Patterning of L1_0 FePt Nanoparticles with Ultra-High Coercivity for Bit-Patterned Media

Zhengong Meng,*† Guijun Li,*‡ Hon-Fai Wong,§ Sheung-Mei Ng,§ Sze-Chun Yiu,* Cheuk-Lam Ho,*∥ Chi-Wah Leung,*∥ Ian Manners*‡ and Wai-Yeung Wong*‡∥

L1_0-ordered FePt nanoparticles (NPs) with ultra-high coercivity were directly prepared from a new metallopolyyne by using a one-step pyrolysis method. The chemical ordering, morphology and magnetic properties of the as-synthesized FePt NPs have been studied. Magnetic measurements show the coercivity of these FePt NPs is up to 3.8 T. By comparison of the NPs synthesized under Ar and Ar/H_2 atmosphere, the presence of H_2 in the annealing environment would influence the nucleation and promote the growth of L1_0-FePt NPs. Application of this metallopolyyne for bit-patterned media was also demonstrated with nanoimprint lithography.

Introduction

The volume of hard disk drive (HDD) has increased exponentially from 5 megabytes (MB) in the first IBM 350 disk storage unit to multiple terabytes (TB) in the disk drives currently available in the market. The storage capacities of conventional perpendicular magnetic recording systems are hardly to be further increased because it is not easy to maintain a high signal-to-noise ratio (SNR) below 10 nm/bit due to the thermal instability of magnetic metal alloy materials.1 Thus, it is important to develop new data recording architectures for increasing the areal density as well as the data stability in HDDs. Bit-patterned media (BPM) system, in which a single magnetic bit is recorded on a pre-defined single magnetic dot, has the higher SNR due to the absence of transition noise and erase bands, and it has emerged as a promising technology for extending magnetic data storage density beyond 1 Tb/in^2.2 As reported in the Advanced Storage Technology Consortium, the novel storage architecture by combining BPM and Heat-Assisted Magnetic Recording (HAMR) will lead to 10-terabit-per-square-inch (Tbpsi) areal density by 2025. Furthermore, as demonstrated by Hitachi Global Storage Technologies (HGST), BPM will be improved towards higher areal density by utilizing nanolithography to break magnetic media down into small regions or bit “islands” on a platter’s surface.3

Recently, the main preparation methods of BPM include electron-beam lithography (EBL),4 directed self-assembly of block copolymer,5-8 self-aligned double patterning9 and nanoimprint lithography (NIL),10-13 etc. Among these, NIL allows the fabrication of large-area nanometer scale patterns rapidly as BPM possesses good features such as low production cost, high throughput and high resolution.14,16 Generally, there are two main steps in NIL patterning: the pre-patterning of the substrate with pillar features and the deposition of the magnetic film on the features.15,17,19 For making BPM with a continual magnetic thin film by NIL, the photoresist must first be spin-coated and patterned using NIL. Then, either the magnetic thin film is etched away (a subtractive process) or the thin film is deposited and lifted off (an additive process).20 A range of nanomaterials have been studied for the magnetic recording layer such as FePt,21 FePd,22 CoPt,23 CoPd24 and CoCrPt,25 etc. In particular, L1_0-type FePt nanoparticles (NPs) with face-centered tetragonal (fct) structures were considered as the promising candidate for the next generation of ultrahigh-density data storage systems due to their large uniaxial magnetocrystalline anisotropy (K_u ≈ 7 × 10^6 J m^-3) and good chemical stability.26-28 The previous approach of synthesizing FePt NPs often relied on vacuum-deposition techniques, however, multi-step procedures were generally required to prepare regular bit patterns.29 Meanwhile, solution phase chemical synthesis was successfully adopted to prepare monodisperse FePt NPs since the first report by Sun et al. in 2000.30 Patterned arrays of FePt NPs have also been fabricated by colloidal self-assembly based on the combination of physical patterning tools with self-assembly, but it is still a challenge for the mass production of such arrays as ordering of NPs is typically only over micrometer scale regions. Besides, although this method

