The exchange bias effects of CoFe$_2$O$_4$@NiO nanofibers fabricated by electrospinning

Jianfeng Dai$^{1,2}$, Wei Feng$^{1,3}$, Chen Cheng$^1$ and Xinchao Wen$^1$

$^1$ School of Science, Lanzhou University of Technology, Lanzhou 730050, People’s Republic of China
$^2$ State Key Laboratory of Advanced Processing and Recycling of Nonferrous Metals, Lanzhou university of Technology, Lanzhou 730050, People’s Republic of China
$^3$ Author to whom any correspondence should be addressed.

E-mail: 945936129@qq.com

Keywords: exchange bias, electrospinning, core-shell, pinning effect

Abstract

Exchange bias effect ($H_{EB}$) systems offer various technological application, which has been playing a key role in spintronics. CoFe$_2$O$_4$@NiO with core–shell nanostructure has been synthesized through coaxial electrospinning. The exchange bias of CoFe$_2$O$_4$@NiO is different in the different molar ratio of core to shell, when the ratio of core to shell is 1:3, its maximum value is of 763 Oe at 5 K. Also, the values of $M_r$, $M_s$, $M_r$/Ms and Hc at 300 K and 5 K are first increases then decreases due to the molar ratio of NiO, its pinning effect play a vital role. Its anisotropy and magnetic domain structure have been primarily studied. The improvement of Hc will influence the $H_{EB}$, which has a significant application value in spintronic devices.

1. Introduction

The exchange bias effect is that the hysteresis loop of the ferromagnetic (FM) layer deviates from the magnetic field direction after the system is cooled from the Neel temperature ($T_{Neel}$) of anti-ferromagnetic (AFM). The systems can consist of permanent magnetic/soft magnetic [1], permanent magnetic/anti-ferromagnetic [2], (FM)/(AFM) [3], ferrimagnetic (FIM)/(AFM) [4] film system [5], core–shell system [6], alloy system [7], etc. In 1956, Meiklejohn and Bean [8] discovered the exchange bias effect, which was due to the spin interaction at the interface of Co nanoparticles covered by CoO, and the hysteresis loop moved along the magnetic field axis after the applied magnetic field cooled. Peddis [9] used a new sol-gel auto combustion technique to fabricate CoFe$_2$O$_4$/NiO nanopolymers with different weight ratios of FIM and discussed the interparticle interactions. Rajnish Kumar [10] used a high energy planetary ball mill technique to fabricate CoFe$_2$O$_4$/NiO nanopolymers and studied the interaction between two phases at their interface. If the size of nanofibers is lower than its critical value, the superparamagnetic effect will appear. One of the solutions to overcome this drawback was inducing an anisotropy at the interface of ferri/ferromagnetic and antiferromagnetic phases [11]. Rajendra Mohan et al prepared CoFe$_2$O$_4$@NiO nanocomposite with different weight percentage of NiO varying from 10% to 40% by chemical co-precipitation and studied its exchange bias effect. But it is only 355 Oe and the exchange bias effect size of the core–shell structure we prepared is over 700 Oe [12]. Gokul et al investigated the novel magnetic interactions, such as exchange bias, memory effect and magnetic relaxation dynamics in NiO and 10 wt% Gd doped NiO nanoparticles synthesized by hydrothermal process [13]. Javed et al prepared 1D hybrid ferromagnetic multiferroic core–shell nanostructures using a two-step method, which was complicated and expensive [14]. This work is to fabricate nanofibers with core–shell nanostructure, which will enhance the anisotropy at the interface of CoFe$_2$O$_4$ and NiO. The strong coupling between the shell and core is responsible for the origin of exchange bias effect in the NiO nanoparticles [15, 16].

The main purpose of present work is to study and understand the effect of different ratios of core and shell on exchange bias effect as well as its influence on magnetic behavior. In this work, CoFe$_2$O$_4$@NiO nanofibers with core–shell nanostructure have been prepared by electrospinning method. Spinel CoFe$_2$O$_4$ has large
magneto-crystal anisotropy and chemical stability, anti-ferromagnetic NiO will show size effect at nanometer scale. This technique is more economical and convenient to fabricate samples.

