PAPER

Electrochemical synthesis and magnetic properties of goethite single crystal nanowires

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We present an electrochemical method for the synthesis of iron hydroxide nanowires, together with a detailed structure and magnetic characterization. The nanowires are single crystalline and show the structure of goethite without traces of any other iron oxide or hydroxide. The nanowires are antiferromagnetic, like bulk goethite, but show a small magnetic hysteresis which arises from uncompensated surface spins. Exchange bias is also reported in the nanowires, an effect related to the coupling between the antiferromagnetic bulk and the surface spins, that shows weak ferromagnetism.

1 Introduction

Magnetic nanomaterials are at the forefront of the development of new electronic sensors and devices. For all magnetic applications it is essential to tailor the magnetic properties in the nanoscale which is normally achieved by combining different ferromagnetic and non-magnetic materials in a single nanostructure. For example, in the case of magnetic nanowires, the stacking of ferromagnetic and paramagnetic layers allows to control the magnetization processes, making possible the synthesis of superparamagnetic nanowires.[1] Another widely used approach for controlling the magnetization processes in nanodevices is the use of the exchange bias effect: joining a ferromagnetic and an antiferromagnetic materials together allows to control the coercivity and the magnetization processes of the ferromagnetic material.[2]

Biomedical applications are among the most demanded applications of magnetic nanomaterials due to the potential impact of nanotechnology in diagnosis and therapy. Magnetic nanomaterials can be used as contrast agents in Magnetic Resonance Imaging (MRI)[3] or as therapy agents in hyperthermia[4] or drug delivery.[5] In all cases, the control of the magnetic properties, as well as geometry is crucial. Iron oxides are biocompatible materials and, therefore, very interesting materials for their use in these applications. In fact, they are the most used magnetic materials in biological applications. However, to tailor the magnetic properties of the magnetite using exchange bias it is important to synthesize an antiferromagnetic material that should be easily nanostructured.

Goethite (α-FeOOH) is one of the most thermodynamically stable iron oxides at ambient temperature and therefore it is widespread in nature. Due to this, most of the studies of its magnetic properties have been done on large natural crystals, finding that it behaves as an antiferromagnetic material with a Néel temperature of about 400 K.[6,7] Only recently has nanostructured goethite been synthesized. In particular, goethite nanorods have been produced by wet-chemistry methods and their structural and magnetic behavior have been reported.[8]

Electrodeposition has been used for the integration of metallic and magnetic materials in electronics devices for years. This technique, combined with e-beam lithography[9] or nanoporous templates, also allows the synthesis of materials in the nanoscale. In particular, the use of nanoporous alumina[10,11] or polycarbonate templates[12] is one of the most extended techniques for the synthesis of nanowires. In this sense, different strategies based on electrodeposition have been followed for the synthesis of iron oxide nanowires. Iron oxide nanowires can be grown by thermal oxidation of previously electrodeposited nanowires.[13] However, this approach has one main drawback when dealing with tailoring magnetic properties and applications: the nanoporous template used for the synthesis of nanowires has to be removed before the annealing, impeding the growth of any other material and losing the order of the structure. Following the work on the electrodeposition of iron oxide thin films,[14] nanowires can be directly electrodeposited into the pores of a template. Magnetite polycrystalline nanowires have been already synthesized following this procedure.[15]

In this work, we propose an electrochemical route for the synthesis of goethite single crystalline antiferromagnetic nanowires, based on previous works of electrodeposition of goethite thin films.[14] Apart from the antiferromagnetic nature of goethite, the study of the magnetic properties of the

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nanowires show a ferromagnetic contribution which is intrinsic to goethite nanowires.

2 Experimental

Iron hydroxide nanowires have been electrodeposited into the pores of a polycarbonate membrane supplied by Sterlitech. The thickness of the membrane was 6 μm and the nominal diameter of the pores was 100 nm with pore density of 4×10^8 cm^{-2}. Before electrodeposition, a thin Au film was thermally evaporated on one side of the template in order to act as a working electrode. The electrolyte used for the electrodeposition of the nanowires was 0.04 M $K(CH_3COO)$ and 0.01 M $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ with a pH of 6.5 adjusted by the addition of $Na(OH)$. All the chemicals were of analytical grade, used without further purification and were mixed in deionized water. The synthesis was carried out at 90 °C in a galvanostatic mode, applying a constant density current of 2 mA cm^{-2} (during 7200 s). A platinum mesh was used as a counter electrode. This procedure for the electrodeposition of iron hydroxide is similar to the one described by Martinez et al.[14] According to this previous work, the synthesis of α-FeOOH films would proceed via the oxidation of Fe^{2+} ions by the reaction:

