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Exchange bias effect in $CoCr_2O_4$/NiO system prepared by two-step method

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ABSTRACT

$CoCr_2O_4$/NiO has been successfully synthesized through two-step method. X-ray diffraction results present the coexistence of $CoCr_2O_4$ and NiO with pure formation. Micrographs measured with scanning electron microscope and transmission electron microscope display the homogeneous and dense morphology with two kinds of nanoparticles. Exchange bias effect is observed in the sample. The exchange bias field is about 872 Oe at 10 K. As measuring temperature increases, exchange bias effect is weakened with decreasing coercive field. In addition, exchange bias field and the shift of magnetization show the linear relationship with increasing cooling field. The exchange bias behavior can be attributed to the exchange coupling at the disordered interfaces in the sample.

1. Introduction

As one kind of coupling phenomena, exchange bias (EB) effect is defined as the shift of magnetic hysteresis loop with respect to the field and magnetization axes. It is usually induced by the exchange anisotropy at magnetic interfaces [1]. The importance of EB effect in applications, such as spintronic devices, magnetic recording media and overcoming the superparamagnetic limitation, has attracted considerable attention [2,3]. In addition, the lack of fundamental understanding also makes the study of EB effect as an interesting subject. To date, EB effect has been widely investigated both theoretically and experimentally in various heterostructure systems, which include core-shell structure, layered films, nanostructures and so on [4–6].

In addition, considering from the variety of research objects, more and more materials show the EB effect. However, transition metal oxides with spinel structure are rarely reported to present the EB effect. Bulk chromium oxide $CoCr_2O_4$ can exhibit the paramagnetic to ferrimagnetic transition at 93 K [7]. As a typical 3d transition metal oxide, NiO displays the nonmagnetic t_{2g} state above 525 K. Moreover, the e_g-orbital degrees of freedom can be coupled to lattice distortions at the interface through exchange coupling mechanisms [8]. So, we speculate that the appearance of EB effect may be possible in the coexisting structure of $CoCr_2O_4$ and NiO due to their interesting magnetic properties. Based on the statement, we try to synthesize $CoCr_2O_4$/NiO composite to study the EB effect. To avoid impurities, two-step method is used during the experimental process. In this study, evident EB effect is shown in $CoCr_2O_4$/NiO at 10 K. What is more, EB behavior is also related to the measuring temperature and the applied cooling field.

2. Experimental procedure

$CoCr_2O_4$/NiO was fabricated using two-step method. The staring material NiO was of analytical pure grade. $CoCr_2O_4$ was synthesized through sol-gel process. Firstly, $Co(NO_3)_2{\cdot}6H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$ and citric acid were dissolved in distilled water with stirring. pH~7 was adjusted by adding ammonia. The solution was thoroughly homogenized to form sol. Subsequently, the sol was heated to get gel and dried to form precursor powders. Then, the powders were ground and calcined at 400 °C for 5 h. Finally, the calcined powders were annealed at 750 °C for 3 h to obtain $CoCr_2O_4$. Eventually, $CoCr_2O_4$/NiO sample was formed through high energy ball milling for 72 h with the calculated component ratio of $CoCr_2O_4$: NiO=1: 9.

Crystal structures were investigated by x-ray diffraction (XRD, Philips X′pert pro). The morphology was characterized by scanning electron microscope (SEM, JSM-5610LV) and transmission electron microscope (TEM, JEM-2100F). Magnetic measurements were measured through physical property measurement system (PPMS, Quantum Design).

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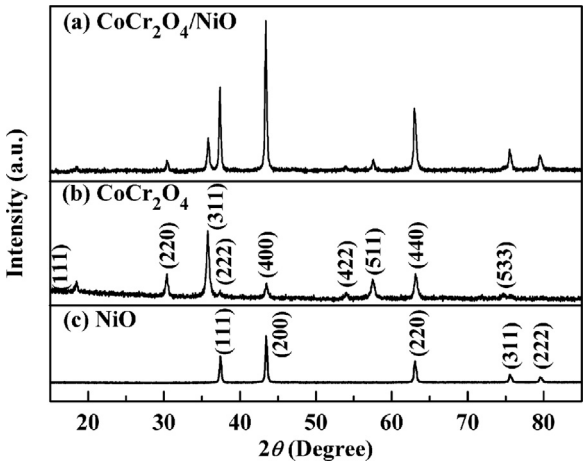

Fig. 1. XRD patterns of $CoCr_2O_4$/NiO (a), $CoCr_2O_4$ (b) and NiO (c).