---

* Institute of Molecular Functional Materials, Department of Chemistry and Institute of Advanced Materials, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, P. R. China. E-mail: rywywong@hkbu.edu.hk; clamho@hkbu.edu.hk; Fax: +852-3411-7348
† Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, P. R. China. E-mail: dennis.leung@polyu.edu.hk
‡ School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK E-mail: ian.manners@bristol.ac.uk
§ Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, P. R. China. E-mail: wai-yeung.wong@polyu.edu.hk
∥ These authors contributed equally.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x
demonstrates the feasibility to produce nanocrystals with smooth morphologies, the dual-source precursors involved such as Fe(CO)$_5$ or Fe(acac)$_3$ and Pt(acac)$_2$, also bring about the difficulty for stoichiometric control.$^{30,32}$ Recently, single-source organometallic precursors such as (CO)$_3$Fe(μ-dppm)(μ-CO)PtCl$_3$ and FePt(CO)$_4$dppmBr$_2$ were reported,$^{33-37}$ in which the atomic ratio of Fe and Pt could be easily controlled. In such case, the precursors would decompose at the same decomposition temperature and the two types of metal atoms are homogeneously distributed in the organic framework at the molecular scale, which would be beneficial to prevent the agglomeration of FePt NPs.

Metallopolymers are of intense interest owing to their ability of being easily processed and fabricated into films.$^{38-40}$ We have previously reported a series of Fe,Pt-containing metallopolymers as precursors to prepare L1$_0$-FePt NPs by the one-pot pyrolysis under an inert atmosphere.$^{10,41,42}$ These single-source polymer precursors could also be used as photoresist to afford micro- or nano-patterns by EBL or NIL.$^{43,44}$ However, the coercivities of the as-synthesized FePt NPs are still relatively low, which would restrict their potential for magnetic data recording media. With the effort of searching for new approaches of preparing highly ordered FePt NPs, a new strategy by optimizing the synthetic process is reported in the present study. Here, a new bimetallic polymetallayne polymer P of Fe and Pt was designed and synthesized, in which a ferrocene was symmetrically bonded to the aromatic ring through a freely-rotating O-bridge. This molecular design not only improves the overall solubility of the resulting polymer in common organic solvents, but also increases the solution processability of the polymer for the fabrication of nanoscale patterns by NIL.

Results and discussion

Synthesis and characterization of L1$_0$-FePt nanoparticles

The synthesis of metallopolymer P was carried out by the Cu(I)-catalyzed dehydrohalogenation reaction between PtCl$_2$(4,4’-dinonyl-2,2’-bipyridyl) and the diethynyl ligand 3 (Scheme 1). Ferrocene as the Fe source in P was bonded to the phenyl ring by a freely-rotating O-bridge, which can improve the solubility of the resulting polymer in common organic solvents. In addition, the diethynyl ligand 3 has a symmetrical structure, and therefore the two terminal acetylenic protons show similar reactivity, which can facilitate the final polymer to get a higher molecular weight and further enhance the

![Scheme 1. Synthetic routes of FePt-containing polymer P.](image-url)
interactions among different polymer molecules.

The polymer P as a single-source precursor of FePt NPs, which was put in a ceramic boat, was placed in a tube furnace. The tube was purged for 30 min, and then heated to 800 °C and kept for 1 h under an Ar/H₂ (v/v = 95/5) atmosphere. The resulting black powder containing FePt NPs were removed from the furnace after cooling the tube slowly to room temperature. The as-synthesized FePt NPs were then characterized by the wide-angle X-ray diffraction (XRD) and transmission electron microscopy (TEM) to investigate the phase and morphology.

