Effect of Each Layer on Anisotropic Magnetic Properties of Nd/Fe/Polyamide 66 Three-Layer Coaxial Nanocables

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ABSTRACT: One-dimensional (1D) Nd/Fe/polyamide 66 (Nd/Fe/PA66) three-layer coaxial nanocable arrays with high aspect ratio and highly anisotropic magnetization were successfully prepared via layer-by-layer deposition in the anodic aluminum oxide template. The morphology, chemical composition, and magnetic properties of Nd/Fe/PA66 nanocables were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and vibrating sample magnetometry. The effects of 1D nanocables on the magnetic properties of the assembled ordered arrays have been systematically investigated. The structural properties of these nanostructures are investigated as a function of the geometrical parameters. The magnetic anisotropy of Nd/Fe/PA66 nanocables has been significantly enhanced owing to the doped Nd that possesses a larger spin-orbital coupling and leads to a synergistic effect with Fe to enhance anisotropy energy.

1. INTRODUCTION

In recent years, magnetic nanostructures have played an important role because of their potential applications in nanoelectronics devices, high-density recording, biological sensors, and high-frequency sensors.1–4 Magnetic nanomaterials have been extensively studied because of their magnetic anisotropy in applications.5 Magnetic materials with different magnetization anisotropies are often genetically determined by the preparation methods and dimensions (i.e., the diameter or the length).6,7 It is difficult to obtain and maintain homogeneous and pure one-dimensional (1D) nanowires because of oxidation and adsorption during fabrication and application processes; therefore, in many cases, ferromagnetic metals were compositized with other materials to prepare various nanocomposites, such as multisection nanowires, nanocables and alloys.9–14 Therefore, it is promising and interesting for researchers to prepare various structural magnetic nanomaterials with high magnetic anisotropy, giant magnetoresistance, or multifunction nanomaterials.5,15,16 For example, multisection ferromagnetic nanowires, such as Ni–Fe/Cu/Co/Cu, Ni–Fe/Cu, Co/Cu, Fe/Cu, and Co/Cu/Co/Cu,9–13 have magnetic properties and giant magnetoresistance effect. Nanocables are typical of 1D composite materials, and a lot of literatures have reported the preparation and applications, for instance, Fe/Fe–dimethylsulfoxide nanocables; the arrays of nanocables showed an obvious anisotropy with the easy magnetizing axial parallel to the length of nanocable.12 Fe/carbon nanotubes (Fe/CNTs) have electromigration effect and can be used as memory devices and nanopipettes.17–19 Fe/Pd nanocables have a prominent catalytic activity in ligand-free C–N bond formation in water. As is known to all, Nd–Fe–B composite is a famous permanent magnet. Inspired by this, few lectures have reported the preparation methods of rare earth metal-doped nanomaterials and studied their magnetic property.20–23 The results showed that the magnetism changed with the increase of rare earth metals; nevertheless, the fabrication of ferromagnetic nanowires or nanocables doped with rare earth metals has been less reported.

In this report, we introduced the preparation method of Nd/Fe/PA66 three-layer nanocable arrays with different magnetic anisotropies. The outermost-layer nanotubes, which can protect metal nanomaterials from being oxidized, were fabricated by solution wetting the anodic aluminum oxide (AAO) template. PA66/AAO nanotubes served as a “second template” to deposit the middle-layer Fe nanotubes. Fe/PA66/AAO nanotubes served as a “third template” to deposit the internal-layer Nd nanowires to form Nd/Fe/PA66 nanocables. In addition, the magnetism of Fe nanotubes, Fe/PA66 nanotubes, and Nd/Fe/PA66 nanocables was studied systematically.

