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journal homepage: www.elsevier.com/locate/jmmmCharge ordering and exchange bias behaviors in Co_3O_4 porous nanoplatelets and nanoringsJ.C. Debnath^{a,*}, Jianli Wang^b, R. Zeng^{b,c}^a Institute for Frontier Materials, Deakin University, Geelong, VIC 3216, Australia^b Institute for Superconductivity and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia^c School of Materials Science and Engineering, Faculty of Science, UNSW, Sydney NSW 2052, Australia

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ABSTRACT

We present the synthesis of $\alpha\text{-Co}_3\text{O}_4$ porous nanoplatelets and hexagonal nanorings using microwave-assisted hydrothermal and conventional chemical reaction methods. The x-ray diffraction (XRD) and refinement analyses indicate the $\alpha\text{-Co}_3\text{O}_4$ crystal structure, and the x-ray photoelectron spectrum (XPS) indicates the high purity of the samples. The M–T (including $1/\chi\text{-T}$) curves indicate an antiferromagnetic transition at about 35 K in both kind of samples but the interesting finding was made that a charge-ordered (CO) state appears at 250 K for the nanoplatelets sample whereas it is inattentive for the nanorings. The antiferromagnetic transition temperature T_N is lower than that of the bulk $\alpha\text{-Co}_3\text{O}_4$ single crystal due to the nanosized structures. We observed quite significant exchange bias for nanorings. The exchange bias behavior of the $\alpha\text{-Co}_3\text{O}_4$ hexagonal nanorings is consistent with an antiferromagnetic (AFM) Co_3O_4 core and spin-glass like shell.

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1. Introduction

The key to the successful design of magnetic structures for application is the ability to manipulate and control magnetic properties. The basic energies involved are exchange and anisotropy, where the former controls magnetic ordering and the later controls the preferred orientation. Both are phenomenological descriptions of fundamental correlations and energies associated with the electronic and crystalline structure of a material. A powerful technique for modifying and controlling magnetic characteristics is based on the use of magnetic heterostructures with properties governed by the interface region. One of the most interesting interfaces for basic study and application is the interface between a ferromagnet and an antiferromagnet. The exchange coupling at the interface between a ferromagnetic layer and an antiferromagnetic layer often results in an interesting phenomenon called “exchange bias” [1].

When a system consisting of ferromagnetic (FM)-antiferromagnetic (AFM) [1], FM spin glass (SG) [2], AFM-ferrimagnetic (FI) [3], FM-FI [4], AFM-SG [5] and FI-FI [6] interface is cooled with field through the Néel temperature (T_N) of the AFM or glass temperature (TSG) of the SG, exchange bias (H_{EB}) is induced

showing a shift of hysteresis loop $[M(H)]$ along the magnetic field axis. Since its discovery by Meiklejohn and Bean in 1956 [1], H_{EB} has been extensively studied during the past fifty years, partly because of its applications in ultrahigh-density magnetic recording, giant magnetoresistance and spin valve devices [7,8]. The H_{EB} effect is attributed to an FM unidirectional anisotropy formed at the interface between different magnetic phases [7]. Generally, the process of field cooling (FC) from higher temperature is used to obtain FM unidirectional anisotropy in different H_{EB} systems [1–4]. The FM unidirectional anisotropy can also be realized by depositing the AFM layer onto a saturated FM layer [7], by ion irradiation in an external magnetic field [9], or by zero-field cooling (ZFC) with remnant magnetization [10,11]. Application of sufficient large fields may also induce exchange bias [12,13]. In summary, the FM unidirectional anisotropy in these H_{EB} systems is formed by reconfiguring the FM spins at the interface between different magnetic phases. This phenomenon is fascinating not only for technological applications in memories and spin electronics but also for exceeding the super paramagnetic limit in ultrahigh density media [14,15].

