Direct Preparation of Highly Ordered $L1_0$ Phase FePt Nanoparticles and Their Shape-Assisted Assembly

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Chemically ordered $L1_0$ phase FePt nanoparticles has been considered one of the best candidates for future magnetic recording media with areal density beyond 1 Tbit/in^2. However, current preparation methods via phase transformation must overcome many obstacles, including particle agglomeration, twinning and difficulty of easy axis alignment. In this paper, the direct preparation of $L1_0$ phase FePt nanoparticles without phase transformation and particles' aqueous phase self-assembly are reported. The mechanism for $L1_0$ phase formation during nucleation and growth processes are discussed. The unique octahedron shape makes these highly ordered FePt nanoparticles even better choice for advanced magnetic recording media because they tend to form tilted and patterned media simultaneously due to the shape effect.

Index Terms—Biomagnetic, direct ordering, FePt, heat assisted recording media, $L1_0$ phase, magnetic particles, medicine, nanoparticle, patterned media, self-assembly, shape-assisted, SOMA, tilted media.

I. INTRODUCTION

THE rapid development of magnetic recording has introduced various techniques for areal density increasement. Perpendicular recording was proposed more than twenty years ago [1] and has already been in production line. Tilted media were also proposed to solve the writability problem for even higher areal density [2], [3]. Exchange coupled composite (ECC) media were proposed and demonstrated as a new type of media, targeting for 1 Tbits/in^2 [4], [5]. The future extremely high density recording media beyond 1 Tbits/in^2 require further reduction of magnetic grain size and thus materials with ultra-high magnetocrystalline anisotropy are needed to overcome the superparamagnetic limit. $L1_0$ phase FePt with nearly equal atomic ratio fits this requirement and it has been reported that it can be made into chemically disordered A1 phase nanoparticles and form ordered pattern through chemical reduction followed by self-assembly [6]. Unfortunately, the unavoidable ordering process for magnetic as well as crystallographic phase transformation leads to several obstacles for these particles to be applied in recording media. First, upon annealing nanoparticles agglomerate and monodispersity can not be kept. Second, because the phase transformation involves new phase nucleation and growth, a single particle could develop multiple easy axes by forming twinned structures or antiphase boundaries. In order for the particles to be used in recording media, the easy axes should be aligned during self-assembly process, which can not be achieved by assembling the disordered particles directly. To solve these problems, different approaches have been proposed to improve the phase transformation process, including ternary element addition for annealing temperature reduction, removable matrix usage for particle isolation, field annealing for orientation control, etc. However, the phase transformation from A1 to $L1_0$ is from one isotropic state to one anisotropic state, which is not easy to control by adjusting external variables. Recently it was pointed out that the ordering of FePt particles might be kinetically limited [7].

An optimal approach is to prepare $L1_0$ FePt nanoparticles without postdeposition annealing. It has been shown that by increasing the reaction temperature during particles' growth in colloidal method, partially ordered FePt nanoparticles could be made [8]. However particle uniformity became a problem since overheating usually leads to particle agglomeration. Intermatrix synthesis was shown to be able to make isolated $L1_0$ FePt nanoparticles [9]. Again the size distribution is still not very applausive.

In this paper, we discuss the direct preparation of monodispersed $L1_0$ phase FePt nanoparticles using a newly developed gas phase aggregation technique. This technique relies on the subtle control over particle nucleation and growth at the atomic level. Effects of magnetron plasma and inert gas flow are to be addressed. Using these highly ordered FePt nanoparticles, monolayer patterns have been achieved through self-assembly in aqueous solution. *In-situ* self-assembly of these nanoparticles on prepatterned substrate in vacuum can be expected. The unique octahedron shape of these particles brings up a practical opportunity to fabricate tilted and patterned media at the same time.

These nanoparticles are not limited to magnetic media applications. As corrosion resistive permanent nanomagnets, they are more preferable than traditional superparamagnetic particles for nanobiological and biomedical applications.

