Research Article

Synthesis of Carbon Nanofibers with Maghemite via a Modified Sol-Gel Technique

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Carbon nanohybrid material (CNF/ γ -Fe₂O₃) was obtained via a modified sol-gel technique consisting of two steps: functionalization of carbon nanofibers (CNF) in H₂SO₄/HNO₃ followed by synthesis using Fe(NO₃)₃•9H₂O. As a result, the iron content of the CNF/ γ -Fe₂O₃ was increased by more than twice from about 40% to about 87% mass percent, compared to the pristine CNF and oxidized CNF specimens, as proved by energy dispersive X-ray fluorescence. Scanning electron microscopy images exhibited “cumulus” on the CNF/ γ -Fe₂O₃ specimen surface, which showed the highest iron mass percentage, proved by energy dispersive X-ray spectroscopy. Transmission electron microscopy images confirmed attachment of γ -Fe₂O₃ cumulus to the inner and outer surfaces of the CNF walls after synthesis. The characteristic peaks of Fe 2p_{3/2} and Fe 2p_{1/2} appeared in the XPS spectra obtained on CNF/ γ -Fe₂O₃. In addition, X-ray diffraction (XRD) results indicated formation of γ -Fe₂O₃ during the synthesis process. The Raman spectrum of the CNF/ γ -Fe₂O₃ sample displays peaks with positions close to characteristic peaks of highly crystalline and monodisperse maghemite nanocrystallites. The synthesis of CNF/ γ -Fe₂O₃ leads to an increase in the hydrophilicity of CNF and magnetic properties at room temperature.

1. Introduction

In recent years, carbon nanofibers (CNFs) have been implemented in a wide variety of applications from aerospace materials as reinforcement or conductive fillers, used to improve the mechanical, electrical, and thermal properties of polymer matrix composites to energy industry as anode materials for applications in Li-ion batteries to improve energy storage properties and life-cycle. CNFs, as well as the multiwalled nanotubes (MWNTs) and the single-walled nanotubes (SWNTs), are the most common components of the nanocomposites [1–15]. Industrial products made of reinforced polymers demand improvement of the mechanical properties to preserve the structural integrity and the electrical conductivity to dissipate static electricity [16]. However, the above-mentioned carbon nanostructures differ considerably in terms of morphology, size, and price. Applied Sciences, Inc. (ASI) has performed a study which

reports the advantages of using CNFs instead of CNTs. Stacked-cup carbon nanotubes, also known as CNFs, have a structure, which consists of graphene layers stacked in conic sections with walls angled 20° along the axis of the fiber. This structure provides exposed edge planes on the interior and exterior surfaces of the fiber, which promotes the chemical functionalization. In contrast, the CNT consists of an assembly of concentric cylinders of graphene. CNFs typically have a few tens of microns length and diameters from 30 to 100 nm with an aspect ratio greater than 100. On the other hand, CNTs typically have smaller diameters and lengths in comparison with CNF. CNFs can be commercially available at a much lower cost and high volumes in comparison with CNTs. The CNF material is easy to handle and overcomes all the main challenges resulting from dispersion, processing, and handling normally associated with other carbon nanomaterials (CNMs) [17–20]. The CNF material is considered as a reinforcement

or conductive nanofiller for preparation of composites due to the nanofiber mechanical (tensile strength ~ 3 GPa), and physical properties (electrical conductivity ~ 103 S/cm) [21].