$$Fe^{2+} + 2H_2O \rightarrow \alpha\text{-FeOOH} + 3H^+ + e^-$$

A Scanning Electron Microscope (SEM) JEOL JEM 6335 was used to study the morphology of the nanowires. Before measuring the nanowires, the polycarbonate template was removed with dichloromethane. X-ray diffraction patterns were collected using a Philips X'Pert Pro MPD diffractometer in the grazing incidence mode (GIXRD). High Resolution Transmission Electron Microscopy (HRTEM) and Selected Area Electron Diffraction (SAED) on a JEOL JEM-3000F were also used to study the morphology and the crystalline structure of the nanowires. The nanowires were released from the templates for the HRTEM characterization. Firstly, the Au layer was removed by contacting the Au layer with liquid Hg and washing with deionized water several times. Afterwards, the polycarbonate membrane was dissolved with dichloromethane. Finally, the suspension was centrifuged to separate the nanowires and the polycarbonate and new clean dichloromethane was added.

Magnetic measurements were performed in a Quantum Design SQUID Magnetometer. Thermal evolution of magnetization was measured under an applied field of 10 kOe in two steps: from 5 K to 300 K using a cryostat and from 300 K to 650 K using a furnace. The thermal evolution of magnetization was also measured in the low temperature range under zero-field cooled (ZFC) and field cooled (FC) conditions. Samples were cooled to 5 K in zero field and warmed up to room temperature in 100 Oe (ZFC curve). Then, samples were cooled down again to 5 K in a field of 20 kOe and warmed up in 100 Oe (FC curve). Hysteresis loops were also recorded at 300 K and 5 K up to a
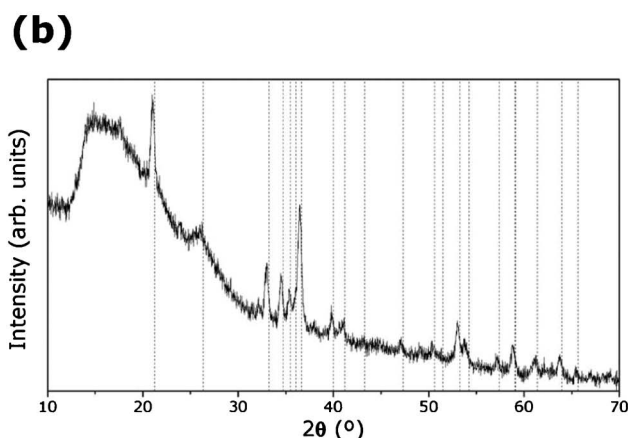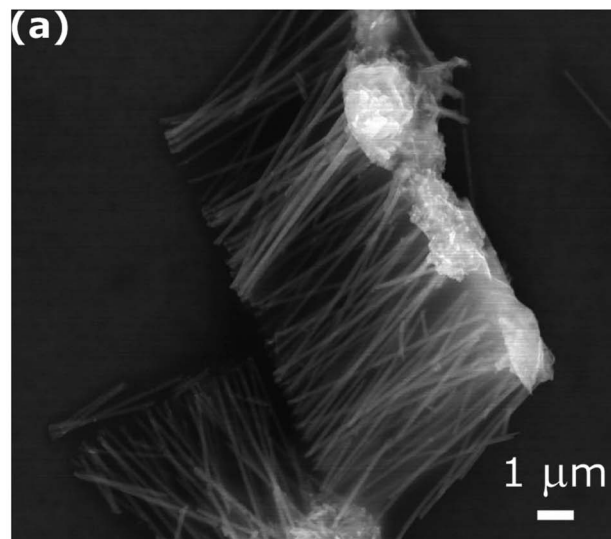

Fig. 1 (a) Scanning electron micrograph of an array of goethite electrodeposited nanowires released from the template. (b) X-ray diffraction pattern of a collection of goethite nanowires randomly oriented in the holder. The dashed lines indicate the position of the goethite reflections according to the card 00-029-0713.

field of 20 kOe. All measurements were carried out with the nanowires randomly oriented in the field.

3 Results and discussion

By the method of synthesis described above – electrodeposition into the pores of a template – we are able to obtain a large density of nanowires, as the SEM images demonstrate (Fig. 1a). The nanowires have quite a smooth surface with a very narrow diameter distribution, with a mean value around 175 nm. The length of the nanowires depends on the electrodeposition time. In the case of this study, it is approximately 6 μm.