The representative TEM micrographs of the as-synthesized FePt NPs at low and high resolution are shown in Figure 1a and 1b. The NPs had regular shapes with good contrast at low magnification, and were evenly dispersed on the amorphous carbon matrix, which could immobilize and protect the FePt alloys. The sizes of the resultant NPs were statistically analyzed from a wide area, as shown in Figure 1c. The mean size was about 12.7 nm with a standard deviation of 1.4 nm, which was in good agreement with the calculated results determined by the (111) diffraction peak position in the powder XRD (PXRD) spectrum. The measured lattice fringes of 0.221 and 0.283 nm from the high resolution TEM image (Figure 1b) of the individual single-crystal NPs are consistent with the d-spacing known for the (110) and (111) planes of fct FePt NPs, which reveals that the resultant FePt NPs possess a highly ordered, fct structure.

Figure 1d shows the PXRD patterns of the resultant FePt NPs. Well-resolved diffraction peaks were observed and indexed to the typical peaks of FePt (JCPDS Card no. 043-1359) alloys. The appearance of the strong (001) and (110) peaks in the curve suggests that the NPs have a chemically ordered fct structure, and the obvious splitting of the (200)/(002) and (220)/(202) pairs of reflections indicates that the L1₀ phase has a very high degree of ordering. The mean crystallite size was estimated to be 12.9 nm from the full width at the half-maximum of the (111) peak by the Scherrer analysis.

The composition of the resulting nanomaterials was studied by energy-dispersive X-ray (EDX) elemental analysis. The EDX result (see Supporting Information, Figure S1) shows that the ratio of Fe to Pt in NPs was around 0.45:0.55, which is within...
the experimental error for the ratio determined by the (111)
diffraction peak position in PXRD.

The magnetic hysteresis loop was measured at room
temperature on a physical property measurement system
(PPMS) and the result is shown in Figure 2. The saturation
moment (Ms) was obtained when the external field up to 9 T
(1 T = 10 kOe) was applied. The magnetic properties of the as-
synthesized FePt NPs revealed a ferromagnetic feature. In
addition, it was found that the NPs had a room-temperature
coercivity $H_c$ of 3.6 T and a saturated moment $M_s$ of 19.8
emu/g. Such a large coercivity further verified that the NPs
indeed showed highly ordered L1$_0$ structure. As compared
to the FePt NPs prepared from the similar methods reported
in the literature, the coercivity in the present study was
significantly increased from 1.4 T to 3.6 T,\textsuperscript{10,41,42} which is even
larger than the value (3.3 T) reported by Sun et al..\textsuperscript{45} To our
knowledge, this value represents the largest magnetic coercivity value for L1$_0$-FePt NPs ever reported. We believe
that the main difference lies in the fact that the fct FePt NPs
herein were synthesized under an Ar/H$_2$ atmosphere, where
the H$_2$ could be adsorbed on the surface of the seeds of NPs
during nucleation to hinder seed aggregation and further
promote the growth on the seed surface.\textsuperscript{46} Furthermore, since
the Fe and Pt sources were alternately linked with the organic
linkages, this would promote the formation of fct FePt NPs as
the L1$_0$-FePt phase can be considered as the superlattice of Fe
and Pt atoms stacked along the [001] direction.

To verify this hypothesis, FePt NPs were also synthesized
according to the previously reported pyrolysis conditions: P
was pyrolyzed for 1 h under an Ar atmosphere to prepare the

Figure 2. Magnetic hysteresis loop measured at room
temperature of the fct-FePt NPs.

![Magnetic hysteresis loop measured at room temperature of the fct-FePt NPs.](image)

Figure 3. (a) SEM image of regular line arrays of the polymer P patterned on the Si substrate; (b-d) SEM, 2-D and 3-D AFM images of
the as-synthesized ferromagnetic line pattern of FePt NPs after pyrolysis under an Ar/H$_2$ (v/v = 95/5). 3D AFM image size 5 × 5 μm$^2$.

