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journal homepage: www.elsevier.com/locate/jmmmMagnetic properties of NiFe₂O₄/carbon nanofibers from Venezuelan petcokeSarah Briceño^{a,*}, Pedro Silva^a, Wilmer Molina^a, Werner Brämer-Escamilla^a, Olgi Alcalá^a, Edgard Cañizales^b^a Laboratorio de Física de la Materia Condensada, Centro de Física, Instituto Venezolano de Investigaciones Científicas IVIC, Apartado 20632, Caracas 1020-A, Venezuela^b Área de Análisis Químico Inorgánico, PDVSA, INTEVEP, Los Teques 1070-A, Venezuela

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ABSTRACT

NiFe₂O₄/carbon nanofibers (NiFe₂O₄/CNFs) have been successfully synthesized by hydrothermal method using Venezuelan petroleum coke (petcoke) as carbon source and NiFe₂O₄ as catalyst. The morphology, structural and magnetic properties of nanocomposite products were characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), vibrating sample magnetometry (VSM) and electron paramagnetic resonance (EPR). XRD analysis revealed a cubic spinel structure and ferrite phase with high crystallinity. HR-TEM reveals the presence of CNFs with diameters of 4 ± 2 nm. At room temperature, NiFe₂O₄/CNFs show superparamagnetic behavior with a maximum magnetization of 15.35 emu/g. Our findings indicate that Venezuelan petroleum coke is suitable industrial carbon source for the growth of magnetic CNFs.

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1. Introduction

Carbon nanofibers (CNFs) have gained increasing attention in the last few years due to their high strength, chemical purity and chemical inertness; these features make them ideally suitable for use as a catalyst support. CNFs consist of a typical non-graphitizing carbon as expected from the nature of the precursor [1]. To date, various petroleum products, such as methane, xylene and benzene, are being synthesized CNFs [2]. Petcoke is a by-product of the upgrading process for Oil-sand derived bitumen and is the most abundant byproduct of oil refining in Venezuela accounting for up to 30 wt% of all products. It is also highly contaminated with metal compounds and particularly sulfur which forms sulfur dioxide upon combustion, which make petroleum coke very cheap [3]. Effort has been directed towards using petcoke in the production of carbon nanotubes [4], water purification [5], catalyst support and environmental applications [3]. Due to its large carbon content (80%) and relatively low ash content, this petcoke can be converted to a value-added product such as CNFs, which may have many catalytic applications. One of the most important factors in the synthesis of CNFs is the catalyst employed. Nickel ferrite NiFe₂O₄ is an inverse spinel in which half of the ferric ions occupy the tetrahedral sites (A-sites) and the rest occupy the octahedral

sites (B sites). Thus, the compound can be represented by (Fe_{1.0}³⁺[Ni_{1.0}²⁺Fe_{1.0}³⁺]O₄²⁻, where the round and the square brackets represent A and B sites, respectively [6]. Previously the present authors reported on the obtention of NiFe₂O₄/AC from petcoke [7]. In this work we report on a new way to produce carbon nanostructures by exploiting the petcoke as carbon source using NiFe₂O₄ NPs as a promising way for a high value-added utilization of Venezuelan oil residue.

2. Materials and methods

2.1. Preparation of NiFe₂O₄

NiFe₂O₄ ferrite nanoparticles were synthesized by the thermal decomposition method. The experimental setup consisted of a system reflux under N₂ atmosphere using a 250 mL condenser and heating mantle. The procedure consisted of mixing Fe(acac)₃ (2 mmol), 1,2 hexadecanediol (10 mmol), oleic acid (6 mmol), oleylamine (6mmol), and benzyl ether (20 mL). The nuclei formation and the growth of the Nps were obtained. When temperature was increased to 200 °C for 30 min with a blanket of Ar, heated to reflux 265 °C for another 30 min. The black-brown mixture was cooled to room temperature by removing the heat source. Under ambient conditions, ethanol (40 mL) was added to the mixture, and a black material was precipitated and separated

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via centrifugation [8]. The obtained samples were dried at 60 °C for 24 h.

2.2. Preparation of NiFe₂O₄/CNFs

Venezuelan petcoke from the INTEVEP – PDVSA Company was used as raw material and mixed with NiFe₂O₄ NPs at a mass ratio of 1:1 in distilled water, followed by the addition of 6 M KOH solution at pH 12. The mixture was then transferred into a Teflon lined stainless steel autoclave of 100 mL capacity. The sealed tank was heated and stirred at 200 °C for 2 h. The resulting black precipitates were collected by filtration and dried in an oven for 24 h at 60 °C. This mixture was heat-treated in a quartz reactor with a programmable furnace from room temperature to 960 °C at a heating rate of 10 °C/min for 2 h; the sample was then allowed to cool down to room temperature under N₂ flow.

2.3. Characterization methods

Phase identification and average size of the samples were examined at room temperature using a polycrystalline sample brand X-ray diffractometer model Bruker D8 Focus using Cu K radiation ($\lambda = 1.5406 \text{ \AA}$) and resolution of 0.02° in 2θ . The size and morphology of particles was examined by a high-resolution transmission electron microscope JEOL JEM 2100 with filament of hexaborure of lantane at 200 kV. Magnetic characterization was made in a homemade vibrating sample magnetometer and the EPR measurements were carried out in a BRUKER EMX spectrometer.