The alignment and dispersion of the CNFs in the matrix are the main challenges to obtain the desired properties. These challenges can be overcome by changing the CNFs chemical composition to create a nanohybrid material with unique characteristics, which allow easy handling. It has been reported that functionalized carbon nanofibers can be aligned in composite materials using AC electric field, which leads to significant decrease of the electrical resistivity in the direction of the aligned CNFs and to increase of the compressive modulus and compressive strength [22]. It is well known that a magnetic field may align small and light objects parallel to that field. Therefore, the use of nanohybrid material with magnetic properties in a polymer matrix composite can significantly enhance the composite structure properties through alignment of the nanomaterial in the polymeric matrix by magnetic field during the material processing. The fabrication of carbon nanohybrid materials composed with metal oxides has been widely studied implementing the use of different techniques such as electrospinning followed by a thermal treatment and modified sol-gel. Previous researches have reported the application of electrospinning technique to fabricate CNF/ γ -Fe₂O₃ for Li-ion batteries as high performance anode material. On the other hand, the use of modified sol-gel technique has also been reported using MWCNTs as the base to create a nanohybrid material in order to improve the material properties of polymers [8–15, 23–25]. Nevertheless, no researches have been reported about the implementation of the same technique using CNFs, which could result in better synthesis results due to the CNF's morphology, in addition to the low cost of the nanohybrid material. CNFs have been functionalized with magnetite (Fe₃O₄) by a coprecipitation method in order to align them in an epoxy matrix, resulting in a higher electrical conductivity along the direction of the alignment [26]. Maghemite, γ -Fe₂O₃, is a member of the same iron oxide family as magnetite (Fe₃O₄) and the main difference between these two oxides is the presence of only ferric (Fe³⁺) ions in the maghemite allotropic form, while both ferrous (Fe²⁺) and Fe³⁺ ions are found in magnetite. Maghemite cannot be oxidized at normal operation conditions and is more stable than magnetite; moreover, it has ferromagnetic properties and can be used to impart magnetic properties in functionalized CNFs. In this work, we describe the synthesis of maghemite carbon nanofibers (CNF/ γ -Fe₂O₃) via a modified sol-gel technique applying an iron salt as a precursor, followed by calcination.

The resulting nanohybrid material was characterized and compared to the starting CNFs and oxidized CNF materials using dispersion analysis, magnetism exposure, energy dispersive X-ray fluorescence (EDXRF), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) X-ray diffraction (XRD), and Raman spectroscopy.

TABLE 1: Carbon nanofiber properties.

Parameter	Quantity
Fiber diameter, nm	≈ 100
CVD carbon overcoat present on fiber	Slight
Surface area, m ² /g	45
Dispersive surface energy, mJ/m ²	85
Moisture, wt. %	<5
Iron, ppm	<14,000
Polyaromatic hydrocarbons, mg PAH/mg Fiber	<1
Surface area, m ² /g	Slight

2. Materials and Methods

2.1. Materials. The CNFs used in this study were Pyrograf PR-24-XT-PS from Applied Sciences, Inc. According to the specifications, these CNFs have an average diameter of about 100 nm and a minimal chemically vapor deposited (CVD) layer of carbon on the surface of the fiber over a graphitic tubular core. The CNF properties are shown in Table 1. The chemicals used for the synthesis of CNF/ γ -Fe₂O₃, such as propylene oxide, iron (III) nitrate nonahydrate (Fe(NO₃)₃•9H₂O), and sulfuric and nitric acid, were purchased from Valrep, SA de CV and used as received.

2.2. Functionalization. CNFs were immersed in a mixture of H₂SO₄/HNO₃ (3:1) at room temperature. The mixture was gently homogenized by magnetic stirring for 5 min followed by 3 h in an ultrasonic bath and upheld for 24 h. The mixture was then 50% diluted with deionized water and filtered with a 0.20 μ m polytetrafluoroethylene (PTFE) membrane with the aid of a vacuum pump. The oxidized CNFs (CNF-COOH) were rinsed in deionized water until reaching pH 5.5 and dried overnight under a vacuum at 50°C [27–33].

2.3. Synthesis of CNF/ γ -Fe₂O₃. Synthesis of the CNF/ γ -Fe₂O₃ was performed by first adding 0.65 g of Fe(NO₃)₃•9H₂O to 20 ml of ethanol and magnetic stirring until the Fe(NO₃)₃•9H₂O was dissolved completely. The iron salt solution was then added to a suspension of oxidized CNF (CNF-COOH) with a mass ratio of 4:1 (Fe(NO₃)₃•9H₂O:CNF), stirred, and sonicated for 90 min. 20 mL of 1.2 mM sodium dodecylbenzenesulfonate (NaDDBS) was added to the solution and stirred for 30 min. Then 1.2 mL of propylene oxide was added and the stirring continued for 30 min. The resulting mixture remained in an oven for 3 days at 100°C. The powder was repeatedly centrifuged at 7000 rpm, for 5 min each time, to reach the ethanol pH. After this, the powder was dried overnight at 50°C. As a final step, the powder was calcined in a furnace under an argon atmosphere at both 500°C and 600°C for 2 h.

Electrospinning technique followed by a thermal treatment is the simplest low cost method for fabrication of CNFs at scalable rate. The fabrication of CNF/ γ -Fe₂O₃ with outstanding results has been demonstrated by other researches in which γ -Fe₂O₃ is attached to the CNFs outer surface [9]. Nevertheless, electrospinning technique will result in

TABLE 2: EDS mass percentage results of CNF/ γ -Fe₂O₃ specimen.