II. NOVEL NANOPARTICLE DEPOSITION TECHNIQUE

In order to prepare monodispersed nanoparticles, the nucleation and growth processes should be separated either in time domain or in space domain. In many of the conventional techniques, such as colloidal methods, nucleation rate can be controlled by adjusting reaction reagents or environmental parame-
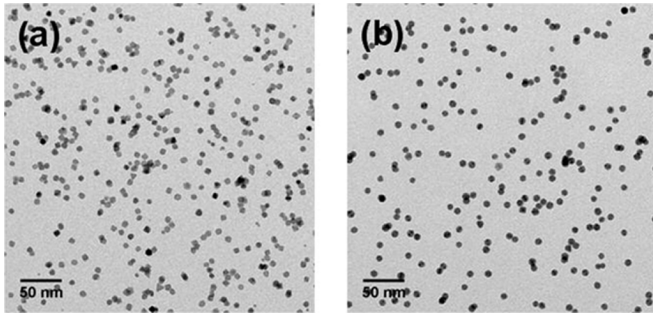
Fig. 1. Discharge current dependence of FePt nanoparticles. (a) 0.52 A; particles are faceted. (b) 0.2 A; particles are basically sphere-like.
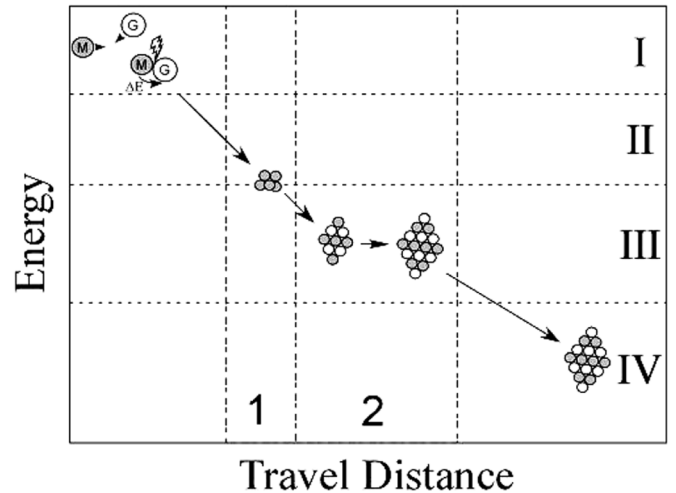

Fig. 2. Steps for directly preparing $L1_0$ FePt nanoparticles using gas phase aggregation. (I) Gas phase or liquid phase. (II) A1 phase stable. (III) $L1_0$ phase stable. (IV) Diffusion limit region. Column 1: Nucleation. Column 2: Growth. Particles formed within I plus II or IV only will be in the chemically disordered A1 phase.
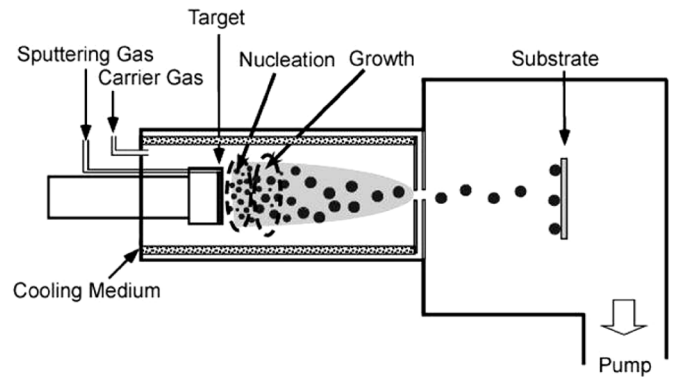

Fig. 3. Schematic view of the gas aggregation source for depositing magnetic nanoparticles. Note that the nucleation and growth are separated both in time and space domains. The thermal environment for particle growth can be adjusted by modifying the magnetron head itself.

ters to separate particle nucleation from growth, bringing about narrow size distribution.

