2011

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Recommended Citation

Zeng, Rong; Wang, J Q; Chen, Zhixin; Li, Wenxian; and Dou, S. X.: The effects of size and orientation on magnetic properties and exchange bias in Co₃O₄ mesoporous nanowires 2011, 07B520-1-07B520-3. <https://ro.uow.edu.au/engpapers/3137>

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Citation: *J. Appl. Phys.* **109**, 07B520 (2011); doi: 10.1063/1.3548831

View online: <http://dx.doi.org/10.1063/1.3548831>

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The effects of size and orientation on magnetic properties and exchange bias in Co_3O_4 mesoporous nanowires

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(Presented 15 November 2010; received 29 September 2010; accepted 27 October 2010; published online 28 March 2011)

Co_3O_4 mesoporous nanowires with average single crystalline grain sizes of about 8 nm, 12 nm, 25 nm, and 45 nm were synthesized by sintering of microwave-assisted hydrothermal processed belt- $\text{Co}(\text{OH})_2$ precursors at 300–500 °C for 2 h. Microstructure analysis was conducted by x-ray diffraction, x-ray photoelectron spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM), field emission SEM (FESEM), transmission electron microscopy (TEM), and high resolution TEM (HRTEM) to confirm the composition, structure, and orientation in the nanowires. Systematic magnetic measurements have also been conducted on the nanowires. It was found that the size and orientation have significant effects on the magnetic and exchange bias properties. The interesting finding was made that room temperature ferromagnetism appeared at 350 °C in the high orientation samples. Systematic comparison and analysis of the relationships among the grain size, microstructure, orientation (texture), surface electric structure (O vacancies), and defects with magnetic properties (ferromagnetism, coercive field, exchange bias, etc.) are presented in this work. © 2011 American Institute of Physics. [doi:10.1063/1.3548831]

I. INTRODUCTION

Cobalt oxide, especially as tricobalt tetraoxide (Co_3O_4) nanomaterial, which is among the most extensively studied oxides, is arousing increasing interest in multidisciplinary fields, such as energy storage, specifically Li-ion batteries;^{1–4} and environmental science, specifically catalysts.^{5,6} Doped Co_3O_4 is also of interest as a multiferroic material⁷ and as a parent compound for other layer-structured cobalt oxides, e.g. Na_xCoO_2 in the thermopower field⁸ and as a superconductor.⁹ Co_3O_4 is an example of an important *p*-type semiconductor with direct optical band gaps at 1.48 and 2.19 eV.¹⁰ In addition to its magnetic behavior, it is also a very important magnetic semiconductor^{8,11} and multiferroic material for multifunctional electronic devices and information storage applications.

Here, we report the preparation, microstructure, and magnetic properties of Co_3O_4 mesoporous nanowires. Systematic comparison and analysis of the relationships among the grain size, microstructure, orientation (texture), and surface defects with magnetic properties (ferromagnetism, coercive field, exchange bias, etc.) are presented in this work. It is found that, the size and the orientation have significant effects on the magnetic properties and exchange bias in the Co_3O_4 mesoporous nanowires, and it is interesting to find that room temperature ferromagnetism (RTFM) appears in this Co_3O_4 low temperature antiferromagnetic (AFM) material from modifying its orientation, as well.

II. EXPERIMENTAL DETAILS

All the reagents used in the experiment were analytically pure. Cobalt hydroxide nanowire precursor was prepared

by a precipitation and microwave hydrothermal process. The experimental details will appear elsewhere. The precursor powders were calcined at 300 °C to 500 °C in air for 2 h to form different mesoporous nanowires with different particle sizes.

The morphology and structure of the as-prepared samples were characterized by powder X-ray diffraction (XRD; GBC MMA, Cu $K\alpha$ radiation, 40 kV, 25 mA), field emission scanning electron microscopy (FESEM; JEOL JSM7500FA, 15 kV), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and selected area electron diffraction (SAED; JEOL 2011F, 200 kV).

The magnetic measurements for the samples were carried out using the vibrating sample magnetometer (VSM) option of a Quantum Design 14 T Physical Properties Measurement System (PPMS) in the temperature range of 5–305 K at applied fields up to 5 T.

III. RESULTS AND DISCUSSION

The mesoporous nanowire samples with average single crystalline grain size of about 8 nm, 12 nm, 25 nm, and 45 nm were prepared by calcining $\beta\text{-Co}(\text{OH})_2$ nanowire precursors at 300, 350, 420, and 500 °C, respectively, for 2 h. The particle size/grain size was determined by combining FESEM (images not shown here) and TEM and HRTEM, images from which are shown in Figs. 1(a)–1(d); about 30 grains of each sample were collected to determine the average grain size for different methods (FESEM, TEM, and HRTEM). The obtained Co_3O_4 samples are respectively defined as W300, W350, W420, and W500, based on the respective sintering temperatures. We examined the crystallographic nature of the porous Co_3O_4 nanowires using HRTEM observation.