3. Results and discussion

3.1. Structural properties

3.1.1. XRD

The XRD patterns of (a) petcoke, (b) NiFe₂O₄ and (c) NiFe₂O₄/CNFs nanocomposite, are shown in Fig. 1. The pattern of the petcoke in Fig. 1 (a) shows a broad peak around $2\theta = 26^\circ$ of graphite structure. This broad peak can be indexed to the peak (111) Bragg reflection derived from petcoke (JCPD 75-1621). XRD pattern of the NiFe₂O₄ Nps and NiFe₂O₄/CNFs nanocomposites is shown in Fig. 1(b) and (c) respectively. These samples present many strong and sharp crystalline peaks attributed to the face-centered cubic Ni Fe₂O₄ phase (PDF #100325). The XRD patterns of sample NiFe₂O₄ exhibited the reflection plans (220), (311), (400), (511) and (440) that indicate the spinel cubic structure. Fig. 1(c) also shows an obvious transition of NiFe₂O₄ Nps from amorphous to the crystal phase with the thermal treatment at 960 °C. The intensity (I) of the peaks increases with the calcination process. This can be attributed to the increase of the rate of crystal growth as a result of expansion of volume and reduction of the supersaturation of the system at elevated temperature.

3.1.2. HR-TEM

NiFe₂O₄/CNFs nanocomposites were further examined by HR-TEM. The low-magnification HR-TEM indicated that the samples prepared from petcoke were composed of carbon nanofibers and NiFe₂O₄ NPs. Fig. 2(a) and (c) shows the (NiFe₂O₄) NPs in the range of $5 \pm 2 \text{ nm}$. In Fig. 2(b) we can observe the formation of the CNFs from the NiFe₂O₄ NPs. Fig. 2(d–f) indicated that the nanoparticles define the diameter of the CNFs as previously reported by [10]. From Fig. 2 it can be inferred that the growth of CNFs from petcoke in the present study is most likely based on the above formation mechanism.

The probable process could be described as follows: firstly, CO was produced in according to reactions (3) and (4) during the

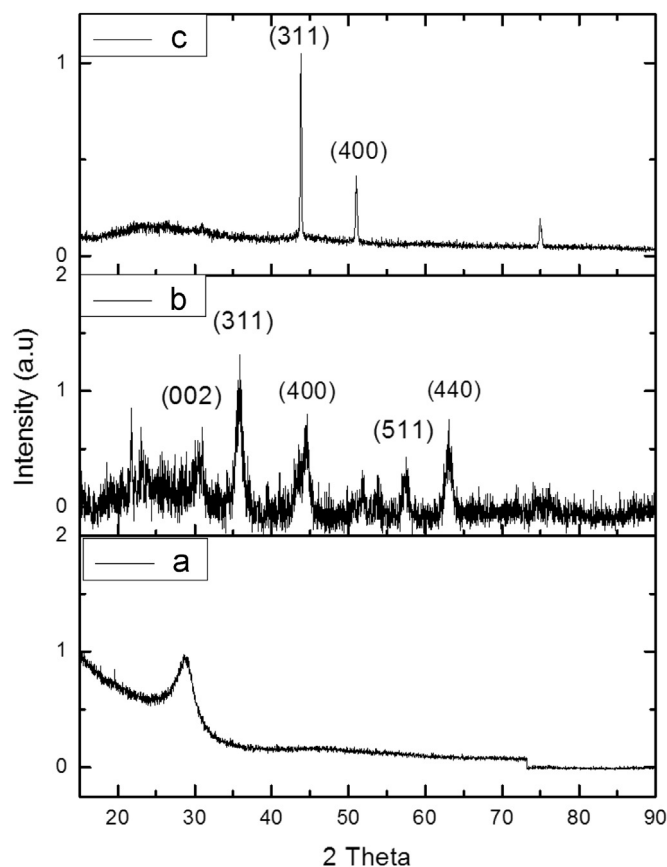
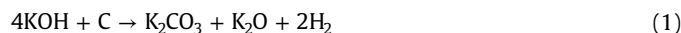


Fig. 1. XRD patterns of (a) petcoke, (b) NiFe₂O₄ and (c) NiFe₂O₄/CNFs.

activation of the petcoke with KOH [11]:



the resulting CO was transformed to CNFs at 960 °C in reaction (5) catalyzed by NiFe₂O₄ NPs that were impregnated into sample from hydrothermal reaction reactor in activation process:



The second possibility is that a new graphene cap forms on the surface of a nanoparticle (Fig. 2(b)) in which an already nucleated nanofiber has encapsulated the nanoparticle, and thus the nanofiber growth has terminated. That the termination is more effective at higher temperatures could be explained in terms of a higher carbon concentration in the particle at higher temperature leading to more frequent nucleation of a second graphene cap. This mechanism could also explain the presence of CNFs [12].

3.2. Magnetic properties

EPR spectra of petcoke as received from INTEVEP-PDVSA (Fig. 3 (a)) show a very intense central line associated with an organic free radical with $g = 2.00621$ and linewidth of 0.7 mT at 300 K. The inset consists in a set of lines that correspond to vanadylporphyrins V⁴⁺ with a hyperfine coupling constant of 7.2 mT. EPR spectra of NiFe₂O₄ (Fig. 3(b)) consisted of a asymmetric broad signal with linewidth of 106 mT.

The EPR spectra of NiFe₂O₄/CNFs annealed at 960 °C show two signals: one absorption at low-field, typical of systems with

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