Synthesis and Characterization of Iron Oxyhydroxide Nanowires

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A very simple method of synthesis of goethite, $\alpha - FeOOH$, nanowire is reported. To fabricate the nanowires, an anodized alumina nanoporous template (AAO) is used. AAO has pores with an average diameter of 60 nm. The synthesis is based on a self-combustion reaction of the chemical precursor ($Fe(NO_3)_3$ saturated solution) which occurs inside the nanopores. The geometry of AAO determines the morphology of the nanowires and the confinement conditions in which the heat treatment determines the composition of the nanostructure. The nanowires are characterized using scanning electron microscopy, high resolution transmission electron microscopy and magnetometry [magnetization versus applied field (M versus H)]. TEM analysis indicates that nanowires are composed of several $\alpha - FeOOH$ single crystals. The nanowires have a clear magnetic oriented structure.

***Index Terms*—Iron oxide, iron oxyhydroxide, nanowires, structural and magnetic properties.**

I. Introduction

NANOWIRES are nanostructured materials in which length is the dominant dimension. They are interesting not only because of their unique properties [1]–[3] but also for their prospective use in technological applications (field effect transistors, sensors, nanolasers, solar cells, magnetic information storage and spintronics) [4]–[9]. The success of these applications is directly related to the synthesis method. The main techniques for nanowire fabrication are lithography [10] and electrodeposition [11], while the chemical methods have been less used.

Investigations about iron oxyhydroxide nanowire fabrication is a topic of scientific interest. Several studies concerning beta and gamma phase oxyhydroxide nanowires ($\beta - FeOOH$ and $\gamma - FeOOH$) have been done [12]. Amorphous and crystalline (orthorhombic phase) goethite ($\alpha - FeOOH$) nanowires, with diameters between 10 and 80 nm, and 0.6 to 1.2 μm of length, have been obtained by laser ablation and hydrothermal techniques [13]–[15]. However, some parameters, like periodic arrays of nanowires, cannot be controlled and the possible techniques to order them require several steps.

Synthesis methods of goethite nanowires have received much interest as an intermediary for obtaining hematite nanowires, however, growing procedures are often complicated and/or expensive [13], [16], [17]. A simple method for obtaining nanowires right from synthesis process is lacking. The aim of this paper is to report a very simple method for obtaining by chemical synthesis $\alpha - FeOOH$ nanowires and their structural, morphological and magnetic properties. This work provides evidence that the composition of the nanowires consists of several $\alpha - FeOOH$ single crystals.

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II. Materials and Methods

Nanoporous anodic aluminum oxide templates (AAO) with an average pore diameter of about 60 nm, prepared by two-step anodization technique [18], was used to grow nanowires (NWs). For this, the chemical precursor of the nanostructure should fill the AAO pores. This process consists of two steps: the preparation of the precursor and the filling of the nanopores.

The chemical precursor preparation was 6 g of $Fe(NO_3)_3 \cdot 9H_2O$ dissolved in 2 ml of distilled water to form a nearly saturated solution (equivalent to 75% in weight).

The filling of the AAO's nanopores was done under vacuum. The nanoporous template was put into a test tube inside of a kitasato flask and a vacuum pump was connected to it. For ten minutes vacuuming was done (around 10^{-2} Torr). Keeping the vacuum, the nitrate ferric solution was added inside the test tube, and the AAO was submerged for ten minutes. When the air inside the nanopores was removed, the pores were filled by the saturated solution.

The AAO template filled with the nitrate ferric solution was taken out of the test tube and a heat treatment in two steps was done: 1) 80 °C for 24 hours to achieve a slow and complete dehydration 2) 300 °C for 3 hours to decompose the precursor and to form NWs within the AAO's nanopores.

The sample (filled AAO template) was divided into two parts. One of them was treated with 1 M NaOH solution to dissolve the AAO and release the nanowires. NWs were collected by transmission electron microscopy (TEM) grid and characterized by high resolution transmission electron microscopy (HR-TEM) with a resolution of 1.7 Å. The other part of the sample was analyzed by commercial scanning electron microscopy (SEM). The magnetic characterization was done using a SQUID magnetometer. The magnetization versus applied magnetic field was done at 5 K and 300 K, up to 3 Tesla.

III. Results and Discussion

Fig. 1 shows the SEM images of AAO template with NWs inside the pores. The AAO template has an average pore diameter of about 60 nm. Nanopores are nearly uniform and hexagonally arranged. The AAO template was broken to show the NWs

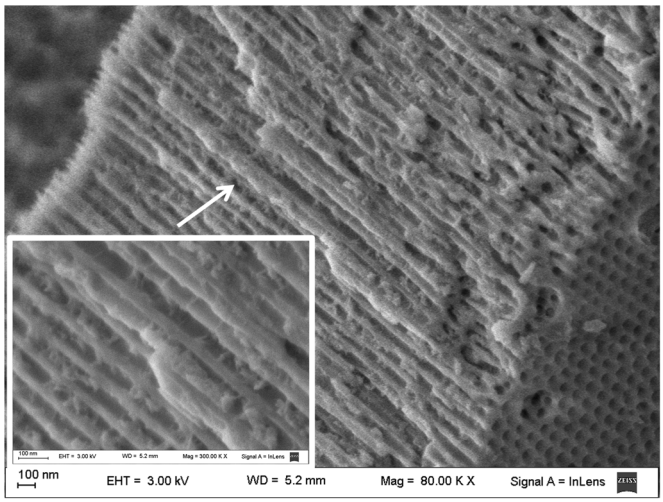

Fig. 1. SEM image of AAO template with nanowires inside of pores of 55 nm diameter average. Inset: Some details are shown.