2. Experiment details

All chemical reagents were analytical grade. The CoFe$_2$O$_4$@NiO nanofibers and nanoparticles were fabricated by coaxial electrospinning method. In the electrospinning process, 0.291 g Co(NO$_3$)$_2$·6H$_2$O and 0.808 g Fe(NO$_3$)$_3$·9H$_2$O were dissolved into the mixed solution of 2.5 g PVP, 3 ml N-Dimethylformamide and 3 ml ethanol. 0.2908 g Ni(NO$_3$)$_2$·6H$_2$O was dissolved into the mixed solution of 2.5 g PVP, 3 ml N-Dimethylformamide and 3 ml deionized water. The ratio of CoFe$_2$O$_4$/NiO is 1:1, we named it as S1, then the ratios of CoFe$_2$O$_4$@NiO were changed to 1:2, 1:3, and 1:4 which were named as S2, S3 and S4 respectively. The obtained precursor solution was transferred to 10 ml glass syringe and connected to stainless steel needles. The coaxial double nozzle electrospinning technology were used, the core needle is longer than the shell needle, and the syringe parameters of core and shell are also different. The flow rate of the core is 0.35 ml h$^{-1}$, while the flow rate of the shell is 0.36 ml h$^{-1}$, which is more conducive to the formation of the core–shell structure. The distance between the needle tip and the aluminum foil collector was 15 cm and the voltage was 17 kv. The precursor fibers were obtained. Finally, the CoFe$_2$O$_4$/NiO precursor fibers were annealed at 773 K (heating rate is 274 K min$^{-1}$) for 4 h, and the CoFe$_2$O$_4$/NiO nanofibers were obtained.

The phase composition of the samples was analyzed by Rigaku d/ max-2400 rotating x-ray diffractometer (XRD). The morphology and distribution of the samples were observed by JEM-6701F scanning electron microscope(SEM) and JEM-1200EX transmission electron microscope(TEM). The basic magnetic properties of the material were measured by MicroSense EV-9 vibrating sample magnetometer(VSM).

3. Results and discussion

3.1. XRD analysis

Figure 1 shows the XRD patterns of CoFe$_2$O$_4$@NiO nanofibers(S1, S2, S3, S4) prepared by electrospinning. As can be seen, the characteristic peaks for both the CoFe$_2$O$_4$ and NiO are observed and no extra peak is detected. As the proportion of NiO increases, the peak becomes sharper and crystallizes well.

3.2. Morphology analysis

Morphology of nanofibers has been studied by employing the SEM techniques. The typical SEM micrograph of CoFe$_2$O$_4$@NiO (S3) has been shown in figures 2(a) and (b), the inset in figure 2(a) is the schematic diagram of electrospinning. It can be found that the average size of nanofibers is about 100 nm. Figure 2(c) is the Energy Disperse Spectroscopy(EDS) pattern of CoFe$_2$O$_4$@NiO nanofibers, the distribution of each element can be clearly seen from the inset. There are only four elements, Fe, Co, Ni, O, and no other extra elements can be detected. Combined with XRD analysis, the samples contain pure phase CoFe$_2$O$_4$ and NiO.
Figure 3 shows the TEM(a), HRTEM(b) and selected area electron diffraction (SAED) patterns of CoFe$_2$O$_4$@NiO nanofibers. As can be seen in figure 3(a), the nanofiber with core–shell nanostructure was obtained. The nanofiber is continuous and smooth, CoFe$_2$O$_4$ and NiO are distributed in core and shell layer uniformly, and the interface of two phases is distinct that we can find the core and shell layer clearly. The average diameter of nanofibers is about 100 nm. The HRTEM image in figure 3(b) confirms the presence of CoFe$_2$O$_4$ and NiO phases. The lattice distance of nickel oxide is 0.2412 nm, which corresponds to the crystal plane (111) of NiO, and the lattice distance of CoFe$_2$O$_4$ is 0.2531 and 0.1713 nm, which correspond to the crystal plane (311) and (422) of CoFe$_2$O$_4$. The inset in figure 3(a) is the SAED patterns of CoFe$_2$O$_4$ and NiO nanofibers.

3.3. Magnetic properties analysis

The hysteresis loops of the nanofibers measured at 300 K are shown in figure 4(a). All samples exhibit typical smooth hysteresis loops, indicating that there is a good interaction on the interface of CoFe$_2$O$_4$ and NiO. Figure 4(b) depicts the magnetic properties of all the nanofibers.

The applied magnetic field is ±5 T, and the inset is hysteresis loops of selected area. As we can see, it is clear that the samples show magnetic hysteresis at 300 K. The saturation magnetization (Ms), coercivity (Hc), magnetic remanence(Mr), Mr/Ms and exchange bias effect (H$_{EB}$) are shown in table 1. The Hc of nanofibers we obtained by electrospinning method first increases then decreases, and reaches the maximum 543 Oe when the mole ratio is 1:3. It is attributed to internal magnetic domains which are arranged along the axis of nanofibers, and NiO(AFM) can cause a pinning effect on CoFe$_2$O$_4$(FIM), so the Hc increases. But an appropriate amount of NiO will increase the coercivity, if the NiO is excessive, it will inhibit the pinning effect, resulting in a reduction of HC. In addition, It can be found that a small amount of H$_{EB}$ (only 1–2 Oe) at 300 K. H$_{EB}$ = (C$_1$ + C$_2$)/2, C$_1$ represents coercivity on the left and C$_2$ represents coercivity on the right of hysteresis loops. It can be attributed to two points, the first is the minor error of measurements, the second is that the T$_{Neel}$ of NiO is about 525 K, the H$_{EB}$ can be observed at 300 K theoretically, but due to the existence of blocking temperature T$_{blocking}$, H$_{EB}$ can be observed obviously when the temperature is lower than T$_{blocking}$. The value of Mr/Ms is reaching its maximum 0.42 at the mole ratio of 1:2, which is an interesting application in magnetic memory device.

