned media) consist of a regular array of magnetic dots, each of which has uniaxial magnetic anisotropy. The easy axis can be oriented parallel or perpendicular to the substrate. Each dot
stores one bit, depending on its magnetization state (i.e., “up” direction could represent 1, and “down” direction could represent 0) [9]. Unlike conventional magnetic media, the grains within each bit patterned are coupled so that the entire element behaves as a single magnetic domain. Ideal patterned media should have a perfect pattern, long range order as shown in Figure 1.

Figure 1 Schematic illustration of ideal patterned media.

In the past decade, several methods have been used to fabricate nanometer scale magnetic dot arrays such as electron beam lithography [9,10], extreme UV lithography [11], X-ray lithography [12], nanoimprint lithography [13,14] and self-assembly of magnetic nanoparticles on a modified surface [5,15]. Among these methods, self-assembly of magnetic nanoparticles have a lot of advantages including highest areal density, low cost and long range order. However, there are issues that need to be resolved before this method will be commercially implemented. The tunable morphology and composition of the particles, the aggregation of the particles due to the high temperature annealing, the orientation of the easy axis and the controlling of the self-assembly of nanoparticles into regular arrays are particularly challenging.

This paper briefly reviews the magnetic properties of FePt nanoparticles, recent progress in chemical syntheses and self-assembly of monodisperse FePt nanoparticles for use as patterned media.

Magnetic properties of FePt nanoparticles

Magnetic recording media must be ferromagnetic. The ferromagnetic behavior can be illustrated by a hysteresis loop as shown in Figure 2a. In the absence of an external field, the magnetic moment of each particle points in different directions and the average magnetic moment is zero. When the magnetic field is applied, the magnetic moment of the particles is
forced to align along the field direction leading to an increase in magnetization. When all magnetic moments point in the same direction as the field, the magnetization is highest at a constant value called the saturation magnetization ($M_s$). However, when the field is removed, the magnetization does not become zero. This residual magnetization is called the remanent magnetization ($M_r$). To reduce the magnetization to zero, the external field must be reversed and increased until the magnetization is zero. This value is called the coercive field ($H_c$).

By contrast, superparamagnetism is described by the hysteresis loop as shown in Figure 2b, the magnetization increases rapidly with an increase in the magnetic field. When the external field is zero, the magnetization is also zero. Hence, superparamagnetic materials cannot be used as magnetic recording media due to the absence of remanent magnetization.

![Schematic illustration of typical hysteresis loops for (a) ferromagnetic and (b) superparamagnetic nanoparticles.](image)

Very small magnetic nanoparticles usually lose their ferromagnetic properties due to the random flip of the magnetization direction under the influence of temperature. The relaxation time of the magnetization orientation of each particle is determined by $\tau = \tau_0 e^{K V / 2 k_b T}$, in which $\tau$ is the relaxation time at one orientation, $\tau_0$ is called the attempt time which is typically $10^{-9} - 10^{-10}$ second, $K$ is the particle’s anisotropy constant, $V$ is the volume of the particle, $k_B$ is Boltzmann’s constant, and $T$ is temperature [16]. In the case of small particles, the term $K V$ becomes comparable to the thermal energy $k_B T$, and therefore, the relaxation time is very short. The magnetization can then fluctuate from one direction to another. As a result, the overall magnetization becomes zero, and the particle is referred to as superparamagnetic.

FePt nanoparticles are suitable materials for magnetic recording applications because of their large uniaxial magnetocrystalline anisotropy (about $7 \times 10^6$ J/m$^3$) and good chemical stability [17]. The FePt nanoparticles with a near-equal atomic percentage of Fe and Pt can be ferromagnetic at room temperature even when the particle size is as small as 3 nm [18]. However, the particles must have a face-centered tetragonal structure (fct) in which the Fe and Pt atoms are arranged in alternate layers along the [001] direction [16] (Figure 3b). Another possible phase of FePt nanoparticle is face-centered cubic (fcc) (Figure 3a) in which the Fe and Pt atoms in the crystal are randomly positioned. In this phase, the particles are superparamagnetic and therefore not appropriate for magnetic recording media.
Figure 3  Schematic illustration of the unit cell of (a) chemically disordered face centered cubic and (b) chemically ordered face centered tetragonal FePt.

Chemical synthesis of FePt nanoparticles

Previously, many researchers have attempted to chemically synthesize monodisperse FePt nanoparticles with controllable size, shape and composition [16-23]. Their results show that the quality of the nanoparticles can be controlled by the reaction conditions. Unfortunately, as-synthesized FePt nanoparticles usually have an fcc structure, leading to no magnetic ordering at room temperature. To achieve a high magnetic ordering, the particles have to be transformed to the fct structure. Such phase transformation typically occurs at high temperature annealing, however this leads to particle aggregation, and wider size distributions. To prevent particle agglomeration, many methods have been developed such as doping with Ag, Au, and Cu in the FePt phase to lower the onset temperature for the fcc to fct phase transformation [24-26], coating FePt with iron oxide [27], SiO$_2$ [28], or MgO [29], direct synthesis of the fct structured particles by a polyol process using high boiling point solvents [30,31], and annealing with salt (i.e. NaCl) [32,33]. Nevertheless, a definitive technique for magnetic recording fabrication has not been achieved yet.

