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Facile synthesis of cobalt ferrite nanotubes using bacterial nanocellulose as template

S. Menchaca-Nal[a], C.L. Londoño-Calderón[a], P. Cerrutti[b], M.L. Foresti[a], L. Pampillo[c], V. Bilovol[c], R. Candal[d], R. Martínez-García[e,*]

[a] Institute of Polymer Technology and Nanotechnology, Faculty of Engineering, University of Buenos Aires—CONICET, Argentina
[b] Department of Chemical Engineering, Faculty of Engineering, University of Buenos Aires, Argentina
[c] Institute of Technology and Engineering Sciences "Hilario Fernández Long", Faculty of Engineering, University of Buenos Aires—CONICET, Argentina
[d] Institute of Physical Chemistry of Materials Environment and Energy, Faculty of Natural Sciences, University of Buenos Aires—CONICET, Argentina
[e] Faculty of Natural Resources, National University of Formosa—CONICET, Campus Universitario, Modulo I, Av. Gutnisky 3200, Formosa, Argentina

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ABSTRACT

A facile method for the preparation of cobalt ferrite nanotubes by use of bacterial cellulose nanoribbons as a template is described. The proposed method relays on a simple coprecipitation operation, which is a technique extensively used for the synthesis of nanoparticles (either isolated or as aggregates) but not for the synthesis of nanotubes. The precursors employed in the synthesis are chlorides, and the procedure is carried out at low temperature (90 °C). By the method proposed a homogeneous distribution of cobalt ferrite nanotubes with an average diameter of 217 nm in the bacterial nanocellulose (BC) aerogel (3%) was obtained. The obtained nanotubes are formed by 26–102 nm cobalt ferrite clusters of cobalt ferrite nanoparticles with diameters in the 9–13 nm interval. The nanoparticles that form the nanotubes showed to have a certain crystalline disorder, which could be attributed in a greater extent to the small crystallite size, and, in a lesser extent, to microstrains existing in the crystalline lattice. The BC-templated-$CoFe_2O_4$ nanotubes exhibited magnetic behavior at room temperature. The magnetic properties showed to be influenced by a fraction of nanoparticles in superparamagnetic state.

1. Introduction

Due to their promising applications in diverse fields of scientific development, different inorganic nanoparticles/biopolymers nanocomposite materials have recently been the focus of much interest from the academic and industrial community (Chen, Yang, Ma, & Wu, 2011; Hassan-Nejad, Ganster, Bohn, Pinnow, & Volkert, 2009; Kroll & Winnik, 1996; Llanes, Ryan, & Marchessault, 2000). For this kind of nanocomposites the most promising applications involve biomedicine uses (Chen et al., 2011), heavy metal separation (Fatyasari, Sureshkumar, & Lee, 2011; Zhoua, Branford-White, Nie, & Zhua, 2009), electronic devices (Aoki, Huang, & Kunitake, 2006) and photovoltaics (Zheng et al., 2013).

The combination of inorganic nanoparticles and cellulose takes benefit from the properties of both components, resulting in new properties due to synergistic effects (Hu, Chen, Yang, Li, & Wang, 2014; Klemm et al., 2006). In this context, nanocellulose is an ideal template to prepare several nanostructures (Hu et al., 2014; Li et al., 2012; Olsson et al., 2010). Recently, nanocellulosics have been successfully used as template for the growth of isolated metal nanoparticles and metal nanotubes (Gu, Liu, Niu, & Huang, 2010; Li et al., 2012; Olsson et al., 2010). Among nanocellulose sources, bacterial nanocellulose is biosynthesized as primary extracellular metabolite by certain bacteria which under proper conditions secrete high-quality cellulose ribbons of microfibrillar bundles. Micrometric-in-length BC ribbons typically show rectangular cross-sections with thicknesses around 3–4 nm and widths in the 70–100 nm interval (Bielecki, Krystynowicz, Turkiewicz, & Kalinowska, 2002). The biopolymer is obtained as a highly hydrated pellicle (97–99%) in the air–water interface of static fermentation vials, and it is recognized for its unique physicochemical, biological and mechanical properties such as high water holding capacity, high crystallinity, high tensile strength and Young modulus, biodegradability, biocompatibility and low thermal expansion coefficient in the axial direction, among others (Castro et al., 2011; Klemm et al., 2011; Putra, Kakugo, Furukawa, Gong, & Osada, 2008). Based on its outstanding properties, BC has a wide range of potential technical applications (Charreau, Foresti, & Vázquez, 2013; Klemm et al., 2011).