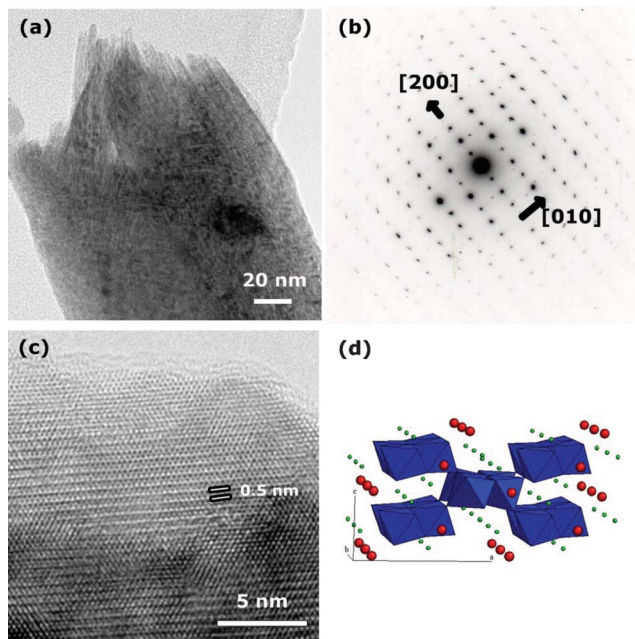Fig. 1b shows the x-ray diffraction pattern of the electrodeposited nanowires. Apart from the broad peak at low angles

Fig. 2 (a) Transmission electron micrograph of the end of a goethite nanowire in which an acicular structure is clearly shown. (b) Selected area diffraction pattern of an individual nanowire. The [200] and [010] directions of the goethite structure are marked in the figure. (c) High resolution transmission electron microscopy image of a nanowire, in which the (002) planes are clearly shown. (d) Schematic of the goethite crystal structure, in which the red spheres are Fe^{3+} ions, the green spheres are H^+ ions and the O^{2-} ions are located on the vertex of the octahedrons.

Fig. 3 Hysteresis loops of nanowires of goethite measured at low (black) and room (red) temperature.

arising from the membrane, all shown peaks can be indexed as goethite (Cod. 00-029-0713). The broad peak that can be seen at low angles is an amorphous contribution, most likely from the amorphous polycarbonate template, because the nanowires were not released from the template for the XRD measurements.

Goethite has an orthorhombic structure with cell parameters $a = 0.9956$ nm, $b = 0.30215$ nm and $c = 0.4608$ nm. The structure is presented in Fig. 2d where the anions (O^{2-} and OH^-) form an hcp array in the [010] direction whereas the Fe^{3+} cations occupy half of the octahedral sites. Goethite natural crystals are normally formed by large crystalline acicular domains, elongated along the [100] directions (a axis). The electrodeposited nanowires reproduces this acicular structure. In the end of the nanowires we can find similar structures than the one reported in ref. 16 (see TEM image in Fig. 2a), which means that the growth modes of the nanowires reproduces the acicular growth observed in natural goethite.

The HRTEM measurements and SAED diffractograms confirm that the crystalline structure of the nanowires corresponds to the one of goethite, without traces of other iron oxide or hydroxide. Fig. 2b shows the SAED pattern obtained in a nanowire, in which the [010] and the [200] directions of the goethite structure are marked by arrows. The pattern is spotty, which corresponds to a sample with high crystallinity. Similar patterns were obtained measuring in
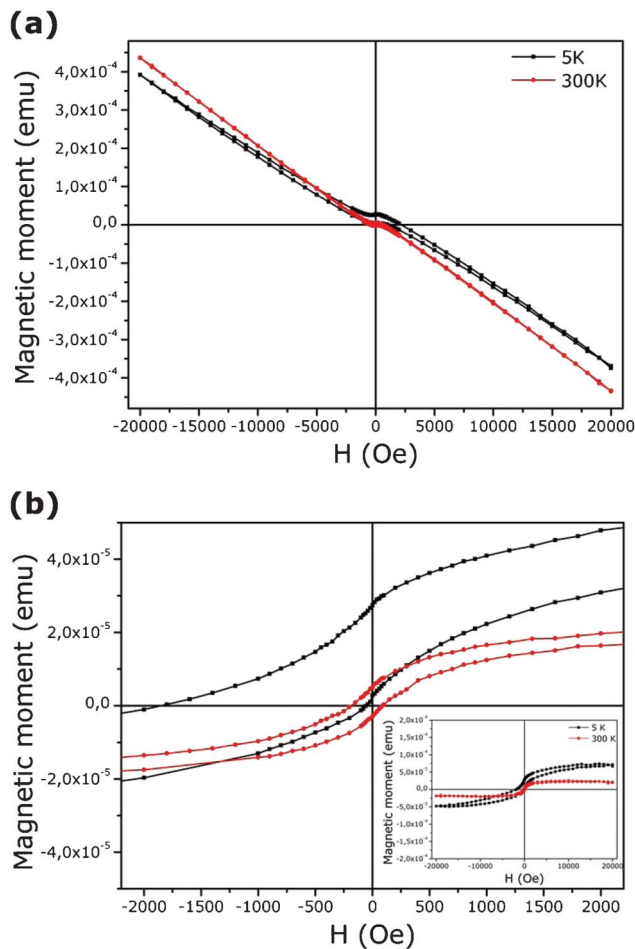
different parts of the nanowire and also in different nanowires. The HRTEM study confirms these results. In the HRTEM image shown in Fig. 2c, rows of atoms separated by 0.5 nm are seen which corresponds to the planar distance (002) of the structure of goethite. Therefore, from the HRTEM and XRD analysis, we can extract that the grown nanowires are single crystal nanowires only composed by goethite.