3. Results and discussion

Fig. 1(a) shows the XRD result of $CoCr_2O_4$/NiO. To clearly prove the pure formation of the sample, XRD patterns of $CoCr_2O_4$ and NiO are also measured as shown in Fig. 1(b) and (c). As a result, NiO and $CoCr_2O_4$ are perfectly matched with the standard PDF cards numbered 01-089-5881 and 00-001-1122, respectively. What is more, the cubic crystal structure with space group Fd-3m is also identified. Compared with the two kinds of single diffraction patterns, both $CoCr_2O_4$ and NiO can be well indexed in Fig. 1(a). It is also revealed that $CoCr_2O_4$ and NiO can be coexistent in one system synthesized through the two-step method. Calculated by Scherrer formula, the average grain size of $CoCr_2O_4$ and NiO are 38 and 102 nm. SEM and TEM micrographs are respectively presented in Fig. 2(a) and (b) with the scale bars of 1 μm and 100 nm. Homogeneous and dense surface morphology of the sample with small particles can be observed in Fig. 2(a). Irregular grain shape with different sizes are displayed in TEM micrograph. Referring to the calculated data of XRD result, it can be clearly found that the larger grains are NiO and the smaller grains are $CoCr_2O_4$. The average size values of the two kinds of grains are consistent with the XRD results.

Magnetic hysteresis loops have been measured at different temperatures with applied cooling field (H_{FC}) of 30 kOe. As shown in Fig. 3(a–c), the measuring temperature are respectively 10, 50 and 90 K. Insets are the corresponding magnified regions at low field of the loops. As temperature increases, hysteresis loops are gradually slim with the decrease in $|H_{C1}|$ and H_{C2}, where $|H_{C1}|$ is the absolute value of H_{C1}. Here, H_{C1} and H_{C2} are the points of intersection of the loop with the field axis. Abstracted from the loops, detailed variation of H_{C1} and H_{C2} is shown in Fig. 3(d). The value of H_{C1} monotonously changes from −5889 Oe at 10 K to −310 Oe at 90 K and that of H_{C2} is decreasing from 4145 to 302 Oe. As a result, the decreased H_C from 5017 to 306 Oe is also obtained from 10 K to 90 K, which is shown in the inset of Fig. 3(d). Here, the value of H_C is quantified as $H_C=(-H_{C1}+H_{C2})/2$. Especially at 10 K, it is evident that hysteresis loop shifts towards negative field direction accompanied with a slight shift to positive magnetization. It is meaning that exchange coupling is existed in $CoCr_2O_4$/NiO. The measured loops are not thoroughly saturated, but they can be considered saturated effectively due to the ascending and descending branches of the closed loops coinciding for high field. That is, EB effect is really observed in $CoCr_2O_4$/NiO. At 10 K, the EB field (H_{EB}) is about 872 Oe, which is quantified as $H_{EB}=(-H_{C1}-H_{C2})/2$. What is more, the value of shift in magnetization (M_{shift}) is about 0.074 emu/g, which is defined as $M_{shift}=(M_{sat(+)}+M_{sat(-)})/2$. $M_{sat(+)}$ and $M_{sat(-)}$ are the magnetization at highest field in positive direction and that of negative direction. With increasing measuring temperature, H_{EB} and M_{shift} are also decreased accompanied with the decreasing H_C.

In details, the temperature dependence of H_{EB} and M_{shift} is plotted in Fig. 4(a). As temperature increases from 10 to 90 K, H_{EB} decreases monotonously from 872 to nearly zero. The similar decreasing tendency is also observed in M_{shift}. Moreover, in order to investigate the exchange coupling in $CoCr_2O_4$/NiO, cooling field influence on EB effect is also studied as shown in Fig. 4(b). With increasing cooling field, linear behavior is observed between H_{EB} and M_{shift}. That is,