* Corresponding author. Tel.: +5411-4342-1396; fax: +5411-4342-1396.
E-mail address: rmartinez@fi.uba.ar (R. Martínez-García).

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Cobalt ferrite ($CoFe_2O_4$) nanoparticles attract interest due to their magnetic properties and their high mechanical and chemical stability (Dorsey, Lubitz, Chrisey, & Horwitz, 1996). Cobalt ferrite is a ferrimagnet with a cubic spinel structure. The Fe^{3+} and Co^{2+}/Fe^{3+} ions occupy the tetrahedral (A sites) and octahedral (B sites), respectively, with a formal ionic distribution that can be represented by $(Fe^{3+})_A(Fe^{3+}Co^{2+})_BO_4^{2-}$ (Valenzuela, 1994). $CoFe_2O_4$ nanotubes have been obtained by electrospinning (Fu et al., 2012), as well as by atomic layer deposition (ALD) onto cellulose (Korhonen et al., 2011) and using anodic alumina oxide (Hua et al., 2007) templates. On the other hand, BC/cobalt ferrite nanocomposites have also been prepared by coprecipitation; however, by this comparatively cheaper and simpler methodology have led to isolated nanoparticles embedded within the nanocellulosics substrate, and not to the formation of nanotubes (Olsson et al., 2010; Zhang et al., 2011).

In the current contribution, a facile procedure for the synthesis of $CoFe_2O_4$ nanotubes is proposed. The method relies on the *in situ* precipitation of metal ions onto freeze-dried bacterial cellulose nanoribbons (nucleation sites). Cobalt chloride and iron chloride salts are used as precursors, being the iron cation in the 3+ state, which differs from previously reported methodologies (Olsson et al., 2010). Moreover, by use of Iron (III) chloride no extra oxidation step for $CoFe_2O_4$ formation is required. The described method leads to homogeneous cobalt ferrite biotemplated-nanotubes. $CoFe_2O_4$ nanotubes obtained by the simple non-expensive methodology herein proposed were characterized by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), Mössbauer spectroscopy, thermogravimetric analysis (TGA) and magnetometry.

2. Experimental

2.1. Microorganism and culture conditions

Inocula were cultured at 28 °C for 48 h in 100 mL Erlenmeyers flasks containing 20 mL of Hestrin and Schramm (HS) medium (%, w/v): anhydrous dextrose (Biopack), 2.0; meat peptone (Britania, Laboratorios Britania S.A.), 0.5; yeast extract (Britania, Laboratorios Britania S.A.), 0.5; anhydrous disodium phosphate (Anhedra), 0.27; citric acid (Merck), 0.15. The pH was adjusted to 6.0 with dilute HCl or NaOH. Agitation (200 rpm) was provided by an orbital shaker.

The fermentation media was HS broth modified by using glycerol (2% w/v) instead of dextrose. The fermentation media was inoculated with 1% v/v of the inoculum culture and distributed in 250 mL Erlenmeyer flasks, keeping the ratio "volume flask: volume medium" in 5:1. The incubation was performed in a shaking water bath (130 rpm) at 28 °C for 15 days. The cellulose pellicles obtained were separated from the culture media by filtration through two layers of cotton gauze and washed at least five times with distilled water. The product was then freeze-dried by use of Christ Alpha 1-4 LD equipment for 48 h to preserve the open porous structure of the cellulose in the dry state. Previous coprecipitation methodologies which led to isolated $CoFe_2O_4$ over BC nanoribbons used lower freeze-dried time intervals, i.e. 12 h (Olsson et al., 2010).