Spectrum	Carbon (C)	Oxygen (O)	Iron (Fe)	Phosphorus (P)	Sulfur (S)	Sodium (Na)
1	44.06	12.51	25.33	1.19	2.73	4
2	36.22	27.33	45.17	1.66	4.23	7.97
3	41.8	12.11	27.92	1.24	2.89	4.15
4	52.49	27.84	51.32	1.06	2.58	4.71
Mean mass (%)	43.6425	19.947	37.435	1.2875	3.1075	5.2075
Sigma	6.7563	8.8230	12.7761	0.2597	0.7590	1.8668

CNFs with a specific morphology (solid fibers) [10]. On the other hand, the use of sol-gel technique has the flexibility to be implemented in different carbon nanomaterials (CNMs) which could bring different results depending on the CNMs used due to differences in morphology allowing the attachment of metal oxides during the synthesis on the inner and outer surfaces of the CNMs in the case of hollow CNFs.

2.4. Characterization Techniques. The elemental composition was analyzed by EDXRF using a Shimadzu EDX-7000. EDS was performed using a Tescan Lyra 3 XMU scanning electron microscope and the chemical composition was determined by XPS using a SPECS high resolution spectrometer with a Mg K α 1.2 ($h\nu = 1253.6$ eV) anode X-ray source operated at 15 kV and an emission current intensity of 20 mA, respectively. Three specimens were prepared for each analysis, CNF, CNF-COOH, and CNF/ γ -Fe₂O₃.

The pressure in the XPS analysis chamber was maintained at 1×10^{-7} Pa throughout the measurements. The analyzed regions were Fe 2p_{3/2}, Fe 2p_{1/2}, O 1s, and C 1s. The binding energy (BE) scale of the spectrophotometer was calibrated using an Au 4f_{7/2} (84.0 eV, BE) substrate. The full width at half-maximum (FWHM) obtained for the Ag 3d_{5/2} (368.3 eV BE) line was 0.9 eV. High resolution spectra were recorded using 20 eV pass energy. A Shirley background subtraction was made to obtain the XPS signal intensity.

SEM and TEM characterizations were carried out using Tescan Lyra 3 XMU and JEOL 2010 transmission electron microscope operating at 200 kV, respectively. In order to compare the suspension stability between specimens, 15 mg of CNF, oxidized carbon nanofibers, and CNF/ γ -Fe₂O₃ were dispersed in 10 ml of deionized water via sonication for 20 min and upheld for 24 h. The magnetic attraction of the CNF/ γ -Fe₂O₃ was tested by placing a magnet close to a glass container with carbon nanomaterial.

3. Results and Discussions

EDXRF analysis results showed a significant difference in terms of iron content between the CNF/ γ -Fe₂O₃ and the rest of the samples. The CNF/ γ -Fe₂O₃ presented an iron content of 86.91% mass percent, which represents an increase of 55% compared to the rest of the specimens. The increment of iron in the CNF/ γ -Fe₂O₃ sample may be attributed to the presence of iron (III) oxide (γ -Fe₂O₃). Figure 1 shows the elemental analysis results for the CNF, oxidized CNF, and CNF/ γ -Fe₂O₃ specimens.

FIGURE 1: Elemental analysis of carbon nanomaterials.

SEM/EDS techniques were used to compare the morphology and composition of CNF, oxidized CNF, and CNF/ γ -Fe₂O₃ specimens. The magnetic carbon nanofibers exhibit “cumulus” seen as bright spots in the SEM image (Figure 2(c)), while the other two types of fibers (Figures 2(a) and 2(b)) do not present this feature. The EDS chemical analysis performed during the SEM analysis of CNF and oxidized CNF (Figures 2(a) and 2(b)) presents a high peak corresponding to carbon and a small additional peak related to oxygen. The spectrum obtained from cumulus region in the CNF/ γ -Fe₂O₃ specimen (Figure 2(c)) showed, in addition to the C peak, the presence of well-defined peaks of O, Fe, Na, P, and S. Table 2 gives results for the mass percentage of elements obtained in four different regions on the maghemite carbon nanofiber, marked with circles in Figure 2(c). Higher iron and oxygen concentrations were found in the cumulus regions, 2 and 4, with values of 45.17, 27.33%, 51.32, and 27.84%, respectively. The results presented in Table 2 may be explained by presence of iron (III) oxide (γ -Fe₂O₃). Indeed, γ -Fe₂O₃ has a molar mass of 159.687 g/mol of which 30% is due to oxygen and 70% to iron with iron to oxygen mass percentage ratio (O : Fe) of 0.43. The results obtained by EDS for the mean mass percentage of oxygen and iron, 19.947 and 37.435%, give a value of 0.53 for the (O : Fe) ratio, similar to