Gas phase aggregation techniques have long been used to prepare nanoclusters [10], [11]. They basically involve an atom source (using thermal evaporation or sputtering or gas phase chemical reaction) and a cooling medium. However, nucleation and growth processes using this type of techniques were hard to control *in situ* and, therefore, the processing of nanoparticles usually happened after deposition [12], [13]. In our case, magnetron sputtering gun is used for atom generation and an inert gas flow is used to cool down the atoms for particle formation [14]. Particles uniformity is ensured by the fact that nucleation and growth are separated in both time and space domains [15]. This separation further provides a chance to directly control particle's nucleation and growth at the atomic level. It is superb to use magnetron sputtering technique to generate atoms because the plasma itself may act as an energy source and inert gas may act as an energy drain. By adjusting the energy source to drain ratio, the thermal environment for nanoparticle nucleation and growth can be gradually adjusted for specific purposes. For example, when the inert gas flow was fixed and the discharge current was decreased, FePt nanoparticles' morphology changed from faceted to sphere-like (Fig. 1). Basically when the energy source was weakened and energy drain was kept, atom diffusion energy was reduced so they could not reach their equilibrium crystallographic sites. The detailed study of this novel technique is described in [16].

FePt nanoparticles prepared by conventional approaches are usually in the chemically disordered A1 phase because when atoms come together to form clusters, they either do not have sufficient energy to diffuse (such as in the colloidal method without intended overheating) or have too much energy to stay quietly on specific crystallographic sites. Upon quenching, the latter will keep the high temperature phase of nanoparticles, which is the A1 phase. As shown in Fig. 2, in order to prepare $L1_0$ FePt nanoparticles directly, the nucleation and growth especially the latter should happen within region III, in which the $L1_0$ phase is stable. The technique described here is a magnetron sputtering based gas aggregation source with the sputtering head modified by using soft iron pieces. The details were reported previously in [17]. In short, both the magnetron plasma and gas flow right above the alloy target surface were manipulated. The nucleation and growth of FePt nanoparticles were found to happen close to target surface and strongly influenced by the thermal environment there. The energy source (plasma)

and drain (inert gas flow) were adjusted so as to ensure atoms to have sufficient energy to diffuse and the inter-diffusion will not be too drastic to disorder the resulted nanoparticles.

III. EXPERIMENTS

FePt nanoparticles were prepared by using a home-built nanoparticle deposition system with a dc magnetron sputtering based gas phase aggregation source (the source itself is schematically illustrated in Fig. 3). The target was iron and platinum alloy with atomic ratio of 50:50 and made by Heraeus Incorporated, Materials Technology Division. The typical base chamber pressure for the source was less than 5×10^{-8} Torr. During deposition, the source pressure was increased to 370 mTorr by feeding argon gas with a flow rate of 17 sccm. A soft iron ring with trigon-cross-section and a cone center piece with height of 3 mm were placed on top of the alloy target during sputtering. The nanoparticles were deposited directly onto silicon substrate as well as carbon-coated copper TEM grid for further characterization.
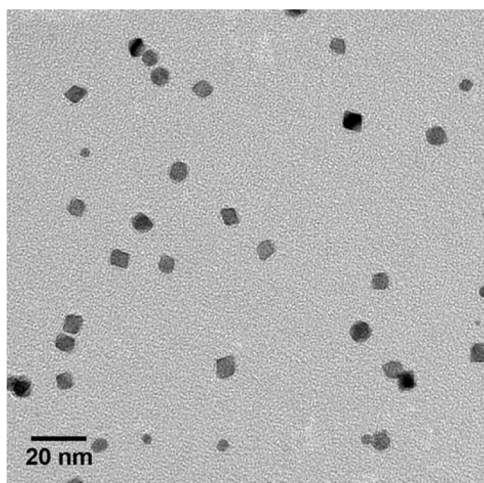
Fig. 4.   TEM micrograph showing the morphology of the directly ordered $L1_0$ FePt nanoparticles. These particles are well crystallized with octahedron shape dominant.

Fig. 5.   TEM selected area electron diffraction pattern of these ordered FePt nanoparticles.

The routine particle morphology and size were characterized by using a transmission electron microscope (FEI Tecnai T12) working at 120 kV. Particle size was measured by taking their projection area and assuming circular shape to calculate effective diameter. High-resolution TEM measurements were carried out by using a FEG-TEM (FEI Tecnai G2 30) operating at 300 kV. X-ray diffraction analysis was performed using a Bruker-AXS microdiffractometer with Hi-Star 2-D area detector and Cu target. The magnetic hysteresis loops of FePt nanoparticles were measured with a Quantum Design MPMS XL sample magnetometer with maximum field of 7 Tesla.

