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Synthesis and Characterization of Feooh by Electrochemical Deposition Techniques

[1] Mr.Chaudhari Devanand Prakash, [2] Prof. Gopal Panda

***Abstract*— A very simple method of synthesis of goethite, α-FeOOH, nanowire is reported. To fabricate the nanowires, an anodiezed 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(NO3)3 satured solution) which occurs inside the nanopores. The geometry of AAO determines the morphology of the nanowires, and the confinement conditions in which occurs the heat treatment determines the composition of the nanostructure. The nanowires are characterized using scanning electron microscopy (SEM), high resolution transmission electron microscopy (HR-TEM) and magnetometry (magnetization vs. applied field (M vs. H)). TEM analysis indicates that nanowires are composed of several α-FeOOH single crystals. The nanowires have a clear magnetic oriented structure.**

***Keywords*— 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 nanowires fabrication are lithography [10] and electrodeposition [11], while the chemical methods have been less used.

Investigations about iron oxyhydroxides nanowires fabrication is a topic of scientific interest. Several studies concerning beta and gamma phase oxyhydroxide nanowires (β-FeOOH and γ-FeOOH) have been done [12]. Amorphous and crystalline (orthorhombic phase) goethite (α-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 can not 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 report a very simple method for obtaining by chemical synthesis of α-FeOOH nanowires and their structural, morphological and magnetic properties. This work provides evidence on the composition of the nanowires consist of several α-FeOOH single crystals.

II. MATERIALS AND METHODS

Nanoporous anodic aluminum oxide template (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 way for the chemical precursor preparation was: 6 g of $Fe(NO_3)_3{\cdot}9H_2O$ was 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 a previous vacuum 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 nanopores was removed, the pores were filled by the saturated solution.

The AAO template filled with the nitrate ferric solution was taken out to the test tube and 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 a Transmission Electron Microscopy (TEM)

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grid and characterized by a High Resolution Transmission Electron Microscopy (HR-TEM) with a resolution of 1.7 Å. The other part of the sample was analyzed by a 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

Figure 1 shows the SEM imags 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 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 figure 1 inset. It is noted that the nanostructure is not compacted, it consist of agglomerates.

Figure 2a shows the TEM image of NWs after the AAO template has been dissolved. TEM image of a single nanowire is shown in figure 2b. 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 AAO template the diameter of NWs remains about 55 nm, but, in some case the length decrease since 2 µm to around 200 nm. This could be due to th 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. Figure 3 shows a 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 α-FeOOH single crystal. In this way, the measured interplanar distance, d = 2.2 Å (plane (210)), d = 3.3 Å (plane (120)), 4.1 Å (plane (110)), and d =2.5 Å (plane (021)) are in good agreement with goethite crystal [19]. These observations are consistent with those reported by Meng Fei et. al. for goethite nanowires obtained by other method [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 effect is associated with disorder due to surface/volume ratio. In this context, the atoms locted in the surface are not in the regular configuration as are 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 satured solution) occurs in confinement conditions (inside the AAO pore substrate, with previous vacuum), in 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, α-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 figure 4 appear the magnetization vs. applied magnetic field (M vs. H) measurements made at 5 K. The external magnetic field was applied parallel (parallel geometry) and perpendicular (perpendicular geometry) to NWs. Diamagnetic component, due to the AAO template, was subtracted to show only the ferromagnetic signal. Inset of the figure 4, shows details close to zero magnetic field applied.

The curves corresponding to both geometry show clear differences. For parallel geometry M vs. H curve saturates at 20000 Oe, indicating 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 α-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 article.

Magnetization as function of temperature is showed in figure 5. The zero field cooled magnetization curves for parallel and perpendicular geometry are different. Curve corresponding to parallel geometry shows a steady descent until T ≈ 65 K. For perpendicular geometry curve, a similar behavior is observed, in the sense of a descent to a minimum at T ≈ 20 K. Large difference in magnetization, almost eight

times bigger for the parallel geometry shows that the system is not isotropic, as should be the case for an ensemble of nanometre-sized nanoparticles. This is clearly indicative of a magnetic texture. Derivatives of the M vs. T curves show a critical temperature at 21 K, which is the same for both geometries, which could be indicative of a magnetic transition. Meaning of such feature is under study.

IV. CONCLUSIONS

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

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