2.2. $CoFe_2O_4$ nanotubes synthesis

Previously freeze-dried BC pieces (20 mg) were immersed for 15 min in 200 mL of a freshly prepared solution 0.02 mol of $FeCl_3{\cdot}6H_2O$ (Anedra, Research AG S.A) and 0.01 mol of $CoCl_2{\cdot}6H_2O$ (Anedra, Research AG S.A). The system was maintained at room temperature. The molar ratio remained 2:1 [Fe]/[Co] in the precursor salts (Tourinho, Franck, & Massart, 1990). Almost immediately, BC color changed from white to orange. The solution containing the BC was then heated at 90 °C for 3 h. This process helps to promote the transformation of soluble initial metal hydroxides to insoluble metal oxyhydroxide complexes that in later stages convert into $CoFe_2O_4$ (Olsson et al., 2005). BC was subsequently transferred to a solution of 1.2 M NaOH (Laboratorios Cicarelli, Reagents S.A) and the system was kept at 90 °C for 6 h. The color of BC changed rapidly from orange to black, which indicated the formation of cobalt ferrite. The product obtained was then washed with distilled water repeatedly to remove counterions, and finally dried at room temperature for 96 h.

2.3. Characterization methods

Samples were coated with a thin layer of gold using an ion sputter coater, and their morphology and structure were analyzed with a Field Emission Scanning Electron Microscope (FE-SEM, Zeiss Supra 40) with field emission gun operated at 3 kV. The gray-scale imaging process was developed to determine the porosity of the samples by using a scanning probe image processor ImageJ-1.46r (Schneider, Rasband, & Eliceiri, 2012). The X-ray diffraction (XRD) patterns were recorded in a Rigaku diffractometer with Cu Kα radiation in a 2θ range from 10° to 100°. Thermogravimetric analysis (TGA) of previously dried (110 °C, 1 h) samples was conducted in a TGA-50 Shimadzu instrument. Temperature programs were run from 25 °C to 800 °C at a heating rate of 10 °C/min, under nitrogen atmosphere (30 mL/min) in order to prevent thermoxidative degradation. Magnetic properties were analyzed using a Physical Property Measurement System (PPMS, Quantum Design). Magnetization curves as a function of applied field were obtained at different temperatures (5 and 300 K) between −40 and 40 kOe. M_S values were expressed per gram of magnetic mass as emu/g $CoFe_2O_4$. A ^{57}Fe Mössbauer spectrum was recorded in transmission geometry at room temperature using a $^{57}Co/Rh$ α-ray source mounted on an electromagnetic transducer with a triangular velocity form. The hyperfine structure was modeled by least-squares fitting procedure of Gaussian lines. The isomer shift (IS) values were referred to α-Fe at 300 K.

3. Results and discussion

3.1. $CoFe_2O_4$ nanotubes synthesis

The nanocellulosic template used in the current contribution was freeze-dried bacterial nanocellulose. Freeze-dried BC nanoribbons have high affinity for water. When the three-dimensional BC network contacts the aqueous precursor solution, the nanoribbons are negatively charged due to the presence of hydroxyl groups moieties that are exposed to the surface of the fiber. Metal precursors (Fe^{3+} and Co^{2+} ions) thus bind to cellulose nanofibrils via electrostatic (i.e., ion-dipole) interactions between the hydroxyl groups (electron-rich oxygen atoms) of BC and the electropositive transition metal cations (Shilin, Qiufang, Dandan, Tengfei, & Xiaoya, 2012). The formed oxyhydroxides act as nucleation points for the growing of nanoparticles that form the nanotubes. The relatively low temperature (90 °C) used in the synthesis contributes to the formation of homogeneous nanotubes using BC as template. The chosen temperature leads to slow nucleation and growing of the particles that form the nanotubes and contributes to obtaining homogeneous structures. During the later drying process, the initially swollen cellulose nanoribbons are dried, leading to the formation of hollow metal oxide structures with dried cellulose nanoribbons remaining in their interior.