The first evidence of exchange bias was reported in the charge ordered (CO) manganite $\text{Pr}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$ among mixed valent perovskites, where ferromagnetic (FM) droplets are spontaneously embedded in the antiferromagnetic (AFM) background [16]. The exchange bias effect has recently been reported in another CO manganite, where the strong cooling field dependence of the exchange bias effect is ascribed to the spontaneous lamellar FM/AFM

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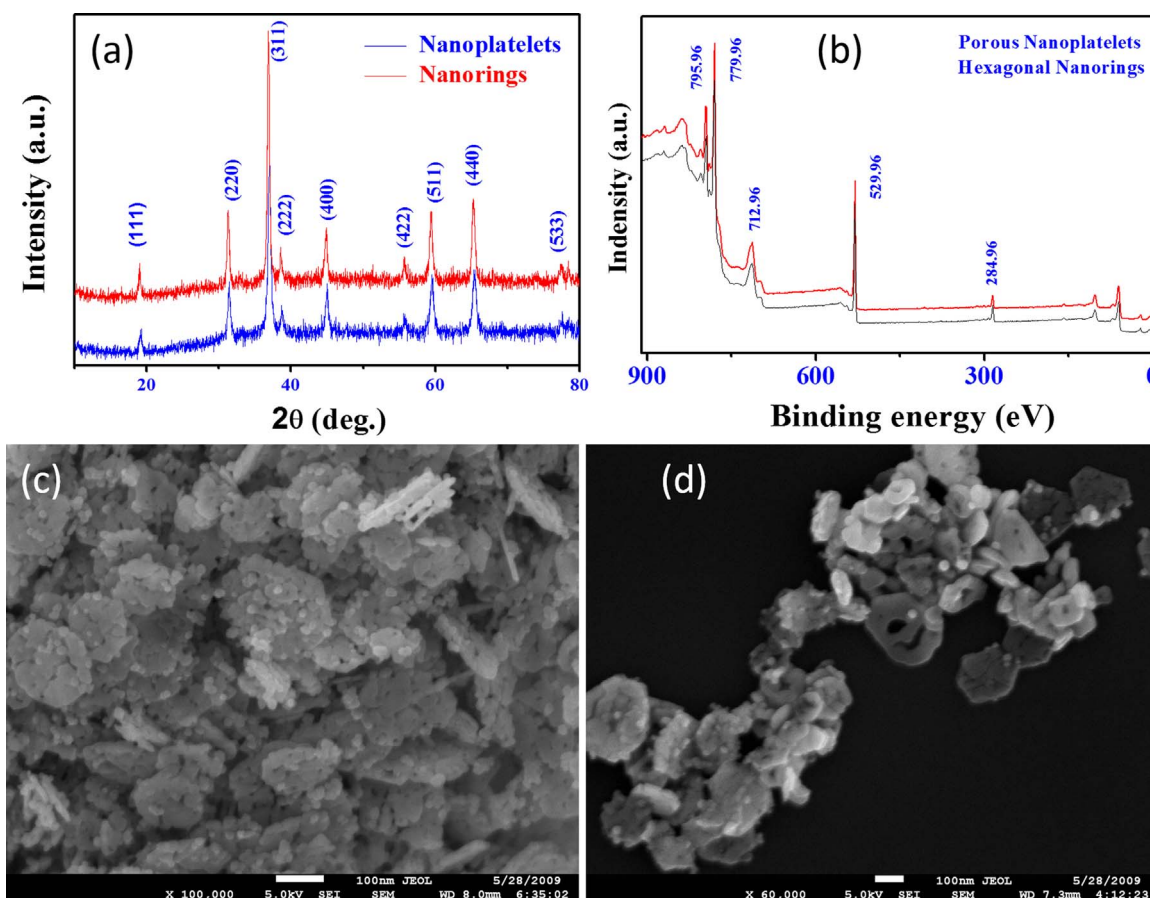


Fig. 1. XRD (a), XPS (b) spectrums and FESEM, images of α - Co_3O_4 porous nanoplattlets (c) nanorings (d).