IV. DIRECT PREPARATION OF MONODISPERSED HIGHLY ORDERED FePt NANOPARTICLES

FePt nanoparticles prepared without the soft iron ring and cone are in the chemically disordered phase as shown in [18], [19]. Here, the added soft iron pieces have two basic functions. First they changed the surface magnetic field distribution, which in turn adjusted the ion and electron distribution of the magnetron plasma. The second function is that the argon gas flow was modified so that the local argon molecules have a more uniform distribution for steady nucleation and growth.

At an appropriate condition as requested by Fig. 2 the chemical ordering was achieved simultaneously with particle formation.

Fig. 4 shows the morphology of the highly ordered $L1_0$ phase FePt nanoparticles randomly distributed on carbon coated TEM grid. They are monodispersed with size distribution of 11% [17]. The average size can be adjusted by taking different deposition parameters, for example, the discharge current density. These particles are in their ordered phase as evidenced by the (110) and (001) superlattice diffraction spots in the TEM electron diffraction pattern (Fig. 5).

These ordered FePt particles show high magnetocrystalline anisotropy. The magnetic property measurements of one typical sample showed that the coercivity at room temperature (300 K) was 8.25 kOe. With the decrease of temperature, coercivity
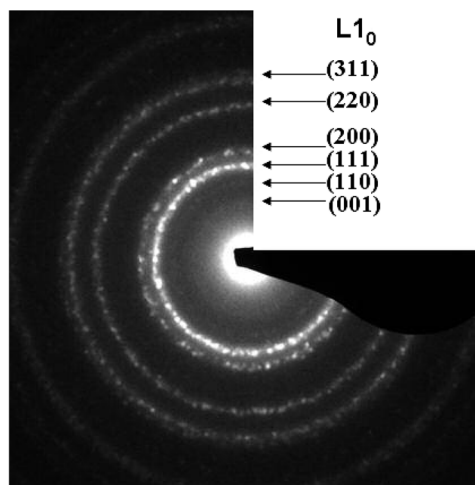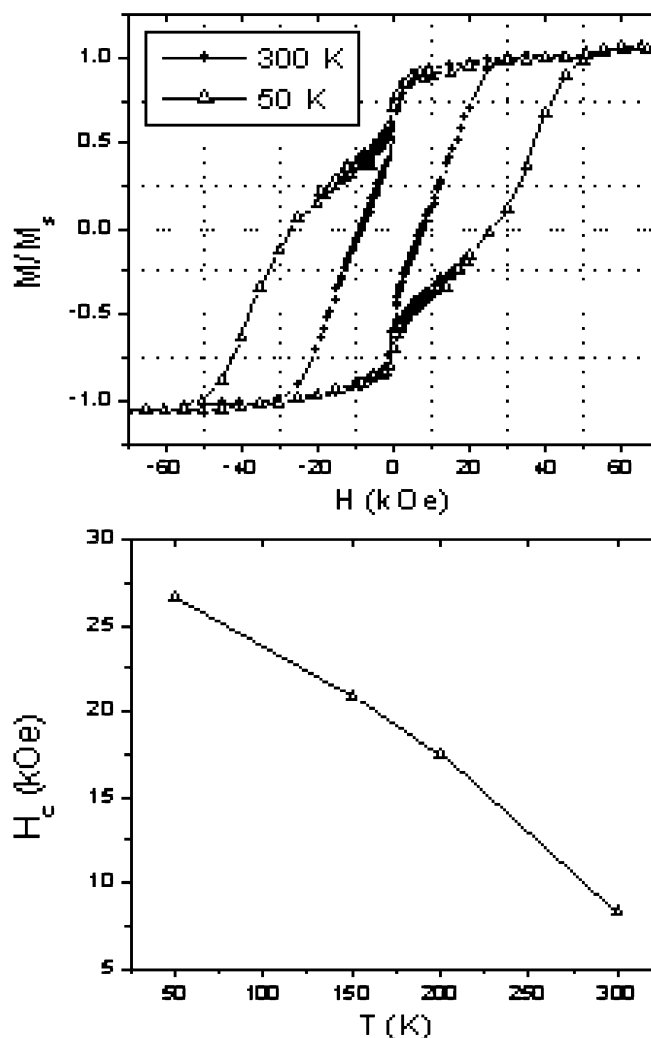