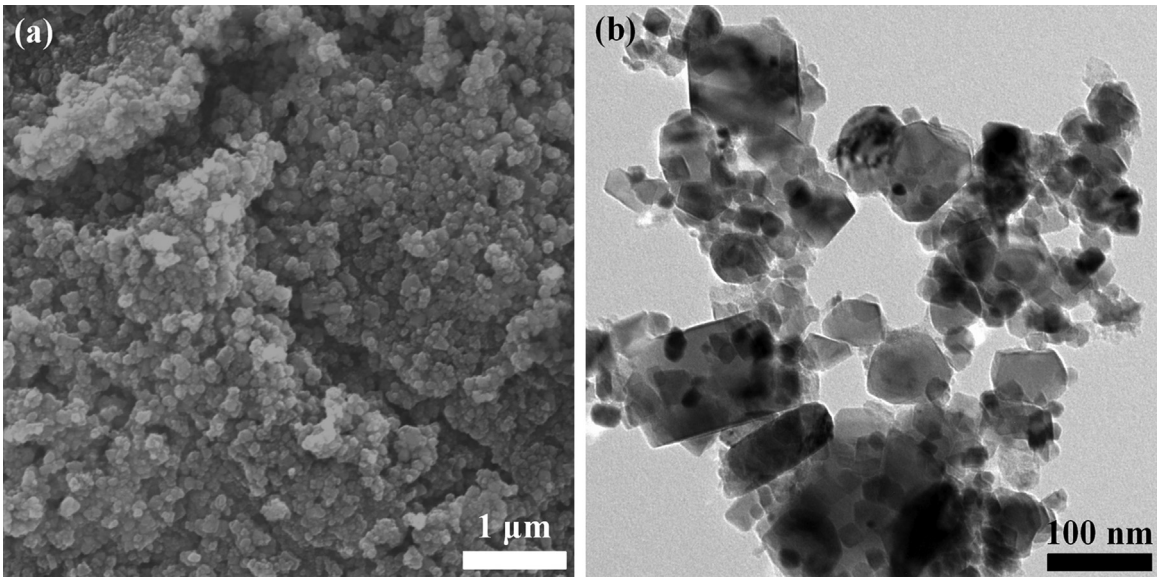

Fig. 2. SEM (a) and TEM (b) micrographs of $CoCr_2O_4$/NiO.

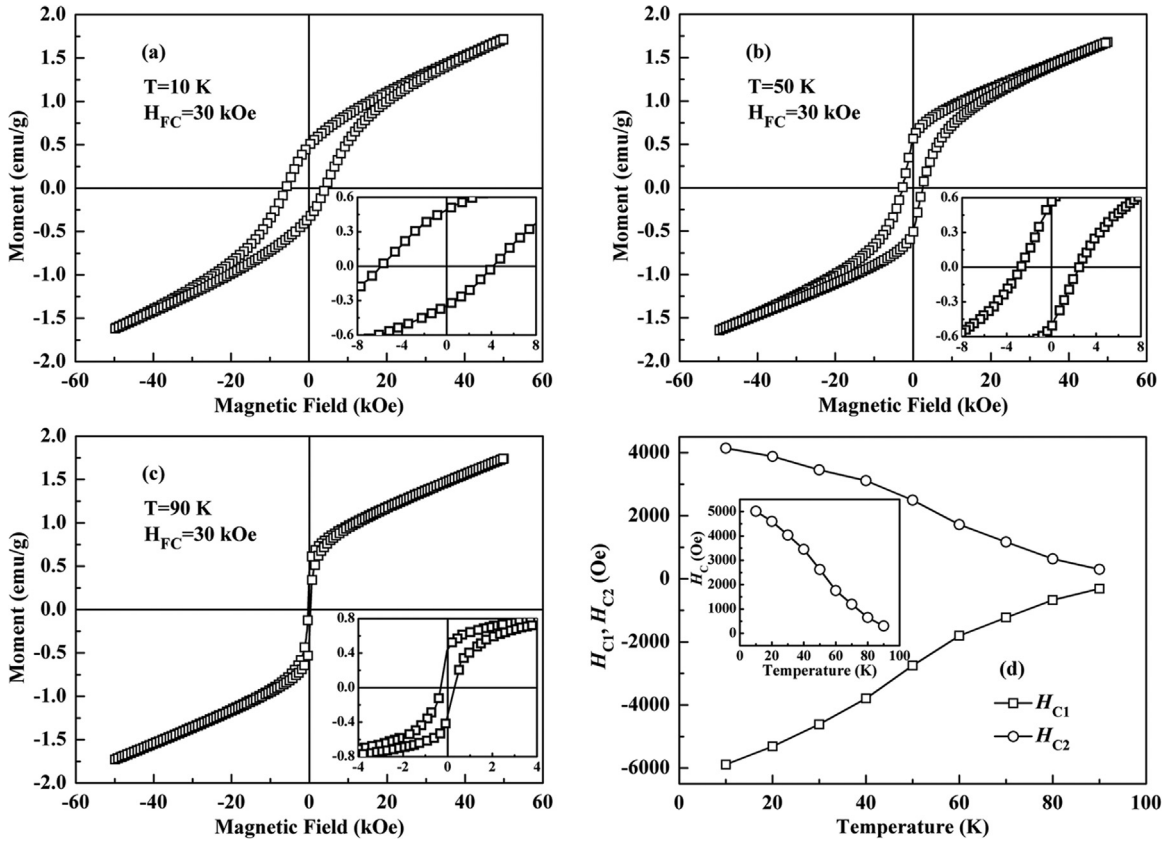

Fig. 3. Magnetic hysteresis loops measured at 10 (a), 50 (b) and 90 K (c) applied with 30 kOe field. Insets are the corresponding magnified regions at low field of the loops. (d) Variation of H_{C1} and H_{C2} with increasing measuring temperature. Inset is the variation of H_C with increasing measuring temperature.

similar change tendency of H_{EB} and M_{shift} is obtained, which is consistent with the variation during the increase in measuring temperature.