phase separation in $\text{Y}_{0.2}\text{Ca}_{0.8}\text{MnO}_3$ [17]. The exchange bias effect is also reported for cluster-glass (CG) compounds $\text{La}(\text{Ba}, \text{Sr})\text{CoO}_3$, which is attributed to the cluster-glass state consisting of FM and spin-glass (SG) phases [18–20]. Recently the exchange bias phenomenon has been detected in another CG compound, where the H_{EB} effect is observed in the case of 30% Fe substitution in LaMnO_3 [21,22].

Cobalt (II, III) oxide (Co_3O_4) is described by a formula unit AB_2O_4 ($A \rightarrow \text{Co}^{2+}$, $B \rightarrow \text{Co}^{3+}$) and exhibits a normal spinel crystal structure ($Fd\bar{3}m$) with occupation of tetrahedral A sites by Co^{2+} and octahedral B sites by Co^{3+} . The magnetic moment arises largely due to Co^{2+} ions because of spins, with a small contribution from spin–orbit coupling [23]. Conversely, Co^{3+} ions have no permanent magnetic moment as a consequence of the splitting of 3d levels by the octahedral crystal field and complete filling of t_{2g} levels. Two paths for the super exchange interaction between Co^{2+} ions have been suggested: A–O–A with $z_1=4$ neighbors and A–O–B–O–A with $z_2=12$ neighbors (O stands for the oxygen O^{2-} ion) but without specifying their relative strengths [23]. Cobalt (II, III) oxide (Co_3O_4) has many functional applications, which include magnetic materials, solar energy absorbers, electrochromic devices, solid-state sensors, and heterogeneous catalysts [24–28]. In particular, Co_3O_4 nanoplatelets, nanorings, nanowires and nanorods have attracted wide interest.

A number of exchange bias studies have been reported recently for Co_3O_4 : (a) Zeng et al. [29] reported the effects of size and orientation on magnetic properties and exchange bias in Co_3O_4 mesoporous nanowires; (b) Salabas et al. [30] studied exchange bias anisotropy in nanocasted Co_3O_4 nanowires; and (c) Benitez et al. [31] stated the evidence for core–shell magnetic behavior in anti-ferromagnetic Co_3O_4 nanowires. Mesoporous Co_3O_4

nanostructures have been extensively studied for exchange bias [32–35]. The exchange bias has also been observed in pure Co_3O_4 nanoparticles [36,37]. As per our knowledge no study has been done on Co_3O_4 nanoplatelets and nanorings.

In this letter we report the charge ordering and exchange bias behaviors in Co_3O_4 porous nanoplatelets and nanorings where the antiferromagnetic transition temperature T_N is lower than that of the bulk α - Co_3O_4 single crystal. The magnetic measurements include exchange bias (H_{EB}), training effects, and the thermo-remnant magnetization (TRM) have been performed. It was found that, the core–shell structure with the shells exhibiting spin-glass-like behaviors, and charge-ordering significantly influence the exchange bias behaviors.

2. Experimental procedures

All chemicals were analytical grade reagents purchased from Sigma-Aldrich. The α - Co_3O_4 porous nanoplatelets and hexagonal nanorings were synthesised by using microwave-assisted hydrothermal and conventional chemical reaction methods [38]. The phase identity of the prepared products were characterized by X-ray diffraction measurements were conducted at room temperature using a mini materials analyzer x-ray diffractometer made by GBC Scientific Equipment, Inc. The morphology of the as-prepared samples were characterized by field emission scanning electron microscopy (FESEM; JEOL JSM7500FA, 15 kV), high-resolution TEM (HRTEM), and selected area electron diffraction (SAED; JEOL 2011F, 200 kV). Magnetic properties of Co_3O_4 nanoplatelets and nanorings were measured by using the vibrating sample magnetometer (VSM) option of a Quantum Design 14 T

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