DOCTORAL THESIS

Metallopolymers as precursors to magnetic metal alloy nanoparticles: synthesis, characterization, lithographic patterning and device fabrication

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Metallopolymers as Precursors to Magnetic Metal Alloy Nanoparticles: Synthesis, Characterization, Lithographic Patterning and Device Fabrication

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Abstract

Magnetic NPs with sizes ranging from 2 to 20 nm in diameter represent an important class of artificial nanostructured materials, since the NP size is comparable to the size of a magnetic domain. They have potential application in data storage, permanent magnetic nanocomposites, and biomedicine. FePt alloy NPs have attracted extensive recent attention because of their remarkable magnetic properties. In particular, $L1_0$ (face-centred tetragonal or fct) phase FePt NPs exhibit a giant magnetocrystalline anisotropy K of ca. 7 $\times$ 10^6 $J \cdot m^{-3}$, one of the highest values among the known hard magnetic materials. These features make the fct FePt NPs very desirable in the field of ultra-high-density information storage and high-performance permanent magnets.

Chapter 1 presents a brief overview on the background, basic theory and development of $L1_0$ phase FePt NPs and bit patterned media for perpendicular magnetic data recording.

In chapter 2, a series of FePt-containing metallopolymers were designed and synthesized. The strategy we adopted to synthesize the metallopolymers incorporating Fe and Pt atom is: anchoring Fe on the backbone of the ligand by using ferrocene as the starting material and then bringing two acetylide groups to the ligand as the terminal group to form bimetallized metallopolyyne with Pt atom. After pyrolytic treatment of these FePt-containing metallopolymers, the corresponding $L1_0$ phase FePt NPs can be synthesized with the atomic ratio of Fe and Pt close to 1. XRD, TEM, EDX and magnetization analysis for characterizing these NPs were carried out.

More importantly, we selected one FePt-containing metallopolymer with excellent

solubility in common organic solvents for patterning studies via nanoimprint lithography (NIL) at low cost and high throughput. As a result, very orderly nanoline pattern and nanodot pattern of FePt-containing metallopolymer can be generated. Controlled pyrolysis of the patterned FePt-containing metallopolymer gives rise to patterned $L1_0$ phase FePt NPs array with high shape conformity. The vibrating sample magnetometer (VSM) results indicate that the patterned FePt NPs possess a coercivity as large as 1.4 T at room temperature. The magnetic force microscopy (MFM) image of the nanodot pattern also indicates that the patterned $L1_0$ phase FePt NPs are capable of exhibiting very strong magnetic response, which suggests great potential to be utilized directly in the fabrication of bit patterned media (BPM) for the next generation of magnetic recording technology. We also patterned this metallopolymer through UV photolithography (UVL), which implies that it can also be utilized directly as a negative-tone resist to fabricate FePt NP array patterns with high *K* by both electron beam lithography (EBL) and UVL.

Chapter 3 presents an alternative way for the one-step generation of $L1_0$ phase FePt NPs through pyrolyzing polymer blends of individual Fe-containing polymer and Pt-containing polymer with an atomic ratio of Fe:Pt (1:1). Thus a wide range of metallopolymers with good solubility can be used to synthesize FePt NPs. XRD, TEM, EDX and magnetization analysis for characterizing these NPs were also carried out. Similarly, we also performed nanopatterning of the polymer blends and pyrolysis of the as-prepared patterned polymer blends. TEM, AFM and MFM measurements indicate the resulting ceramic pattern is of high shape fidelity and is also magnetic for application as a new platform for BPM.

In chapter 4, a series of porphyrin-based metallopolymers were designed and synthesized. Taking advantage of the template effect of porphyrin, various metal atoms can be incorporated into the porphyrin ring, thus coupling with different atoms reside outside of the porphyrin ring, and diverse metal alloy NPs can be generated. For the FePt NP case, XRD measurements prove that the structure of the resulting alloy NPs is still chemically ordered $L1_0$ phase.

In chapter 5, a series of NP2-type ligands and their corresponding Co^{II} and Ni^{II} complexes were designed and synthesized. From the crystal structures of these metal complexes, we have found that NP2 ligands exhibit dual coordination modes. The dual coordination modes are due to the geometric preference of the metal center: Co^{II} (tetrahedral) and Ni^{II} (square planar). The EPR experiments and UV/vis absorption spectra illustrate the role of solvent (MeCN versus THF) in modulating the dual coordination modes of NP2 ligands to Co^{II} complexes, which best exhibited by the unusual crystal *Cc* structure containing two conformers in a single unit cell. Besides, we also have successfully attached one Co complex onto the Si(111) surface, which would be explored for the engineering of organic catalyst for water splitting at the molecular level.

Chapters 6 and 7 present the concluding remarks and the experimental details of the work described in Chapters 2–5.

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