Fig. 6.   (Top) Magnetic hysteresis loops measured at two different temperatures. The coercivity increases from 8.25 kOe at 300 K to 26.5 kOe at 50 K. (Bottom) Coercivity as a function of measurement temperature.

constantly increased and reached a value of 26.5 kOe at 50 K. The saturation field was 53.5 kOe at 50 K (Fig. 6). The kinks
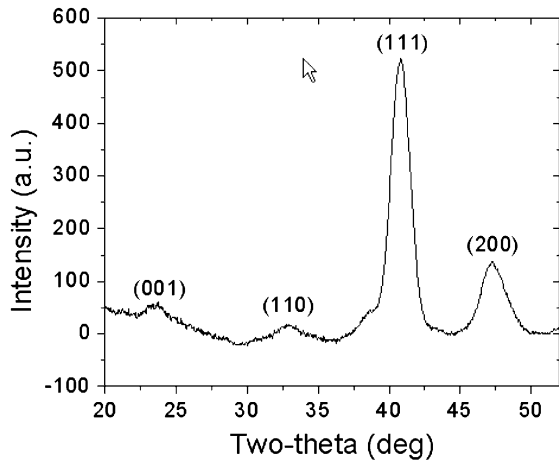
Fig. 7. X-ray diffraction spectrum of the FePt particles sitting on naturally oxided silicon substrate. The crystallite size calculated using Scherrer equation and the (111) peak is about 7 nm, which is consistent with the size measured by TEM.
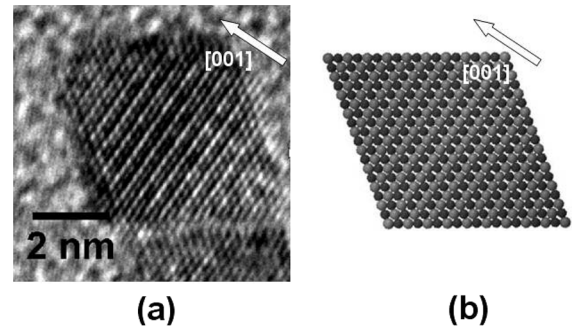

Fig. 8. (a) HRTEM micrograph of a single ordered FePt nanoparticle with its easy axis (c-axis) lying in plane. (b) Corresponding structure model showing the crystallographic orientation of particle.
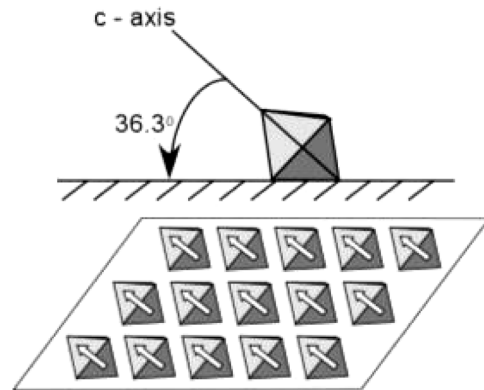

Fig. 9. (Top) Schematic view of one octahedron shaped ordered FePt nanoparticle lying with its easy axis tilted 36.3° away from the substrate plane. (Bottom) A proposed patterned media with tilted magnetic recording.

around zero magnetic fields can be attributed to either the particle shape effect or some ultra small particles. For faceted particles, such as here FePt nanoparticles with octahedron shape, the magnetization may switch nonuniformly because of the existence of sharp corners. By fitting the coercivity versus temperature data to Sharrock's equation [20], the magnetocrystalline anisotropy was roughly estimated to be 2.6×10^7 erg/cm^3. Because of the unique faceted shape (octahedron) for the as-prepared FePt nanoparticles, a nonuniform switching is suspected to be responsible for the low coercivity, for which the Sharrock equation may not be directly applied. Further micromagnetic study is under way.