FIGURE 2: (a) EDS analysis of CNF specimen, (b) oxidized CNFs, and (c) maghemite carbon nanofiber (CNF/ γ -Fe₂O₃). Insets show SEM images of analyzed area, respectively.

that of γ -Fe₂O₃. The small percent of Na, P, and S detected in the CNF/ γ -Fe₂O₃ specimen is a result of the chemicals used in the CNF/ γ -Fe₂O₃ synthesis. EDS analysis showed the presence of iron in the CNF/ γ -Fe₂O₃ specimen, which was not observed in the rest of the specimens (see Figure 2). SEM images of the magnetic carbon nanofiber specimen exhibited “cumulus” on the surface (see Figure 2(c)) in which the EDS data were collected. It was found that the highest mass percentage of iron comes from the cumulus areas, which may be explained by the presence of iron (III) oxide (γ -Fe₂O₃).

Additional information for the CNFs and CNFs/ γ -Fe₂O₃ morphology was obtained by transmission electron

microscopy (Figure 3). The image of the CNF specimen (Figure 3(a)) shows bare fiber walls without attached particles, in agreement with the specification of the starting material. In contrast, the CNFs/ γ -Fe₂O₃ specimen exhibits high concentration of cumulus attached to the inner and outer surface of the walls (Figure 3(b)). The inset in Figure 3(b) shows a high resolution TEM image of the CNF/ γ -Fe₂O₃ specimen. Randomly distributed cumulus of maghemite nanoparticles is clearly seen. The γ -Fe₂O₃ nanoparticles are distributed very close to each other due to the absence of reactive species used during the functionalization process which can cause electrostatic interactions. From the high resolution image the outer diameter of the CNF was determined to be about 70 nm,

FIGURE 3: (a) TEM image of CNF specimen and (b) maghemite CNF (CNF/ γ -Fe₂O₃). Inset in (b) shows high resolution image of CNF/ γ -Fe₂O₃.

close to the specification value, the wall thickness was in the 13–15 nm range, and the maghemite nanoparticle size was 10 ± 1.5 nm in the inner space of the hollow CNFs and up to 22 nm for the cumulus on the external surface [34–36].

XPS spectra were obtained on CNF, functionalized CNF, and CNF/ γ -Fe₂O₃ specimens in order to determine the chemical composition and the degree of oxidation, iron (II) or iron (III), of the iron oxide nanoparticles. Figure 4(a) shows XPS survey spectra of the three materials with characteristic peaks for Fe 2p_{3/2} and Fe 2p_{1/2} in addition to carbon C 1s (285 eV) and oxygen O 1s. The positions of the Fe 2p_{1/2} and Fe 2p_{3/2} peaks, determined from the high resolution XPS spectrum (Figure 4(b)), were at 725 and 711 eV BE, respectively, which are in good agreement with the values reported for γ -Fe₂O₃ in the literature [37–39]. High resolution spectra of the O 1s peak are presented in Figure 4(c). The O 1s peak of the CNF material has a maximum at about 533 eV, which can be related to water absorption [40]. The functionalized CNF spectrum was deconvoluted in two peaks, at 533 eV and at 531.2 eV, which corresponds to OH hydroxyl group [41]. The spectrum of CNF/ γ -Fe₂O₃ was deconvoluted in three peaks, the water related and hydroxyl group peaks and one additional peak resulting from oxygen in iron oxide at 530.1 eV [42–44]. The positions of the Fe 2p_{1/2} and Fe 2p_{3/2} peaks support the formation of γ -Fe₂O₃ in the carbon nanohybrid material.