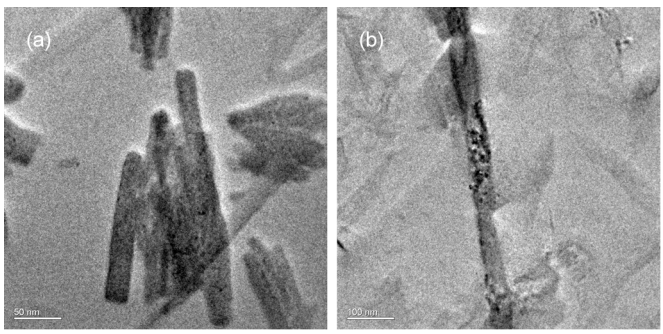

Fig. 2. TEM images of (a) nanowires. (b) Nanowires are formed by nanoparticle arrays.

morphology. The diameter of the NWs is about 55 nm, which closely fits the nanopore size of the AAO template, and, inside AAO, the length is between 1.5 and 2 μm. Thus, the length/diameter ratio of the nanowire is over 40. Details are shown in the Fig. 1 inset. It is noted that the nanostructure is not compacted, it consist of agglomerates.

Fig. 2(a) shows the TEM image of NWs after the AAO template has been dissolved. The TEM image of a single nanowire is shown in Fig. 2(b). It can be seen that NWs consist of several nanoparticles (NP) in a compact array. The NP size distribution is wide between 5 and 10 nm. Outside the AAO template the diameter of NWs remains about 55 nm, but, in some cases, the length decrease from 2 μm to around 200 nm. This could be due to the preparation method for TEM analysis. After dissolution of AAO, the nanowires remain in NaOH solution and they must be put in the TEM grid with a syringe, which could produce the break of NWs.

From several HR-TEM images, an analysis by the fast Fourier transform (FFT) technique was done (over 50 TEM images were analyzed). A common feature is observed in most of the FFT graphs corresponding to the nanoparticles that form the nanowires. Fig. 3 shows an HR-TEM image and the FFT graphs of goethite nanoparticle arrays in the border of NW.

The TEM characterization confirms that NWs are formed by $\alpha-$FeOOH single crystal. In this way, the measured interplanar

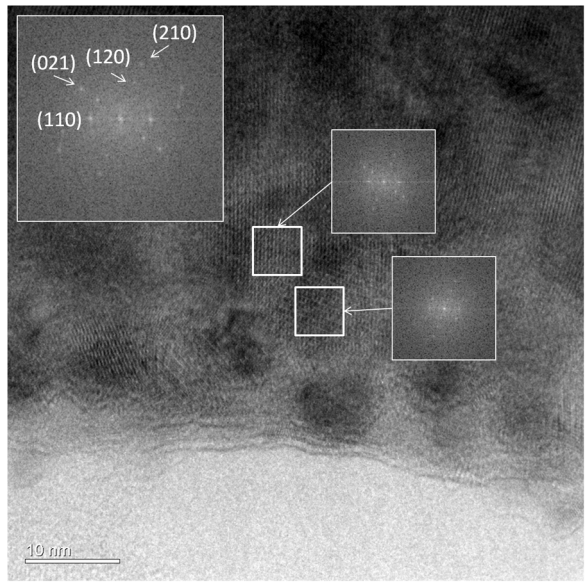

Fig. 3. TEM image and fast Fourier transform (FFT) of goethite nanoparticle arrays in the border of nanowire. Inset: Interplanar distances of some observed reflection (indexed FFT) corresponding to $\alpha-$FeOOH [16], [19].

distance, $\mathrm{d} = 2.2$ Å [plane (210)], $\mathrm{d} = 3.3$ Å [plane (120)], $\mathrm{d} = 4.1$Å [plane (110)], and $\mathrm{d} = 2.5$ Å [plane (021)] are in good agreement with goethite crystals [19]. These observations are consistent with those reported by Meng Fei *et al.* for goethite nanowires obtained by other methods [16]. However, some of the measured angles associated between those planes have different values if compared with those calculated from the theoretical relationships [20]. Such an effect is associated with disorder due to surface/volume ratio. In this context, the atoms located on the surface are not in the regular configuration as in a bulk crystal. For example, in NPs of 5 nm the number of unit cells on the surface represents approximately 70% of total volume.