The hysteresis loops of the goethite nanowires measured at room temperature and 5 K with a maximum applied field of 20 kOe are shown in Fig. 3a. It can be seen that, in spite of its antiferromagnetic nature, a small hysteretic behavior can be observed for low applied magnetic fields. For a better display of this behavior, the linear diamagnetic contribution has been subtracted (inset of Fig. 3b) and the central part of the hysteresis loops, corresponding to small applied fields, has been enlarged (Fig. 3b). Whereas the hysteresis loop measured at room temperature is fully saturated, for the one measured at low temperature it is not, which indicates the presence of a strong magnetic anisotropy at low temperature. Coercivity at room temperature is 170 Oe in agreement with previous results reported for goethite.[6,17–19]

The most interesting feature of the hysteresis loop is the exchange bias effect, shown by the shift of the loop in the magnetic field axis.[20] In natural goethite crystals, the presence of exchange bias has been attributed to the presence of hematite phase inclusions, that were detected by XRD measurements.[6] The coupling of these hematite inclusions with the goethite crystals were responsible for the observed shift in the hysteresis loops. However, in the nanowires reported in this paper, the XRD and HRTEM measurements only revealed the presence of a single goethite phase.

To have a deep insight into the magnetic properties of the synthesized nanowires, thermal evolution of magnetization has been measured and analysed under different magnetic applied fields. Thermal evolution of magnetization under a large applied field is shown in Fig. 4a – low temperature – and Fig. 4b – high temperature. Apart from a large drop below 50 K, magnetization is almost constant up to 345–350 K. Around this value, magnetization decreases abruptly, indicating a phase transition, most likely related to the Néel temperature of goethite. There is a new drop in magnetization around 560–580 K due to the goethite dehydration that forms hematite, α-Fe_2O_3.[6,7,21,22] Additional information about the magnetic properties at low temperature can be extracted from the FC–ZFC curves (Fig. 4c). The FC curve decreases with increasing temperature and ZFC shows a slight maximum at 50 K. This can be related with the existence of a superparamagnetic phase with a blocking temperature around 50 K. This would also explain the drop in the magnetization at high field observed before in Fig. 3a. In any case, what is most remarkable is the absence of any other transition up to room temperature.

Thermal evolution of magnetization, studied from 5 K to 650 K, has shown only features that can be directly related to goethite. The large drop around 350 K corresponds to the transition from antiferromagnetic to paramagnetic behavior – Néel temperature. Although Néel temperature has been reported for bulk goethite to be 400 K,[6,7,23] a smaller Néel temperature is expected in the nanowires. Due to the lack of symmetry close to the surface, the antiferromagnetic coupling between atoms in a nanostructure is smaller than in a bulk material, leading to a smaller value of Néel temperature in nanowires. This effect has been observed in other antiferromagnetic oxides.[24] The other clear magnetic transition observed in the thermal evolution of magnetization can be ascribed to the goethite dehydration, as mentioned before.

