The effects of size and orientation on magnetic properties and exchange bias in Co3O4 mesoporous nanowires

Rong Zeng  
*University of Wollongong, rzeng@uow.edu.au*

J Q Wang  
*University of Jinan, China*

Zhixin Chen  
*University of Wollongong, zchen@uow.edu.au*

Wenxian Li  
*University of Wollongong, wenxian@uow.edu.au*

S. X. Dou  
*University of Wollongong, shi@uow.edu.au*

Follow this and additional works at: [https://ro.uow.edu.au/engpapers](https://ro.uow.edu.au/engpapers)  
Part of the Engineering Commons  

**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.  
The effects of size and orientation on magnetic properties and exchange bias in Co3O4 mesoporous nanowires

Citation: J. Appl. Phys. 109, 07B520 (2011); doi: 10.1063/1.3548831
View online: http://dx.doi.org/10.1063/1.3548831
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v109/i7
Published by the American Institute of Physics.

Related Articles
Microwave and mechanical properties of quartz/graphene-based polymer nanocomposites
Appl. Phys. Lett. 102, 072903 (2013)
Influence of the supersaturation on Si diffusion and growth of Si nanoparticles in silicon-rich silica
J. Appl. Phys. 113, 063519 (2013)
Comb-drive micro-electro-mechanical systems oscillators for low temperature experiments
Influence of the embedding matrix on optical properties of Ge nanocrystals-based nanocomposite
Fabrication of Bi2Te3 nanowire arrays and thermal conductivity measurement by 3ω-scanning thermal microscopy

Additional Information on J. Appl. Phys.
Journal Homepage: http://jap.aip.org/
Journal Information: http://jap.aip.org/about/about_the_journal
Top downloads: http://jap.aip.org/features/most_downloaded
Information for Authors: http://jap.aip.org/authors

ADVERTISEMENT
The effects of size and orientation on magnetic properties and exchange bias in Co$_3$O$_4$ mesoporous nanowires

R. Zeng,1,a) J. Q. Wang,1,2 Z. X. Chen,1 W. X. Li,1 and S. X. Dou1
1Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia
2School of Materials Science and Engineering, University of Jinan, Jinan 250022, China

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

Co$_3$O$_4$ 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-Co(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$_3$O$_4$) 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 super capacitors,5 metallic oxide, is arousing increasing interest in multidisciplinary nanomaterial, which is among the most extensively studied Co$_3$O$_4$ is also of interest as a multiferroic material7 and as a superconductor.9 The parent compound for other layer-structured cobalt oxides, e.g., NaxCoO$_2$ in the thermopower field8 and as a superconductor.9

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 β-Co(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$_3$O$_4$ 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$_3$O$_4$ nanowires using HRTEM observation.
Fig. 1(a) shows part of a porous Co$_3$O$_4$ 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$_3$O$_4$ 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., 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, 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$_3$O$_4$ 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 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 ($H_{ex}$) 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 of an increase with increasing calcining temperature.
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 structure 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 $Co^{3+}$ 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. 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 have found room temperature ferromagnetism in $Co_3O_4$ and identified the original microscopic mechanism as due to $Co^{3+}$ 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 $Co^{3+} – O_2$ vacancy complex, since the satellite peak of 2p3/2 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).