2. RESULTS AND DISCUSSION

The morphology of PA66 nanotubes is shown in Figure 1. Figure 1a shows that the PA66 nanotubes formed ordered arrays without AAO template supporting. Figure 1b shows that the PA66 has a good nanotube structure with a continuous and
uniform pipe wall. The morphology and structure of Fe nanotubes and Fe/PA66 coaxial nanotubes are shown in Figure 2. These nanotubes were separated by dissolving alumina in NaOH aqueous solution. Figure 2c,d shows pure Fe nanotubes. It can be seen that the nanotubes are array structures, the diameter of Fe nanotubes is about 200 nm, and the wall is thin and continuous. Figure 2a shows the scanning electron microscopy (SEM) image of Fe/PA66 coaxial nanotubes. The length of the two nanotubes is almost same, and the ends of Fe nanotubes are open. The coaxial nanotube is confirmed by the transmission electron microscopy (TEM) image (Figure 2b), and the Fe nanotube is coated tightly by PA66 nanotubes. The patterns of selected area electron diffraction (SAED) (Figure 2b,d) indicate that the Fe nanotube is a polycrystalline structure. Furthermore, some Fe nanoparticles that attached on the inner wall of the PA66 nanotubes can be seen. Fe nanoparticles with magnetism could form various kinds of magnetic domain and distribute optionally onto the inner wall of the PA66 nanotubes before the formation of Fe nanowires; the phenomenon also appears in Figure 2d and Ni nanotubes, which may be the intrinsic characteristics of ferromagnetic metals.

Fe/PA66 coaxial nanotubes can be used as templates to prepare other new materials. Nd was deposited in the above coaxial nanotubes to prepare three-layer coaxial nanocables. The morphology and structural features of Nd/Fe/PA66 are shown in Figure 3. The SEM image shown in Figure 3a clearly depicts that the nanostructure is a core/shell nanocable array and the length of the nanocables is almost the same. The core is almost a solid wire. It is confirmed that Nd nanowires occupied almost all Fe/PA66 nanotubes. However, few nanotubes still exist. Above-mentioned microscopic structures were proved by the typical TEM images, as shown in Figure 3b. The TEM image reveals that the nanocable is a high aspect ratio 1D structure (>40), and it can be seen that most are solid, and few are a tubular structure, which is resulted by two possible cases as follows: one is that few PA66 nanotubes were blocked by the PA66, and the metal ions could not be deposited into; and the other is that few PA66 nanotubes or Fe/PA66 nanotubes at the edge of the AAO template could not be deposited into by the metal ions. From the zoom-in TEM image (Figure 3c), it is clearly shown that the nanocable consists of a bright PA66 nanotube shell and a dark Nd/Fe nanowire core. It is proved that the materials of the core and shell are different. The Nd nanowire grew out of the Fe/PA66 nanotube, which is seen from the top of the Nd/Fe/PA66 nanocable. The SAED pattern, which is marked by a red circle, as shown in Figure 3c, reveals that the Nd nanowire belongs to a single-crystal structure. However, the crystal form of the Nd/Fe/PA66 composite belongs to a polycrystalline configuration (the area marked with the red square in Figure 3c). The SAED pattern is mainly from Fe materials. The reason may be that the sample is thick and electron beam cannot pass through it.

The crystalline structure of Nd/Fe/PA66 nanocables was characterized by X-ray diffraction (XRD) (Figure 4). Crystalline phases of PA66 can transfer in the limited space. Only γ crystalline phase exists in the PA66 nanotubes at room temperature as revealed by the presence of the γ peak at 24.0°. The absence of α phase is probably because of the preferred formation of γ phase in the space-confined deposition driven by a kinetic factor. Among another five peaks, two distinct peaks observed at 2θ of 44.4° and 64.6° are consistent with the diffraction peaks of (110) and (200) crystalline planes of Fe, respectively. Two distinct peaks observed at 2θ of 64.6° and 77.6° are consistent with the diffraction peaks of (311) and
(206) crystalline planes of Nd, respectively. Another two diffraction peaks (2θ of 38.2° and 81.7°) were introduced by the sputtered Au film used for electrodeposition.

Magnetization reversal in ferromagnetic nanotubes can be determined by the angular dependence of the coercive field in ordered arrays of ferromagnetic nanotubes, and the two most common magnetization reversal modes can be modeled by coherent rotation or curling. Generally, for magnetic nanowires, magnetization reversal is different from magnetic nanotubes about the field angle.