Based on above results, the mechanism of EB effect should be related to the disordered interface regions between $CoCr_2O_4$ and NiO. With the special synthesis method and thermal treatment, $CoCr_2O_4$ and NiO can be homogeneously dispersed in the sample as shown in the micrographs. As a result, the formation also provides the evident increase in interface regions. Different from the whole magnetic domains in sample grains, interface regions with the intermediate structural disorder layers can lead to strong anisotropy. Thus, antiferromagnetic uncompensated spins provided by NiO will be formed at the interfaces. During field cooling process below the transition temperature of $CoCr_2O_4$ and NiO, uncompensated spins with different coupling strength can be existed, which include the frozen and rotatable spins. Once the magnetic reversal begins, rotatable uncompensated spins can coupling with the adjacent ferrimagnetic moments in $CoCr_2O_4$ grains and follow the moment rotation. On the other hand, the frozen uncompensated spins can act as the pinning center and pin the adjacent ferrimagnetic moment, leading to the appearance of H_{EB}. Those frozen spins are pinned along field direction and cannot rotate with the field direction, giving rise to the M_{shift} in hysteresis loops, which is also a good evidence of the existence of uncompensated spins. With the increase in measuring temperature, monotonous drop of H_{EB} and M_{shift} is related to the decrease in exchange anisotropy at the interface regions. The consistent change tendency of H_{EB} and M_{shift} with temperature increasing and the linear relationship of them during the change of cooling field reveal that H_{EB} with M_{shift} is determined by the quantity of uncompensated pinned spins at the disordered interfaces.

4. Conclusions

$CoCr_2O_4$/NiO within nanoscale has been successfully synthesized with pure formation of the two coexisted phases. SEM and TEM micrographs present the homogeneous and dense morphology with two kinds of grain sizes. EB effect is observed accompanied by the left shift in field axis and positive shift in magnetization. It can be attributed to the coupling interaction at disordered interfaces between $CoCr_2O_4$ and NiO in the sample. In addition, H_{EB} and M_{shift} display the gradual decrease with increasing temperature due to the weakening in exchange coupling. The consistent change tendency between H_{EB} and M_{shift} also proves that the uncompensated spins are their same origin in EB effect.

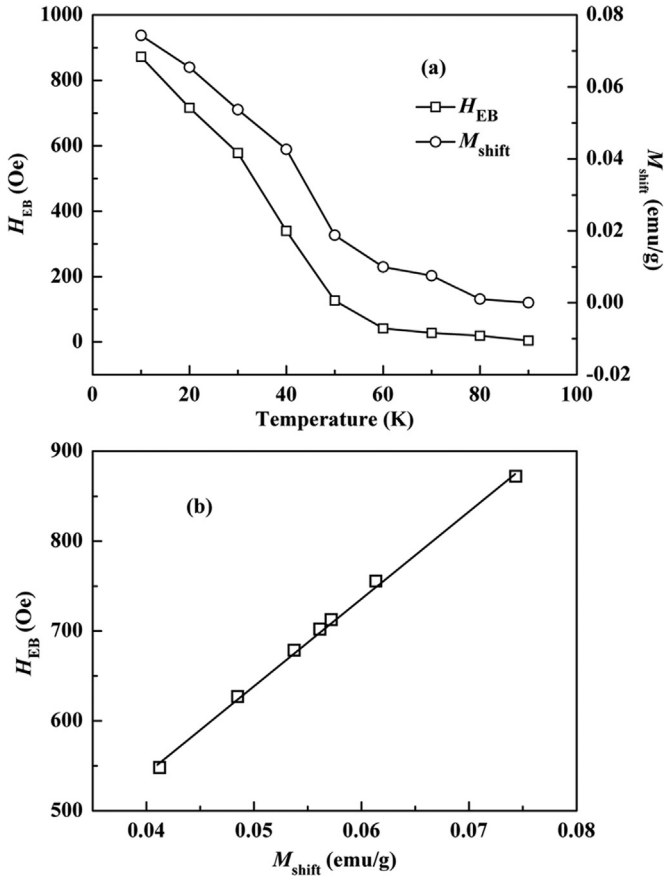

Fig. 4. (a) Variation of H_{EB} and M_{shift} with increasing measuring temperature. (b) The relationship between H_{EB} and M_{shift} measured with different applied cooling fields.

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