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Fig. 1(a) shows part of a porous Co_3O_4 W300 nanowire. Except for a little coarseness in the particle size, there is not much difference in the HRTEM observations of W350, W420, and W500 nanowires. Fig. 1(b) contains an image of a section of a porous Co_3O_4 W350 nanowire. It is interesting to note that the nanowires consist of layers of nanosheets with a few 0.47 nm (111) atomic plane fringes (white lines) and large amounts of 0.284 nm (220) atomic plane fringes (yellow lines), which directly reflect the exposed outer surface planes. These constituent nanosheets are single crystals 3–8 nm thick. This was confirmed by axial rolling TEM observations of an individual nanowire (images not shown here).

Due to these crystallographic features of our nanostructures, it is difficult to make a precise quantitative determination of the average orientations of the nanosheets by HRTEM, the method employed by Xie et al.,⁵ but they can be determined qualitatively from the SAED patterns, as shown in the insets of Figs. 1(a)–1(d). Here, we introduce a combined facile method to precisely determine the average orientations of nanostructured powder samples, i.e., combining the results of powder XRD with calculation results on the fully random powder diffraction state through the retrieval refinement Fullprof software package; the formula is given in the caption of Fig. 2(a). We also determined textures by another method described in our earlier report on high-temperature superconducting materials,¹² the results showed good agreement with each other.

Fig. 2(a) The texture-determining peaks of porous nanowires prepared at different calcining temperatures. It shows that all the samples exhibit the (110) plane texture, but sample W350 has the highest percentage of texture and the smallest lattice parameter. This means the Co_3O_4 nanosheets mainly grow along the (110) direction and preferentially expose the (110) plane. The optimum temperature among the four is 350 °C in order to obtain the highest (110) plane texture based on the analysis formula using XRD data. Figure 2(b) shows the percentage of texture (as a percentage of surface area), which is estimated to be 64% of the total surface

FIG. 1. (Color online) TEM and HRTEM images of (a) and (c) the W300 sample, and (b) and (d) the W350 sample. The insets in (a) and (b) are the corresponding SAED patterns, and the insets in (d) show the region of the main image in context at lower magnifications.

FIG. 2. (Color online) (a) XRD patterns of 220, 311, 222, 422, 333, and 440 peaks, and Fullprof refinement calculation results, with textures calculated by the following formula: $T_{\text{Orient}} = [(I_{\text{Obs.220}} + I_{\text{Obs.440}}) / (I_{\text{Calc.440}} + I_{\text{Calc.440}})] / (I_{\text{Obs.220}} + I_{\text{Obs.440}})$ or $T_{\text{Orient}} = (I_{\text{Obs.220}} + I_{\text{Obs.440}}) / (I_{\text{Obs.220}} + I_{\text{Obs.311}} + I_{\text{Obs.222}} + I_{\text{Obs.422}} + I_{\text{Obs.333}} - (I_{\text{Obs.220}} + I_{\text{Obs.440}}) / (I_{\text{Obs.220}} + I_{\text{Obs.311}} + I_{\text{Obs.222}} + I_{\text{Obs.422}} + I_{\text{Obs.333}} + I_{\text{Obs.440}})) / (I_{\text{Obs.220}} + I_{\text{Obs.311}} + I_{\text{Obs.222}} + I_{\text{Obs.422}} + I_{\text{Obs.333}} + I_{\text{Obs.440}})$. (b) The calculation average results for the (110) plane textures and the lattice parameter versus calcining temperature for Co_3O_4 porous nanowires. (c) M versus T curves under zero-field cooling (ZFC) and after field cooling (FC) at a field of 1 kOe. (d) M versus H loops of Co_3O_4 nanostructures after 5 T field cooling to 5 K, with the inset showing M-H loops at 305 K for the W350 sample.

area from the texture data analysis; and the change in the lattice parameter as a function of calcining temperature.