Vibrating sample magnetometry (VSM) is employed to investigate the magnetic behaviors of Fe nanotubes, Fe/PA66 nanotubes, and Nd/Fe/PA66 nanocables. The magnetic hysteresis (M−H) loops of the three samples are shown in Figure 4. The magnetic properties can be changed by the geometry. Figures 2 and 3 show that there are distinct differences in the vertical geometry and transverse geometry of the nanotubes or nanocables; therefore, the magnetic properties are obviously different between Fe nanotubes, Fe/PA66 nanotubes, and Nd/Fe/PA66 nanocables (Figure 5). It is obvious that the magnetism along the long axis of nanotubes or nanocables is bigger than that of the vertical direction. That is to say, the direction along the long axis is easily magnetized. It is interesting that the coercivity paralleling to the long axis in the Fe/PA66 nanotube arrays is very small. Taking into consideration of the error of VSM, the magnetization curves pass through the ordinate origin; thus, the coaxial double-nanotube arrays display superparamagnetic nature. It is promising to be used as superparamagnetic materials, which can be used in biological magnetic-perception field. However, from the square shown in Figure 5c, it can be seen that the Nd/Fe/PA66 nanocables have a better magnetic property than Fe nanotubes and Fe/PA66 nanotubes and are more easily magnetized than Fe nanotubes and Fe/PA66 nanotubes. In our previous studies, it has been found that the magnetism of the composite with a nonmagnetic single-crystal metal as cores and a magnetic polycrystal metal as sheaths was enhanced, and the magnetism of the composite with a magnetic polycrystal metal as cores and another magnetic polycrystal metal as sheaths was decreased. Figure 3c displayed that the Fe nanotube as a sheath is a polycrystal and the Nd nanowire as a core is a single crystal. This may be a universal law: magnetism will be enhanced when magnetic polycrystal metals as sheaths coat the nonmagnetic single-crystal metals as cores. The Nd/Fe/PA66 nanocable arrays are in good agreement with the law. The M−H loop shape of Nd/Fe/PA66 nanocables is closer to that of the hard magnetic materials than those of Fe and Fe/PA66 nanotubes. Therefore, the Nd/Fe/PA66 nanocables are suitable for preparing permanent magnetic materials and applications in perpendicular recording media.

According to the M−H loops in Figure 5a–c, the magnetization intensity achieves a maximum value (M_{max}) when the direction of H is parallel to the long axis of nanotubes/nanocables, whereas that has a minimum value (M_{min}) when the direction of H is perpendicular to the long axis of nanotubes/nanocables. The value of M_{max}/M_{min} can be employed to evaluate the magnetic anisotropy of nanotubes/nanocables and determined as 3.18, 1.01, and 5.25 for Fe nanotube arrays, Fe/PA66 nanotube arrays, and Nd/Fe/PA66/AAO nanocable arrays, respectively. It is very easy to be understood. The three systems have the same diameter, which determines the anisotropy energy of the nanowires. The pure Fe nanotube is regarded as a reference. After coating PA66, which shows weak magnetism, the diameter of the Fe nanotube becomes...
thinner and decreases the anisotropy. However, Nd, as a typical rare earth metal, usually possesses a larger spin-orbital coupling, which leads to a larger anisotropy energy. Another reason is that Nd nanoparticles diffused into Fe, which leads to a synergistic effect and enhances the anisotropy energy of Nd/Fe/PA66 nanocables.\(^\text{27}\)

Table 1 shows the magnetic properties of nanostructures consisting of Fe, Fe/PA66, and Nd/Fe/PA66 in AAO templates. We compare the magnetic properties of pure and composite nanostructure arrays in AAO templates. It can be seen that the magnetic properties of the nanotube and nanocable are intrinsic; therefore, the dipolar interaction among the nanostructure is different. From Table 1, the variation in the values of \(H_r\) and \(M_r/M_i\) and in the magnetic hysteresis (\(M-H\)) loops is observed for different nanostructure arrays. Magnetic parameters of the three systems in perpendicular and parallel directions are obviously different. It can be proved that the magnetic anisotropy of Nd/Fe/PA66 nanocables is better than those of Fe and Fe/PA66.

| sample       | \(H_r^c\) (Oe) | \(H_r^p\) (Oe) | \(M_r/M_i^c\) | \(M_r/M_i^p\) |
|--------------|----------------|----------------|---------------|---------------|
| Fe           | 277.1          | 345.7          | 0.0529        | 0.143         |
| Fe/PA66      | 228.6          | 92.39          | 0.116         | 0.0903        |
| Nd/Fe/PA66   | 161.2          | 253.7          | 0.0394        | 0.196         |

3. EXPERIMENTAL SECTION

3.1. Preparation of PA66 Nanotubes and Fe/PA66 Nanotubes. AAO templates were used as purchased from Whatman Corp. The diameter of the pores in the AAO templates is 200 nm, and the depth is about 60 \(\mu\)m. Formic acid was employed as the solvent to prepare 5 wt % of PA66 solution. A drop of PA66 solution was placed on a glass slide, and then, a piece of AAO template was covered on the PA66 solution. The length of the PA66 nanotubes was controlled by the growth time.