Based on the above analysis, the samples were cooled to 5 K with 1 T magnetic field, and then the field-cooled (FC) hysteresis loops are measured, applied field is ±5 T. The hysteresis loops of nanofibers (S1, S2, S3,
Compared with the measured values at 300 K, the similarity is that the Ms and Hc of nano fibers measured at 5 K increases first, then decreases, and reaches its maximum at S3, \( \text{Ms}_{\text{S3}} = 47 \text{ emug}^{-1}, \text{Hc} = 11890 \text{ Oe} \). But the difference is that they are larger than them at 300 K. Also, the large HEB (763 Oe) is observed. Moreover, with the increase of the molar ratio, the HEB keeps increasing, and reaches its maximum until the molar ratio is reaching 1:3 and then decreases. It can be related to the frozen uncompensated spin at the interface between CoFe\(_2\)O\(_4\) and NiO.

**Table 1.** Magnetic properties of nanofibers measured at 300 K.

| Samples | Ms  | Mr  | Hc   | Mr/Ms | HEB |
|---------|-----|-----|------|-------|-----|
| S1      | 26  | 10  | 442  | 0.38  | 1   |
| S2      | 38  | 16  | 476  | 0.42  | 1   |
| S3      | 43  | 8   | 543  | 0.18  | 2   |
| S4      | 31  | 4   | 365  | 0.12  | 2   |

**Table 2.** Magnetic properties of nanofibers measured at 5 K.

| Samples | Ms  | Mr  | Hc   | Mr/Ms | HEB  |
|---------|-----|-----|------|-------|------|
| S1      | 29  | 22  | 4076 | 0.75  | 80   |
| S2      | 41  | 33  | 7649 | 0.80  | 177  |
| S3      | 47  | 32  | 11890| 0.68  | 763  |
| S4      | 35  | 22  | 11343| 0.62  | 593  |

S4) at 5 K are shown in the figure 5(a). Figure 5(b) depicts the magnetic properties of all the nanofibers. Their Ms, Hc, Mr, Mr/Ms and HEB are shown in table 2.

Compared with the measured values at 300 K, the similarity is that the Ms and Hc of nanofibers measured at 5 K increases first, then decreases, and reaches its maximum at S3, \( \text{Ms} = 47 \text{ emug}^{-1}, \text{Hc} = 11890 \text{ Oe} \). But the difference is that they are larger than them at 300 K. Also, the large HEB (763 Oe) is observed. Moreover, with the increase of the molar ratio, the HEB keeps increasing, and reaches its maximum until the molar ratio is reaching 1:3 and then decreases. It can be related to the frozen uncompensated spin at the interface between CoFe\(_2\)O\(_4\) and NiO.
NiO. When the samples were cooled to 5 K, the number of frozen uncompensated spin in anti-ferromagnetic NiO increased. The appropriate amount of NiO will increase the pinning effect on CoFe2O4, but the excessive amount of it will inhibit the pinning effect. The frozen uncompensated spins of NiO accelerate the magnetic domains of CoFe2O4 to inverse. Thus, NiO has a stronger pinning effect on CoFe2O4 at 1:3. In addition, the nanofibers with core–shell nanostructure have high shape anisotropy, which leads to a high $H_{EB}$. Through the above research, it is found that the nanofibers with core–shell nanostructure have a high $H_C$ and $H_{EB}$ in the mole ratio of 1:3 at 5 K. It is attributed to the pinning effect and the frozen uncompensated spins at the interface of CoFe2O4 and NiO. The nanofibers have a high shape anisotropy due to the core–shell nanostructure, which makes the nanofibers have high exchange bias effect.

4. Conclusion

The CoFe2O4@NiO nanofibers were successfully fabricated by electrospinning method. Due to the interaction of two phases, an effective heterogeneous coupling interface has been obtained. The magnetic domains of nanofibers are arranged along the axial direction. the hysteresis loops of the samples at 5 K and 300 K were measured respectively. Magnetic measurements revealed the exchange bias effect of these nanofibers with core–shell nanostructure. With the increase of NiO molar ratio in electrospinning, the exchange bias effect gradually enhances and reaches its maximum at 1:3. Materials with this effect have significant application value in spintronic devices, magnetic random memory, etc.

Acknowledgments

The authors are highly grateful for the support provided by the National Nature Science Foundation of China (No. 11664023) and State Key Laboratory of Advanced Processing and Recycling of Nonferrous Metals of China.

ORCID iDs

Jianfeng Dai https://orcid.org/0000-0002-8747-7586
Wei Feng https://orcid.org/0000-0003-1565-4149
Chen Cheng https://orcid.org/0000-0002-3996-1816

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