The X-ray diffraction spectrum of these $L1_0$ FePt nanoparticles is shown in Fig. 7. The average particle size (correlation length along $< 111 >$ direction) calculated from the peak half width using Scherrer's equation is about 7 nm, which is consistent with the size as measured by TEM of this sample. Using the (001) and (110) diffraction peaks we can get the lattice constants ($a = b = 3.86$ Å and $c = 3.75$ Å). Using the c to a ratio of 0.97 we estimated the magnetrocrystalline anisotropy to be 5.7×10^7 erg/cm^3 [21]. This is different from the estimation based on magnetic measurements. One possible reason is that these particles magnetize nonuniformly because of they are overlapping with each other. The intensity of (111) peak dominates the others and it may be understood by considering the shape of these particles. For face centered tetragonal crystals, the {111} series planes have the lowest surface energy and highest atomic density. Therefore, these particles show faceted octahedron shape with only the {111} planes exposed. This is not contradictory to what proposed by traditional Wulff's construction theorem. The size of these particles is so small that the edge terms in the energy consideration can not be ignored anymore. The usually used truncated-octahedron (TO) shape for theoretical calculation has too many edge terms to be applicable for these nanoparticles. High-resolution TEM images clearly show that these particles are near perfectly octahedron shaped (Fig. 8). When a single octahedron particle lying on a flat substrate (here SiO$_2$/Si), two of its (111) faces will be parallel to the substrate surface, which is an energetically preferred

state. Owing to the symmetry of octahedron objects, every particle lying directly on the substrate surface is preferentially oriented with one sets of its {111} planes parallel to each other. This in-plane texture results in the dominant (111) diffraction.

The future magnetic recording media may benefit from the octahedron shape effect using FePt nanoparticles as the recording material. Tilted magnetic recording is considered to be a good solution for media writability [22] especially for media fabricated with very high anisotropy materials such as FePt. However, easy axis physically tilted media are difficult to prepare because of the various engineering problems involved. It is worth to note that with octahedron shape, these ordered FePt nanoparticles will naturally have their easy axes (the c-axes) tilted 36.3° from the substrate surface (Fig. 9), which in turn results in a near half drop of the switching field. Furthermore, these particles can be assembled to form patterned media, which was again proposed for future extremely high magnetic recording media [23]. By assembling the octahedron shaped $L1_0$ phase FePt nanoparticles into ordered patterns with shape-preferred easy axes tilting, tilted media and patterned media can be achieved at the same time for advanced magnetic recording.

V. TRANSFER OF GAS PHASE FePt NANOPARTICLES INTO AQUEOUS SOLUTION

Current microelectronic industry uses robotic assembly for building devices. When the size of components shrinks down
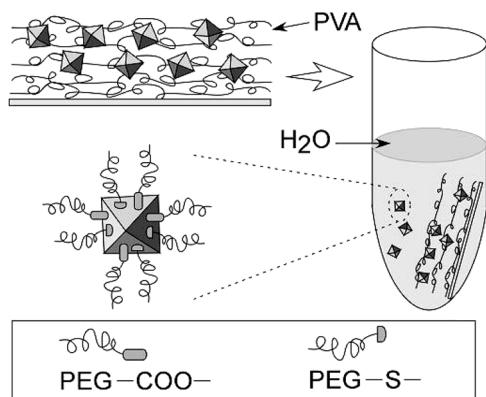
Fig. 10. Solubilization of $L1_0$ FePt nanopariclies into aqueous solution. Particles were deposited onto poly(vinyl alcohol) (PVA) coated substrate with appropriate amount of poly (ethylene glycol) (PEG) based ligands (PEG-SH, PEG-COOH) added. Then, the substrate was immersed in a vial containing the above ligands aqueous solution. Stirred with a shaker then followed by brief sonication, these particles become soluable in water and stable.
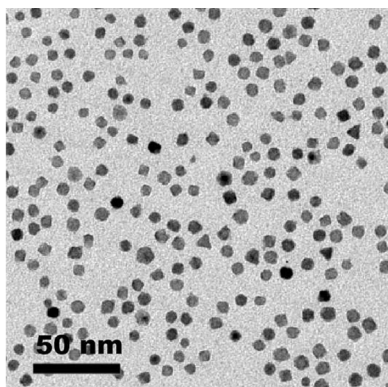