![SEM image of regular line arrays of the polymer P patterned on the Si substrate; (b-d) SEM, 2-D and 3-D AFM images of](image)
FePt NPs. The resultant NPs had a smaller size of ca. 5.3 nm with a standard deviation of 1.2 nm as statistically analyzed from the TEM image (Figure S2), and the atomic ratio 46:54 of Fe to Pt was verified by EDX spectrum (Figure S3). PXRD was also applied to identify the phase and crystallinity of the NPs (Figure S4). The characterization peaks (001) and (110) of fct-phase FePt NPs were observed, but the intensity was relatively weaker for the (001) planes. In addition, the splitting of the (200) and (220) peaks was also not clearly observed. It could be deduced that the resultant FePt NPs were not highly ordered, or existed as a mixture of fcc and fct phases. The magnetic hysteresis loop (Figure S5) was also measured and the resulting lower coercivity of 0.75 T further supported this conclusion. All of these results indicate the merit of introducing H2 in promoting the synthesis of L10-FePt NPs.

**Patterning of L10-FePt nanoparticles by nanoimprint lithography**

Improvement of materials properties to push data storage densities beyond the Tbit/in2 value is important for high-density data storage applications. Therefore, patterning of the L10-FePt alloy NPs with a high degree of order and high Kc is an effective strategy to achieve the goal. In our previous reports, the polymer precursors were successfully patterned on the Si substrate by EBL and NIL, respectively.30, 42 Particularly, NIL was considered as a high throughput process to fabricate various patterns at the nanometer scale. In the present study, a new metallopolymers act as a photoresist, and its saturated solution in chloroform was first drop-casted onto the Si substrate. Then, the poly(dimethylsiloxane) (PDMS) templates, where the stamps used in this study included a line array in one-dimension with a periodicity of 740 nm (feature size of 350 nm) and a dot array in two-dimension with a periodicity of 500 nm (feature size of 250 nm), were casted onto the substrate. After the solvent was evaporated, the templates were lifted off and the reverse patterns of P were left on the substrate. Finally, the highly ordered 2D ferromagnetic arrays were obtained by annealing the prepattern under an Ar/H2 atmosphere.

As displayed in Figure 3, the regular line arrays were fabricated. The SEM images in Figure 3a and 3b show the line patterns of P and ferromagnetic FePt NPs obtained after pyrolysis, respectively. As depicted from Figure 3a, the pattern and structure of the imprinted bimetallic FePt-containing polymer P can be controlled and defined by the stamp. Also, the morphology of the line arrays revealed the same feature size before and after pyrolysis (Figure 3a–3b). However, because the polymer skeleton was collapsed during pyrolysis, and the height of the ferromagnetic line was decreased dramatically from 100 nm to 30 nm after pyrolysis. Figure 3c and 3d illustrate the top view 2D and 3D AFM images corresponding to Figure 3b, respectively, which further proved that the line arrays still preserve the highly ordered patterns after pyrolysis.

In order to isolate each magnetic recording bit under the bit-patterned media architecture, the PDMS template with hole array stamps was used to fabricate the negative patterns with dot arrays. Figure 4a portrays the SEM image of the nanoimprinted polymer P with a nanodot array pattern, in which the periodicity of 500 nm and feature size of 250 nm were observed. The patterned substrate was then annealed for 1 h at 800 °C under an Ar/H2 atmosphere; the polymer precursor was decomposed to form L10-FePt NPs through epitaxial growth. As demonstrated in the AFM images in Figure 4b, the morphology of the dot pattern was preserved after pyrolysis, and the 3D AFM image in Figure 4d intuitively showed the regular patterns of the dot array structure on the substrate. The height of the dot array was measured to be around 10 nm, which was obviously shown by the crosssection profile in Figure 4c. This was relatively small as compared to the depth of the original PDMS mold (80 nm) owing to the collapse of the polymer skeleton during pyrolysis. In addition, the magnetic properties were characterized by magnetic force microscopy (MFM). Figure 4e shows the corresponding MFM image. A nanopattern of magnetization with the same periodicity as the dot array pattern in the corresponding AFM image (Figure 4b) can be observed clearly, which indicates that this dot array nanopattern is magnetic and thereby can be used as a new platform for future perpendicular ultrahigh-density magnetic data recording. Our prototype BPM here provides an areal density of 2.58 Gb in-2. In addition, the higher coercivity means the more stable bits, which renders FePt NPs a good potential to be developed as stable BPM with higher areal density.