Chemical synthesis of FePt nanoparticles mainly involve the thermal decomposition of iron pentacarbonyl $\{\text{Fe(CO)}_5\}$ and the reduction of platinum acetylacetonate $\{\text{Pt(acac)}_2\}$ by a polyalcohol (i.e. 1,2 hexadecanediol) in the presence of solvent such as dioctyl ether or benzyl ether with oleic acid and oleylamine as surfactants [17,19]. The synthetic chemistry is illustrated in Figure 4. Fe(CO)$_5$ is decomposed at high temperature to carbon monoxide and Fe. Pt(acac)$_2$ is reduced to Pt by a reducing agent. A small group of Fe and Pt atoms combine to form clusters that act as nuclei and then the crystal growth process is activated, forming FePt nanoparticles. The surfactants are required for surface passivity and particle stability.
In the procedure described above, the composition of FePt particles is controlled by the Fe(CO)$_5$/Pt(acac)$_2$ ratio. However, some of the Fe(CO)$_5$ does not contribute to the FePt alloy formation since Fe(CO)$_5$ has a low boiling point (103 °C). At high temperature (usually about 300 °C), Fe(CO)$_5$ is actually in the vapor phase and slowly decomposes. Comparing to the shorter time period of the FePt nanoparticle formation, therefore, the consumption of Fe(CO)$_5$ cannot be completed within the synthetic time period. Usually, an excess of Fe(CO)$_5$ is used in the synthesis of FePt nanoparticles with a near-equal atomic percentage of Fe and Pt.

In a study using Fe(CO)$_5$ as a starting material [21], it was found that the surfactants and their concentration, type of solvents, nature of precursors, and heating rate played crucial roles in controlling the size and shape of FePt nanoparticles. At a fixed heating rate, the particle size increases with an increase in surfactants to Pt(acac)$_2$ ratio but beyond a certain concentration of surfactants (the molar ratio of surfactants to Pt(acac)$_2$ was 10) the particle size did not change. They also found that the heating rate of the reaction at about 5 °C/min gave rise to the largest particle size. In addition, when benzyl ether was used as a solvent, spherical particles with narrow size distribution were obtained. By contrast, octyl ether gave faceted cubic shape particles. However, the effect of the solvent on the shape of the particle was hard to find in the particle with particles smaller than 7 nm. The time interval of surfactant injection into the reaction mixture is another factor that influences the particle shape. Using benzyl ether as a solvent, rod shape nanoparticles with few spherical ones were obtained when oleylamine was injected 5 min after injecting oleic acid. However, the same result was not observed when octyl ether was used as the solvent.

An alternative approach to the synthesis of FePt nanoparticles using Fe(CO)$_5$ is to synthesize Pt/Fe$_2$O$_3$ core-shell nanoparticles [34]. The core-shell particles were synthesized by using Fe(CO)$_5$ and Pt(acac)$_2$ as precursors and then were deposited as a monolayer on a substrate using a Langmuir-Blodgett (LB) technique. Annealing at either 550 or 650 °C for 9 h under a gas flow of Ar(95 %)/H$_2$(5 %) in a tube furnace can convert the Pt/Fe$_2$O$_3$ core-shell nanoparticles to FePt nanoparticles.

Although high quality FePt nanoparticles may be synthesized from Fe(CO)$_5$, it is very toxic and a highly flammable liquid at room temperature. Moreover, the exact composition of the FePt particles is difficult to control due to the reaction temperature being above the boiling point of Fe(CO)$_5$. Therefore, less toxic precursors such as Fe(acac)$_3$ and Fe(acac)$_2$ have been tested in the synthesis of monodisperse FePt nanoparticles [21,35-37]. The co-reduction of Fe(acac)$_3$ or Fe(acac)$_2$ and Pt(acac)$_2$ with 1,2 hexadecanediol can produce monodisperse 2-3 nm diameter FePt nanoparticles. For example [27], Fe(acac)$_3$ (0.5 mmol), Pt(acac)$_2$ (0.5 mmol), 1,2 hexadecanediol (5.0 mmol), oleic acid (0.5 mmol), and oleylamine

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**Figure 4** Schematic illustration of FePt nanoparticle formation from decomposition of Fe(CO)$_5$ and reduction of Pt(acac)$_2$. (Adapted from [16])
(0.5 mmol) were mixed in 20 mL of octyl ether at room temperature using standard techniques. The mixer was then heated to reflux at 286 °C for 30 min. Then, the heat source was removed and the product solution was cooled to room temperature under a N₂ blanket. The particles were then purified by centrifugation, e.g., ethanol (~40 ml) was added in the solution and centrifuged again. The supernatant was discarded. The black precipitate was dispersed in hexane (~25 ml), oleic acid (0.05 ml), oleylamine (0.05 ml) and precipitated out by adding ethanol (~20 ml) followed by centrifuging. The product was dispersed in hexane (~20 ml) again and centrifuged to remove any undissolved precipitate, and precipitated out by adding ethanol (~15 ml) and centrifuging. The final product was redispersed in hexane and stored under N₂.

