Physica E 41 (2009) 806–811

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

Synthesis and characterization of single-crystalline α-Fe_2O_3 nanoleaves

Y.Y. Xu [a], D. Zhao [a], X.J. Zhang [a], W.T. Jin [a], P. Kashkarov [b], H. Zhang [a,*]

[a] *Materials Physics Laboratory, State Key Laboratory for Mesoscope Physics, Department of Physics, Peking University, Beijing 100871, China*
[b] *Faculty of Physics, M.V. Lomonosov Moscow State University, Moscow 119899, Russian Federation*

ARTICLE INFO

Article history:
Received 2 December 2008
Accepted 19 December 2008
Available online 6 January 2009

PACS:
61.46.HK
73.63.Nm
61.72.Bb

Keywords:
α-Fe_2O_3
Nanoleaf
Surface
Spectra
Magnetic property

ABSTRACT

By carefully controlling the reacting conditions, including atmosphere, temperature, and time, α-Fe_2O_3 nanoleaves have been synthesized by oxygenating pure iron. X-ray diffraction and transmission electronic microscope analyses demonstrate that the nanoleaves are single crystalline. The X-ray photoelectron spectrum, Raman spectrum, optical absorption spectrum, and photoluminescence spectrum are also carried out to characterize the nanoleaves. Magnetic measurement shows that the blocking temperature of the nanoleaves is about 120 K and the coercivity decreases as temperature increases. The more interesting is that a small exchange bias is found in 2 T field cooling hysteresis loops. This small exchange bias may possibly originate from a different magnetic order on the surface of the nanoleaves or the coexistence of a tiny amount of Fe_3O_4.

1. Introduction

α-Fe_2O_3 is the most stable iron oxide under ambient conditions, which is of significant scientific and technological importance due to its excellent properties, such as a small band gap (2.2 eV), high resistivity to corrosion and low cost. It can, for example, be used as a photoelectrode for solar energy conversion [1], gas-sensors [2], or heterogeneous catalysts [3]. As an antiferromagnetic material, corundum structure α-Fe_2O_3 has the Néel temperature at 950 K and the Morin transition temperature at 263 K [4]. When the dimension decreases to nanoscale, α-Fe_2O_3 has some unusual behavior and attracted more and more attention. Recently, the nanowire of iron oxide has been prepared by direct oxidation of iron [5,6], and the properties of it have been studied in some aspects [7]. Oxidation behaviors of iron have been investigated extensively for over decades. It has been reported that micron-size whiskers or blades of α-Fe_2O_3 are observed to grow out of the oxidized surface of iron at temperatures of oxidation from 400 to 700 °C [8–10]. Following our previous works [5,6], here we report a new nanostructure of α-Fe_2O_3, nanoleaf, and some basic properties of this new kind of nano-α-Fe_2O_3 have been studied. A small exchange bias was first observed in this structure.

2. Experimental

Following our previous work [5,6], the α-Fe_2O_3 nanoleaves were prepared by oxygenating pure iron. After being polished and washed with alcohol in an ultrasonic cleaner, the pure iron substrate was placed into a quartz tube, which was mounted in a horizontal tube furnace. The sample was heated in a flowing gas (19.4% CO_2, 80.43% N_2, and 0.164% SO_2) with a flow rate of 20 mL/min. The relative humidity in the tube, which was controlled by mixing above gas with H_2O vapor and a sensor, was kept at about 95%. The temperature was increased at the rate of 40 °C/min and kept at 500–510 °C for 10 h. Under these conditions we acquired the α-Fe_2O_3 nanoleaves with length of 1–3 μm, thickness of about 50 nm, and width of about 1 μm. Different temperatures were also attempted in order to study the growth mechanism. It was found that the best temperature for growing α-Fe_2O_3 nanoleaves (500–510 °C) was less than that of growing α-Fe_2O_3 nanowires (550–600 °C).

The samples were characterized by X-ray diffraction (XRD) (Philips X'Pert MRD with Cu K_α radiation), field emission scanning electron microscopy (SEM) (FEI Strata DB235 FIB), transmission electron microscopy (FEI Tecnai F30 TEM), and X-ray photoelectron spectroscopy (XPS) (Kratos Analytical Axis Ultra with Mono Al K_α radiation, excitation energy 1486.6 eV). The Raman spectrum (Renishaw-inVia) was collected at room temperature with the excitation of the 514.5 nm wavelength of an Ar+laser. The optical absorption spectrum (240–840 nm) was conducted using

---

* Corresponding author. Fax: +86 10 62751615.
E-mail address: hanzhang@pku.edu.cn (H. Zhang).

1386-9477/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.physe.2008.12.015

an UV–vis–NIR spectrophotometer (UV 3100). The photoluminescence (PL) spectrum (Jobin-Yvon-Spex) was measured at room temperature using a Xe arc lamp (excitation wavelength 325 nm) as the excitation source. The magnetic measurement was conducted using a quantum design magnetic property measurement system (MPMS-XL7). To prepare the sample for magnetic measurement, the nanoleaves from several pieces of sample were taken off in an ultrasonic cleaner using alcohol as solvent and then collected them into a capsule. We may convincingly assert on the reproducibility of our results on the nanoleaves clinched from different substrates and have, in fact, achieved mutually comparable signals from different groups of the nanoleaves prepared in this way.