**Experimental**

**General Procedure and Materials**

All reactions were carried out under nitrogen unless otherwise stated. Commercially available reagents were used as received without further purification. 1,3-Dibromo-2-(bromomethyl)benzene and PtCl2(4,4′-dihydroxy-2,2′-bipyridyl) were prepared by the literature methods.10 Other reagents were purchased and used as received. All reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated glass plates. Compounds were visualized with UV light irradiation at 254 and 365 nm. Separation or purification of products was achieved by column chromatography. NMR spectra were measured in CDCl3 on a Bruker AV 400 NMR instrument with chemical shifts being referenced against tetramethylsilane as the internal standard for 1H, and 13C NMR data. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) using a HP 1050 series HPLC instrument with visible wavelength and fluorescent detectors against polystyrene standards.

**Synthesis of FePt-containing polymer P**
Ferrocenylmethanol: Ferrocenecarboxaldehyde (0.54 g, 2.5 mmol) and NaBH₄ (0.12 g, 3 mmol) were dissolved in EtOH (30 mL), H₂O (1 mL) was then added dropwise to the solution. The mixture was stirred for 1 h and then refluxed for another 2 h. After cooling to room temperature, the solvent was removed and the crude product was extracted by Et₂O (3 × 50 mL). The organic phase was dried and the residue was recrystallized in n-hexane to get the pure product as a yellow solid (0.49 g, 90%).

1H NMR (400 MHz, CDCl₃, δ): 4.24 (t, J = 2 Hz, 2H, Fc-H), 4.20 (t, J = 0.8 Hz, 2H, Fc-H), 4.17 (s, 5H, Fc-H), 1.66 (s, 2H, -CH₂-), 1.60 (broad, 1H, -OH); 13C NMR (100 MHz, CDCl₃, δ): 88.5, 68.4, 68.3, 68.0 (Fc), 60.8 (-CH₂-).

1: To a solution of ferrocenylmethanol (0.43 g, 2.0 mmol) in dry THF (10 mL), NaH (0.12 g, 3 mmol) was added slowly at 0 °C under a nitrogen atmosphere. After stirring for 0.5 h, 1,3-dibromo-5-(bromomethyl)benzene (0.66 g, 2.0 mmol) in THF (10 mL) was added dropwise and the reaction mixture was stirred overnight at 60 °C. The reaction mixture was quenched with saturated aq. NH₄Cl (50 mL) at 0 °C and extracted with CH₂Cl₂ (3 × 50 mL). The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄ and

Figure 4 (a) SEM image of regular dot arrays of P patterned on the Si substrate; (b) 2D AFM image of the as-synthesized ferromagnetic line pattern of FePt NPs after pyrolysis under Ar/H₂ (v/v = 95/5); (c) cross-section of (b); (d) 3D AFM image of (b) and (e) MFM image of (b). AFM and MFM image size 5 × 5 μm².
concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using n-hexane/dichloromethane (1:3, v/v) as eluent to afford a yellow solid (0.69 g, 74%). 1H NMR (400 MHz, CDCl₃, δ): 7.57 (s, 1H, Ar-H), 7.41 (s, 2H, Ar-H), 4.43 (s, 2H, -CH₂-), 4.34 (s, 2H, -CH₂-), 2.44 (t, J = 2 Hz, 2H, Fc-H), 4.18 (t, J = 1.6 Hz, 2H, Fc-H), 4.14 (s, 5H, Fc-H); 13C NMR (100 MHz, CDCl₃, δ): 142.7, 133.0, 129.1, 122.9 (Ar), 82.8, 70.0, 69.5, 68.9 (Fc), 68.7, 68.5 (-CH₂-).