According to previously published works,[6] hematite traces could be presented in goethite crystal, being responsible for the ferromagnetic behavior. In the case of the nanowires reported in this paper, the analysis of the thermal evolution of magnetization allows us to exclude this possibility. Bulk hematite shows a magnetic transition at a temperature of 262 K, called Morin temperature, that could decrease up to 120 K in case of nanostructured hematite.[24] Some authors have reported Morin transitions at values as low as 80 K.[13] In the measurements reported in the paper, no magnetic transition has been observed in the thermal evolution of magnetization
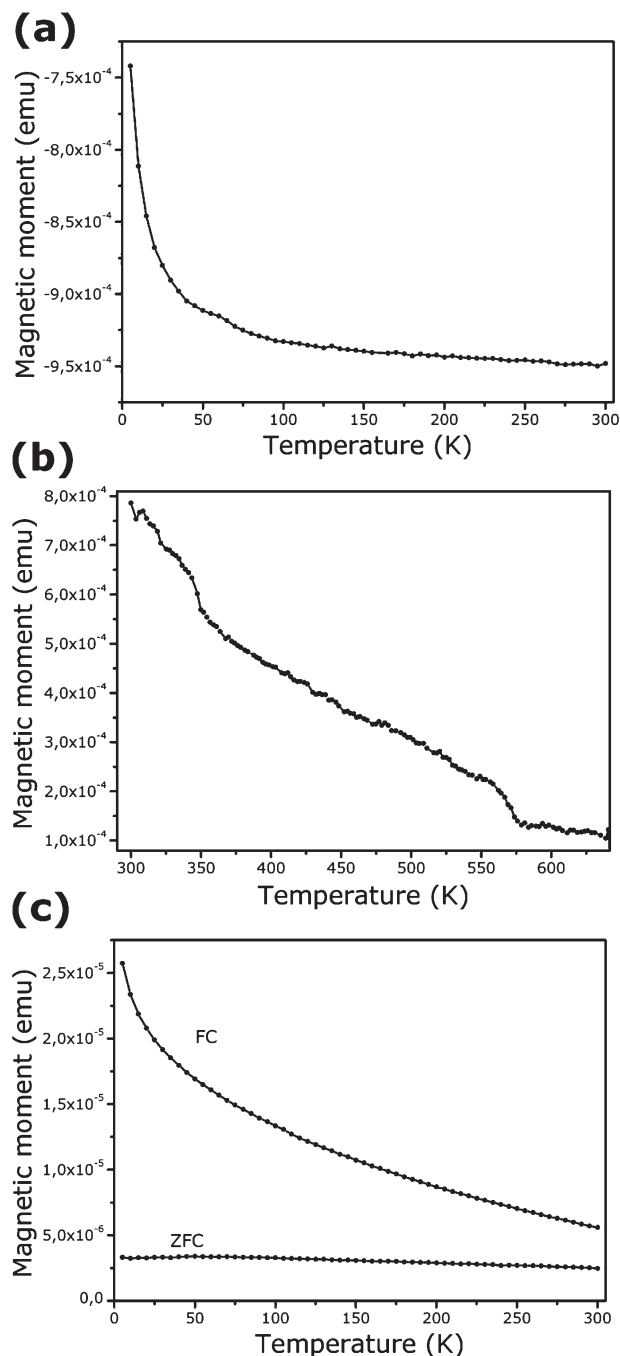

Fig. 4 Thermomagnetic measurements of the synthesized goethite nanowires: (a) Low temperature, (b) high temperature. (c) ZFC/FC warmed up in a 100 Oe field and FC cooled down from 300 K to 5 K in 20 kOe.

in the range 50–300 K which discards the possible presence of hematite magnetic impurities in the goethite nanowires. Therefore, from both structural and magnetic measurements, the nanowires are only composed of goethite.

Putting all the magnetic measurements together, the magnetic structure of the goethite nanowires can be understood as follows. The bulk of the nanowires is antiferromagnetic, although there could be a very weak net magnetic

moment arising from a non-collinear sublattice in the antiferromagnetic structure with a canted angle of $13°$.[25] However, most of the ferromagnetic contribution most likely comes from the nanowire surface, where the magnetic sublattices forming the antiferromagnetic structure may not be compensated. This leads to a ferromagnetic net contribution to the magnetic signal. This magnetic structure – antiferromagnetic bulk and ferromagnetic surface – also explains the observed exchange bias, whose mechanism would be similar to the commonly studied exchange bias effect produced by coupling between an antiferromagnetic and a ferromagnetic materials. Therefore, the observed exchange bias is an intrinsic effect of the goethite single crystal nanowires and can be explained without the need for the presence of any magnetic impurity or inclusion in the nanowires.

4 Conclusions

Single crystalline goethite nanowires have been synthesized by electrochemical deposition using a polycarbonate membrane as a template. The nanowires are antiferromagnetic as expected, but a small hysteresis in their magnetic behavior is observed, arising from uncompensated surface magnetic moments. Exchange bias effect is also observed when measuring the hysteresis loops. Careful structural and magnetic studies discard the existence of other magnetic phase in the nanowires apart from goethite. Thus, the exchange bias is an intrinsic effect of the goethite nanowires related to the coupling between the antiferromagnetic bulk and the surface magnetic moments, that show weak ferromagnetism.

Acknowledgements

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