The magnetic measurement results are shown in Figs. 2(c) and 2(d), in which the magnetization [with zero-field cooling (ZFC) and 1 kOe field cooling (FC)] versus temperature (M–T) curves are shown in Fig. 2(c), and the magnetization versus applied field (M–H) loops (under ZFC and FC) are shown in Fig. 2(d). Figure 3 presents the Néel temperature (T_N), the coercive field (H_C), the exchange bias (H_{EB}) under 1 kOe and 50 kOe FC, and the average grain size (for easy comparison) versus the calcining temperature. From these results, we can conclude: (1) T_N is consistent with previous reports^{13–15} of an increase with increasing calcining

FIG. 3. (Color online) Summary of various properties versus calcining temperature for the samples: (a) the Néel temperature (T_N), (b) the average grain size, (c) the exchange bias (H_{EB}), and (d) the coercive field (H_C) under 1 kOe and 50 kOe FC.

temperature, due to the increasing grain size. (2) The H_{EB} behavior of most of the samples is the same as in Refs. 16 and 17, consistent with an antiferromagnetic (AFM) Co_3O_4 core and a diluted AFM or spin-glasslike shell, except for W350. This sample's H_{EB} behavior presents unusual features, which may be because the magnetic state of the shell is different, e.g. the magnetic state of the shells of W350 nanowires change to ferromagnetic (FM) behavior from normal diluted AFM or spin-glasslike (SGlike) behavior. (3) Sample W350 presents obvious room temperature ferromagnetism, and the ferromagnetic transition is even obvious at high temperature [as shown in the inset of Fig. 2(d)]. This feature may also imply an exchange bias mechanism for nanostructures in which random or local weak FM areas reduce the coupling area of the AFM core with the diluted or spin-glass shell, and then reduce the magnitude of H_{EB} . It also indicates that the AFM/diluted AFM or SG core-shell structure generates stronger H_{EB} than the AFM/FM core-shell structures.

Co_3O_4 has a spinel structure¹⁸ containing Co^{3+} in an octahedral coordination (*O*) and Co^{2+} in a tetrahedral coordination (*T*). Oxygen anions form a distorted face-centered cubic sublattice, in which Co^{2+} cations occupy one-eighth of the tetrahedral interstices and Co^{3+} cations occupy half of the octahedral interstices. HRTEM observations and XRD orientation calculations indicate that the surface mainly presents (111) and (110) planes. Clearly, the (111) planes contain only Co^{2+} cations, while the (110) planes are composed mainly of Co^{3+} cations. In fact, surface differential diffraction studies have proven that the Co^{3+} cations are present solely on the (110) planes.^{19,20} Therefore, for our samples, especially W350, it is most likely that Co^{3+} cations on the exposed surface planes in the *O* position of Co_3O_4 nanostructures are reduced to Co^{2+} cations by surface oxygen deficiency. The subsequent x-ray photoelectron spectroscopy (XPS) results (not shown here) further confirmed this hypothesis, and in addition, several groups of researchers^{21,22} have found room temperature ferromagnetism in Co_3O_4 and identified the original microscopic mechanism as due to Co^{2+} ions replacing Co^{3+} in the *O* positions by different methods. The XPS indicates that (1) the W350 sample is high purity, which can rule out impurity and metallic Co magnetic particle effects; and (2) W350 presents a higher amount of Co^{2+} , which is caused by the Co^{3+} -oxygen vacancy complex, since the satellite peak of Co 2p_{3/2} in W350 is higher than for the other samples.

The surface is the most sensitive part of a material to any kind of treatment or interaction. Properties depending on the surface and its reactivity in the first stages can be completely different; the W300, W420, and W500 nanowires do not present room temperature ferromagnetism (RTFM), while W350 does. This RTFM phenomenon in W350 could arise from the greater amount of (110) planes exposed at the surface, which allows more Co^{3+} exposed at the surface to be reduced to Co^{2+} (since the surface easily loses oxygen, causing oxygen vacancy defects and other defects), and this breaks down the balance in the antiparallel magnetization in the Co^{2+} sublattice because the Co^{3+} is reduced to Co^{2+} at the surface, causing the surface RTFM. Our magnetic measurements support the surface RTFM phenomenon: the main contribution is the bulk AFM, while the weak FM is added

to it and its effects are superimposed [as shown in Fig. 2(d)]. The first principle calculations on the ferromagnetism after the appearance of *O* vacancies on different plane surfaces in Co_3O_4 spinel structures are ongoing.

IV. CONCLUSIONS

In summary, the size and, especially, the orientation have significant effects on the magnetic properties and exchange bias in spinel Co_3O_4 mesoporous nanowires. The effects of size follow normal nanomaterial rules, such as that T_N decreases with size reductions on the nanoscale or with increasing ratio of surface area to volume. The orientation of the nanograins seems to be dominant in terms of effects on the magnetic properties. It is found that improved (110) plane orientation is associated with more (110) planes exposed on the surface, which leads to surface room temperature ferromagnetism in the nanostructures. These results show the importance of refinement control of the surface of nanostructures in the preparation of transition metal oxides as multifunctional nanomaterials.

ACKNOWLEDGMENTS

The authors thank Dr. T. Silver for her help and useful discussions. This work is supported by the Australian Research Council through a Discovery project (project ID: DP0879070).

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