2: To an ice-cooled mixture of 3 (2.05 g, 6.6 mmol) in freshly distilled triethylamine (25 mL) and dichloromethane (25 mL) solution was added Pd(PPh₃)₄ (200 mg) and Cul (50 mg). After the solution was stirred for 30 min at 0 °C, trimethylsilylacetylene (5 mL) was then added and the suspension was stirred for 30 min in an ice-bath before being warmed to room temperature. After reacting for 30 min at room temperature, the mixture was heated to 75 °C for 24 h. The solvent was removed under vacuum and then the residue was redissolved in CH₂Cl₂ at 0 °C. The solvent was removed under vacuum and then the residue was redissolved in CH₂Cl₂ and precipitated from methanol. IR (KBr): 2105 cm⁻¹.

Preparation of FePt nanoparticles

In the metallopolymer P, Fe and Pt sources are evenly dispersed in the same molecule and bonded chemically, which means that P can act as the single-source precursor to prepare FePt NPs. Polymer P was put in a ceramic boat, and was then placed in a tube furnace equipped with temperature and gas-flow controls. The precursor was heated for 1 h under an Ar/H₂ atmosphere at 800 °C. After being cooled to room temperature, black powdery FePt NPs were formed. The resultant nanomaterials were then characterized to PXRD, TEM, EDX and PPMs.

Patterning of FePt nanoparticles

A solution of P in chloroform (20 mg/mL) was prepared and filtered by a syringe with a 0.22 μm pore size hydrophobic Nylon membrane. 20 μL of the solution was drop-casted onto a Si wafer (10 × 10 mm²), which was previously cleaned with acetone. Then, a PDMS template with stamps such as line or dot arrays was immediately imprinted onto the wafer for 5 min under 1 N/cm² of pressure. After removing the template, the reverse stamps of the polymer P were left on the Si substrate. The substrate was annealed to get the ferromagnetic patterns according to the same pyrolysis condition as for the preparation of FePt NPs.

Conclusions

L1₀-FePt NPs with highly ordered crystalline structures were prepared from the single-source bimetallic metallopolymer precursor P. Pyrolysis of P under an Ar/H₂ atmosphere successfully produced the resultant FePt NPs with an ultra-high coercivity of 3.6 T, where the existence of H₂ played an important role in facilitating the formation of the fct phase. The metallopolymer precursor was easily used as a photoresist and could be directly imprinted on the desired substrate. Ferromagnetic 2D line and dot arrays suitable for BPM were patterned, which are potentially useful for high-density data storage applications. In principle, the approach can be readily extended to other L1₀-phase nanocrystals (NC) such as CoPt and FePd. Therefore, the present work opens up a new and general route for the fabrication of highly ordered 2D ferromagnetic NP arrays.

Acknowledgements

W.-Y. Wong thanks the Hong Kong Research Grants Council (HKBU 12302114), Areas of Excellence Scheme of HKSAR (AoE/P-03/08), National Natural Science Foundation of China (Project No. 51373145), Science, Technology, and Innovation Committee of Shenzhen Municipality (JCYJ20140419130507116), Hong Kong Baptist University (FRG2/13-14/083) and the Hong Kong Polytechnic University for financial support. C.-L. Ho thanks Hong Kong Baptist University (FRG2/13-14/078), and the Science, Technology and Innovation Committee of Shenzhen Municipality (JCYJ20140818163041143) for their financial support. We also...
thank the National Natural Science Foundation of China (project number: 21504074). The work in PolyU was supported by the Hong Kong Research Grants Council (PolyU 153015/14P) and PolyU (1-ZE14/1-ZE25).

Notes and references