Fig. 11. TEM micrograph showing the well dispersed FePt nanoparticles, which were functionalized to be water soluble.

to tens of nanometer range and below, current robotic technology can no longer be applied and therefore self-assembly takes its turn. Most of current self-assembly processes rely on the solubilization of nanoparticles by applying certain surfactant molecules. To assemble these $L1_0$ FePt nanoparticles into monolayered structure, their solubilization is the first step.

As shown in Fig. 10, faceted $L1_0$ phase FePt nanoparticles were directly deposited onto PVA (water soluble, $MW = 115\,000$ g/mol) coated glass substrate. The purpose of this PVA layer is to prevent these particles from magnetic agglomeration. Then, the glass substrate was broken into small pieces and collected in a vial containing 3 mL of water and a little PEG-SH, and PEG-COOH ligands (PEG: $MW = 550$ g/mol). Here the two ligands were chosen because PEG-COOH is good for iron atoms and PEG-SH is good for platinum atoms [24]. The vial was stirred with a shaker for 3 h, and then 1 mL of the resulting solution was subjected to sonication briefly. After sonication, the excess polymer matrix and ligands were removed via centrifugation. Then FePt nanoparticles become soluble in water.

One advantage of using polymer based ligands comparing to small molecular surfactants is the variability of ligand length. These $L1_0$ FePt nanoparticles are strong nanomagnets. To prevent them from magetic clustering, large and supportive
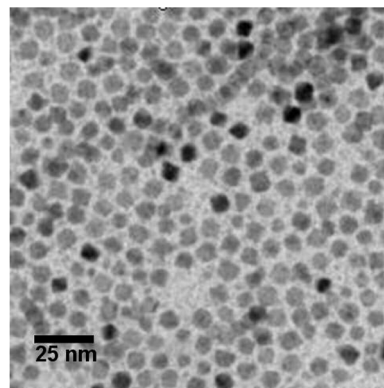

Fig. 12. TEM micrograph showing an ordered patterned formed by self-assembling the $L1_0$ phase FePt nanoparticles.

ligands are desired. By simply adjusting the molecular weight of PEG segment, the interparticle distance could be easily adjusted. Fig. 11 shows a typical TEM image of particles directly deposited from diluted particle dispersion. It can be seen that this approach successfully separated the strong magnetic nanoparticles. Water solubility also provides the chance to use them in biological applications.

VI. SELF-ASSEMBLY OF $L1_0$ PHASE FePt NANOPARTICLES

The water dissolved nanoparticles were used to form patterned structures through self-assembly. About 3 μL liquid droplet was put on an amorphous carbon-coated TEM grid. The solvent water was allowed to evaporate out slowly (about 20 min) in air at room temperature. Then the grid was used for TEM observation. As shown in Fig. 12, particles are packed closely to each other, forming ordered superstructure. The faceted particles are not easily assembled by using small molecular surfactants because of the shape effect. Here, the polymer based ligands work more effectively comparing with the usually used oleic acid/oleylamine combination for FePt nanoparticle assembly. By balancing the ligand and shape effects large area superstructure can be expected. Because these particles are highly ordered with their easy axis along the $\langle 001 \rangle$ direction, an external magnetic field is able to direct their crystallographic orientation. Our preliminary results show that an external dc field of 7000 Oe is able to confine the easy axes distribution within $18°$. The study of magnetic field directed self-assembly is undergoing and detailed results will be reported later.

VII. CONCLUSION

The directly prepared highly ordered $L1_0$ phase FePt nanoparticles with unique octahedral shape and their self-assembly into ordered superstructures are appropriate for fabricating patterned and tilted magnetic recording media targeting for areal density of 10 Tbit/in^2 and above. Although some issues such as long- range-order patterning, disk surface roughness control, signal readback, *et al.* still remain critical engineering problems to solve, the successful preparation of these building blocks forms one solid basis for the continuous areal density increase for future.

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