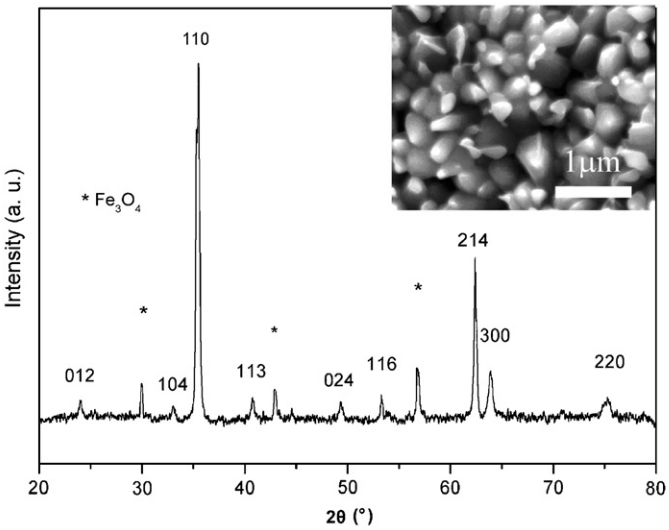

Fig. 1. X-ray diffraction pattern of the nanoleaves. The inset is SEM image of the layer under the nanoleaves, where Fe_3O_4 is located.

3. Results and discussion

A typical XRD pattern of the nanoleaves is shown in Fig. 1. All the significant peaks can be indexed to α-Fe_2O_3 (JCPDS No. 86-0550) except a small amount of Fe_3O_4. The nanoleaves were carefully stuck off substrates by non-magnetic adhesive tape, and then the surface on the substrate was used for SEM analysis. The inset of Fig. 1 is a SEM image of the layer under the nanoleaves, where the Fe_3O_4 pattern is from. It is found that before growing out the nanoleaves, the substrate is firstly oxygenated into Fe_3O_4. Then the nanoleaves grow out from it. Because the penetration depth of our X-ray is about 3 μm, but the length of the nanoleaves is about 2 μm, some Fe_3O_4 under the nanoleaves is reflected (see Fig. 1). The latter experiments of TEM and Raman spectra also support that the nanoleaves are pure α-Fe_2O_3.

The SEM images in Fig. 2 show that there exist two kinds of the nanoleaves. One kind of the nanoleaves is sword-like and

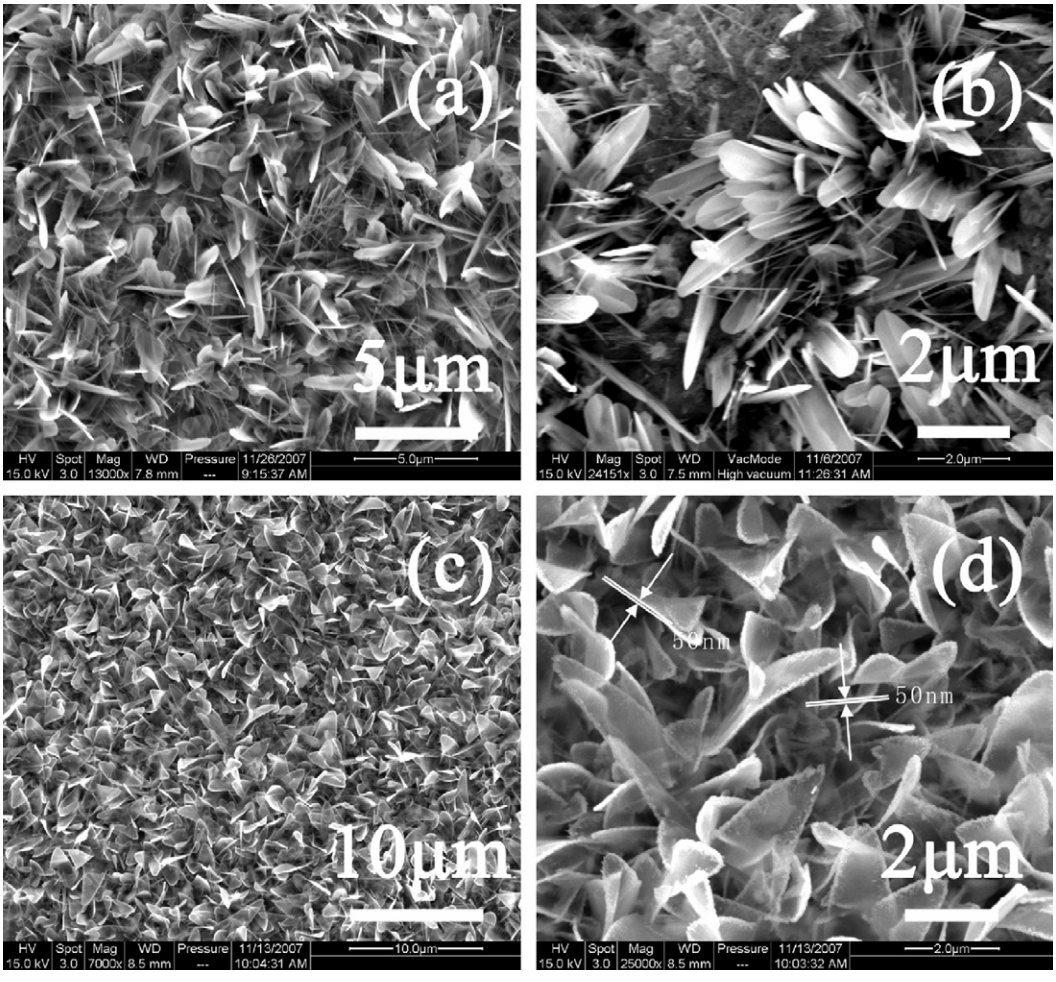

Fig. 2. SEM images of two typical kinds of nanoleaves: (a) and (b) the sword-like nanoleaves; (c) and (d) the board nanoleaves.