The AAO template filled with PA66 nanotubes was used as a "second template" to deposit Fe nanotubes. First of all, the AAO template filled with PA66 nanotubes was treated with formic acid to make the PA66 nanotube to open, and then, a thin film of Au was sputtered on a side of the AAO/PA66 composite membrane to serve as the working electrode.

Electrolyte solution used for the electrodeposition of Fe is composed of 0.6 M FeSO\(_4\)·7H\(_2\)O, 0.2 M H\(_3\)BO\(_3\), and 0.3 M KCl. The AAO/PA66 composite membrane was used as the working electrode and also the template for the deposition of Fe. A platinum plate served as the counter electrode and an Ag/AgCl electrode in saturated KCl solution as the reference electrode. Direct current (dc) electrodeposition at \(-1.2\) V/SCE was employed to deposit Fe in PA66 nanotubes for 15 min to form Fe/PA66 nanotube arrays.

For comparison, Fe nanotubes were also prepared by the dc electrodeposition of Fe in the AAO template at \(-0.8\) V/SCE for 15 min.

3.2. Preparation of Nd/Fe/PA66 Nanocables. The Fe/PA66 composite membrane was used as a “third template” to deposit Nd nanowires. Electrolyte solution is composed of 0.4 M Nd(NO\(_3\))\(_2\), 0.2 M H\(_3\)BO\(_3\), and 0.3 M KCl. dc electrodeposition at \(-0.4\) V/SCE was employed to deposit Nd into Fe/PA66 nanotubes for 40 min to form Nd/Fe/PA66 nanocable arrays.

The preparation process is displayed in schematic diagram (Figure 6).

**Figure 6.** Schematic diagram of the Nd/Fe/PA66 nanocable array; A: AAO template, B: PA66 solution, C: PA66 nanotube, and D: PA66 membrane after the solvent volatilizing.

3.3. Characterization. SEM (JEOL JSM-6390LV), TEM (CM200-FEG equipped with a GIF) were used to characterize the morphology of nanotubes and nanocables. For SEM imaging, all samples were separated by dissolving the alumina membrane in NaOH aqueous solution. For TEM measurement, a drop of (5 \(\mu\)L) diluted sample was dried on a copper grid. The crystalline structure of the obtained materials was determined by XRD (Bruker D8 Advance with a Cu K\(\alpha\) radiation, \(\lambda = 1.5418\) \(\AA\)). Magnetization of nanotubes and nanocables was measured at room temperature (295 K) with a vibrating sample magnetometer (Quantum Design-PPMS). All samples embedded in AAO templates, such as Fe/AAO, Fe/PA66/AAO, and Nd/Fe/PA66/AAO, are closely related to their microstructure and therefore to the growth condition.

4. CONCLUSIONS

In summary, we have prepared Nd/Fe/PA66 nanocable arrays with shape anisotropy and magnetic anisotropy through AAO template-assisted method with polymer solution wetting technique and two-step electrodeposition technique. The two methods offer low cost and a simple way to fabricate nanocable arrays. In an array with all nanocables initially magnetized in the same direction, the magnetostatic interaction between neighboring tubes favors the magnetization reversal of some of them. The Nd/Fe/PA66 nanocable arrays have been demonstrated with high anisotropic magnetization along the long axial direction. The magnetic anisotropy can be manipulated by filling with the rare earth metal Nd. Owing to the hard magnetic material nature of Nd/Fe/PA66 nanocables, these arrays possess the ability of permanent magnet materials. It is anticipated that such a finding provides a facile and effective approach for preparing high-magnetic nanocable arrays for application in perpendicular recording media.

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Notes
The authors declare no competing financial interest.

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