Although Fe(acac)₃ is easier to handle than Fe(CO)₅, it is still very hard to control the size, shape and composition of the particles. Nandwana et al. [21] found that when Fe(acac)₃ was used as a starting material, the particles around 2 nm were always obtained although the amount of surfactant and heating rate were varied. Elkins et al. [35] also found that even the final particle composition was changed by changing the initial mole ratio of the precursors. The initial ratio was not retained in the final product. For example, using a 2:1 mole ratio of the precursors, Fe₄Pt₅₆ particles are produced. To obtain precise composition particles, other precursors and reducing agents have also been studied [38,39]. The initial molar ratio of the metal precursors is carried over to the final product by reduction of FeCl₃ and Pt(acac)₂ mixtures in diphenyl ether by lithium triethylborohydride (LiEt₃BH) in the presence of oleic acid, oleylamine, and 1,2 hexadecanediol at 200 °C. After refluxing at 263 °C, FePt nanoparticles around 4 nm in size were obtained [38]. Fe(CO)₅ can also be replaced by Na₂Fe(CO)₅ which acts as both a reducing agent and Fe source [39]. In this reaction, the anion Fe²⁺ from Na₂Fe(CO)₅ transfers two electrons to Pt²⁺. The Pt²⁺ is reduced to metallic Pt while the Fe²⁺ is oxidized to metallic Fe, which then combine to form FePt. This assures a 1:1 stoichiometry of the final product.

To date, the effective method to control size, shape, and composition of FePt nanoparticles by using low toxic precursors remains a challenge that must be overcome before their potential applications will be fulfilled.

Self assembly of magnetic nanoparticles

A control of the self-assembly of nanoparticles into regular arrays is very difficult particularly in creating long range order, because the interactions of such small particles are not precisely known or controlled [40]. Hence, lithography-assisted self-assembly has been adopted. The pre-patterned substrate is fabricated by lithography techniques and then the template for assembly of nanoparticles is formed by self-assembly of block copolymers [41-45]. Nevertheless, perfect ordering over large areas and circumferential geometry has not yet been achieved. Recently, Park et al. [46] reported that without lithography heating can modify the faceted surface of commercially available sapphire wafers to guide the self-assembly of block copolymers into oriented arrays with a long range order over arbitrarily large wafer surfaces. Areal density in excess of 10 Tbit/in² was obtained as a result. However, this method is not yet the most promising route due to the need for high temperature annealing (1,300 - 1,500 °C) for 24 h and some defects are present. Furthermore, the assembly of magnetic nanoparticles into such arrays has not been studied. Block copolymers are very expensive and require modification of the capping ligands to make the nanoparticles compatible with a specific side of the copolymers, which can be synthetically challenging [47]. Therefore, a controllable, simple, and low cost method to assemble the nanoparticles into regular arrays is still required.

The LB technique is another powerful and simple method to fabricate high-density nanoparticle monolayers and multilayer films with controllable layer numbers and thickness [48]. In principle [49], hydrophobic nanoparticles are assembled at the air-water interface of the LB trough and then the particle layer is compressed by the barriers until the desired surface pressure is achieved. The uniform monolayer can be transformed to a substrate by vertical dipping of the substrate into the densely packed film. In the past decade, many nanoparticle monolayers and multilayers have been prepared by the LB technique such as Au [50,51], Ag [52], γ-Fe₂O₃ [53], and Fe₃O₄ [54,55]. Moreover, FePt
nanoparticle monolayers have been fabricated [56-58]. Wang et al. [56] synthesized monodisperse FePt nanoparticles with a mean size of around 4 nm and then created a monolayer on a glass substrate using the LB technique. They found that the transfer of nanoparticle layers onto a solid substrate surface was quite efficient for the first few layers. Patel et al. [57] dispersed FePt nanoparticles onto the water surface in the LB trough. When the desired surface pressure was achieved, a polydimethylsiloxane (PDMS) stamp fabricated by conventional photolithography was carefully brought into contact horizontally with the water surface. As a result, the pattern was transferred to the silicon substrate. By this approach, micrometer-size circles, lines, and square patterned monolayers and multilayers of FePt nanoparticles may be prepared. Heitsch et al. [58] reported a study of an ordered hexagonal monolayer of FePt nanocrystals fabricated using 3 techniques (LB, Langmuir-Schäfer, and spin coating). The results indicated that the LB technique provided the most ordered superlattice films.

**Conclusion**

This article has reviewed the research and the challenges in the synthesis of FePt nanoparticles for patterned media applications. Chemical synthesis has been shown to be a promising route to produce FePt nanoparticles with a narrow size distribution. However, there are some issues that need to be resolved before their applications will be realized such as less toxic precursors, shape control, precise composition, and prevention of particle agglomeration due to the high temperature annealing. Another task is the control of self-assembly of the particles to provide long range order. Self-assembling on pre-patterned block copolymer substrate and LB technique are possible candidates for success in this area. The novel simple, low-cost, and more effective technique will most likely be discovered in the near future. When this happens, many applications for self-assembled nanoparticles will become a reality.

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