We may assume that the conditions of synthesis, with a heat treatment in air, give rise to the formation of an iron oxide phase instead of an iron oxyhydroxide. However, the self-combustion of the precursor (iron nitrate saturated solution) occurs in confinement conditions (inside the AAO pore substrate, with previous vacuum), where the oxygen-deficient atmosphere is rich in $Fe(NO_3)_3$ decomposition gases. Therefore, there is not enough oxygen to displace the hydroxide group in the iron coordination sphere to form the iron oxide. The goethite crystal could be described as a three-dimensional structure built up with $FeO_3(OH)_3$ octahedral which form large tunnels, spreading out along the direction [010] and where hydrogen atoms are located [21]. In order to obtain ferric oxide, the three hydroxide groups in the octahedral sites must be replaced by oxygen atoms. On the other hand, the oxyhydroxide phases are the major direct hydrolysis products [22]–[26]. The stability of the polymorphs of ferric oxides/oxyhydroxides depends on their energy surface, sizes, and environment. At nanoscale in a hydrated environment, $\alpha-$FeOOH is the most stable phase due to its lower surface energy [27].

Magnetic measurements of NWs arrays inside the AAO template were done. In Fig. 4, we see the magnetization versus applied magnetic field (M versus H) measurements made at 5 K.

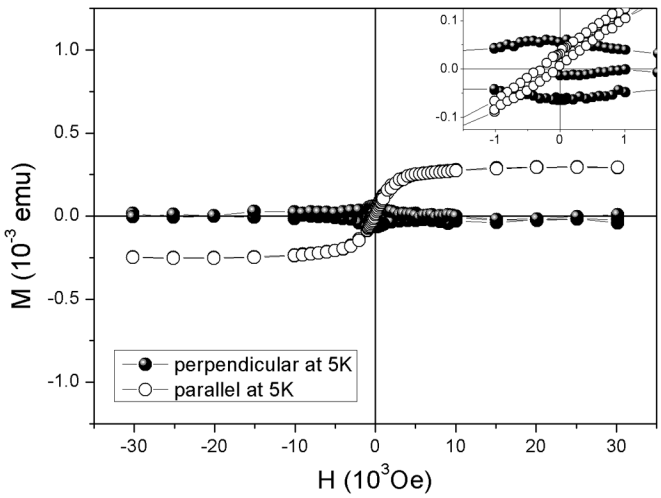

Fig. 4. Hysteresis loops of goethite nanowire arrays measured at 5 K with the applied magnetic field parallel and perpendicular to the nanowires.

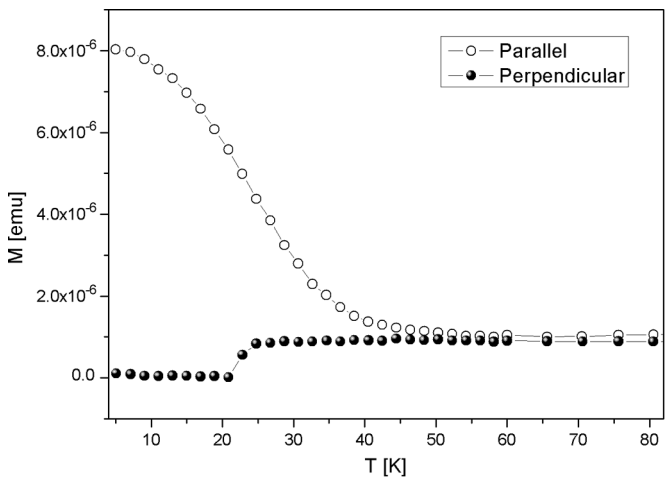

Fig. 5. Magnetization as a function of temperature for nanowires parallel and perpendicular to the applied field.

The external magnetic field was applied parallel (parallel geometry) and perpendicular (perpendicular geometry) to NWs. The diamagnetic component, due to the AAO template, was subtracted to show only the ferromagnetic signal. Inset of Fig. 4 shows details close to zero magnetic field applied.

The curves corresponding to both geometries show clear differences. For parallel geometry M versus H curve saturates at 20 000 Oe indicate the presence of an easy magnetization axis in the direction of such geometry. For perpendicular geometry the value of coercive force is several times higher. This means that the $\alpha-$FeOOH nanowire arrays have magnetic anisotropy. This behavior is like magnetic metal nanowire arrays, which show uniaxial anisotropy with easy axis along the wire [28]. Related studies on these topics will be reported in a future paper.

Magnetization as a function of temperature is shown in Fig. 5. The zero field cooled magnetization curves for parallel and perpendicular geometry are different. Curves corresponding to parallel geometry show a steady descent until T $\approx$ 65 K. For a perpendicular geometry curve, a similar behavior is observed, in the sense of a descent to a minimum at T $\approx$ 20 K. Large differences in magnetization, almost eight times bigger for the parallel geometry, show that the system is not isotropic, as should be the case for an ensemble of nanometer-sized nanoparticles. This is clearly indicative of a magnetic texture. Derivatives of the M versus T curves show a critical temperature at 21 K, which is the same for both geometries, which could be indicative of a magnetic transition. The meaning of such a feature is under study.

IV. Conclusion

Iron oxide nanowires are produced by a very simple chemical method. Structural and magnetic characterizations show clearly a structured nanowire formed by small single crystals of goethite. The nanowires show a preferential magnetic orientation.

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