The three types of specimens were characterized by X-ray diffraction technique. The specimen with iron oxide nanoparticles (curve (3), Figure 5) presents in addition to the (0 0 2) peak of CNF [45, 46] some characteristic peaks for both maghemite and magnetite materials. The XRD spectra do not provide direct evidence for the oxide phase since the intensity of the maghemite specific peaks (2 1 0) at 23.77° and (2 1 1) at 26.10° is very low. Moreover, the second peak is partially covered by the CNF (0 0 2) peak at 26°. An indirect indication can be obtained from the shape of the high-angle

peaks (5 1 1) and (4 4 0). It has been shown by Kim et al. [47] that these peaks are doublets in case of mixture of magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃) phases; for example, the maximum of the (5 1 1) peak varies from 57° for pure Fe₃O₄ to 57.3° for pure γ -Fe₂O₃. For Fe₃O₄/Fe₂O₃ mixture, the intensity of each of these peaks varies, depending on the concentration of the corresponding oxide. The experimental data of each of the (5 1 1) and (4 0 0) peaks in Figure 5 were successfully fitted with a single symmetric peak with maximum at 57.3° and 62.8°, respectively, which is an indirect indication for formation of γ -Fe₂O₃ attached to the CNF during the synthesis. The inset figure in Figure 5 shows the fitting of the (4 0 0) peak.

Figure 6 shows the Raman spectra of CNF, CNF-COOH, and CNF with iron oxide nanoparticles. The spectra of the first two materials display only two broad peaks with maximums at ~ 1315 and 1595 cm⁻¹ corresponding to the two main bands of CNF: the disorder induced D band and the graphite mode G band [45, 48]. In contrast, the specimen with iron oxide nanoparticles shows five additional peaks, at ~ 220 , 290, 400, 485, and 598 cm⁻¹. Peaks, with positions close to the last two bands, have been observed in the spectrum of highly crystalline and monodisperse maghemite nanocrystallites with size of 11 nm [49]; the average size of the synthesized nanoparticles in this work was about 10 nm. The other three peaks (curve (3), Figure 6) are characteristic for hematite, 225, 291, and 411 cm⁻¹ [50]. It has been shown that very low laser power (<1 mW) has to be used in Raman measurements in order to avoid transformation of maghemite to hematite [50, 51]. The measured spectrum of the sample with iron oxide nanoparticles may be explained by the laser power used in these experiments, 12 mW, which most likely caused transformation of the major part of maghemite to hematite.

The synthesis of CNF/ γ -Fe₂O₃ leads to an increase in the hydrophilicity of the CNF. Before synthesis, the dispersion of the CNF in aqueous media was very poor, while after

FIGURE 4: (a) XPS survey spectra of CNF/ γ -Fe₂O₃, CNF-COOH and CNF; high resolution XPS spectra, showing (b) Fe 2p_{1/2} and Fe 2p_{3/2} regions and (c) O 1s region.

synthesis it improved significantly (see Figure 7(a)). This improvement in dispersion is associated with the functionalization procedure used during the synthesis of the CNF/ γ -Fe₂O₃ material. However, the CNF-COOH sample showed a much better dispersion than CNF/ γ -Fe₂O₃ after 24 h, which may be due to the molecular weight increase after the inclusion of γ -Fe₂O₃ to the CNF (see Figure 7(b)).

The three carbon nanofiber materials (CNF, CNF-COOH, and CNF/ γ -Fe₂O₃) were exposed to a magnetic field created by a commercial magnet. The CNF/ γ -Fe₂O₃ specimen showed magnetic properties at room temperature in contrast to the rest of the specimens, which may be

explained by the presence of γ -Fe₂O₃ in the nanohybrid material (see Figure 8).

4. Conclusions

Synthesis of carbon nanofibers functionalized with maghemite nanoparticles via a modified sol-gel technique was successfully performed. The formation of γ -Fe₂O₃ was confirmed by EDXRF, EDS, XPS, XRD, and Raman spectroscopy. In particular, the iron content in the CNF and CNF-COOH determined using EDXRF was 40% and 39%, respectively. According to the supplier's information,

FIGURE 5: XRD spectra of CNF (curve (1)), CNF-COOH (curve (2)), and CNF/ γ -Fe₂O₃ (curve (3)). The inset shows fitting of the (4 0 0) peak with a single symmetric peak with maximum at 62.8°.

FIGURE 6: Raman spectra of CNF (curve (1)), CNF-COOH (curve (2)), and CNF/ γ -Fe₂O₃ (curve (3)).

the CNF material contains iron at a concentration of <14000 ppm. However, after the synthesis process the iron content in the nanohybrid material increased up to about 87%, more than double than the concentration found in the CNF and CNF-COOH specimens.

One of the important physical properties of γ -Fe₂O₃ is its high magnetic permeability. The results of the magnetism experiment showed that only the nanohybrid material reacted to the presence of a magnetic field, which is another indication for the formation of γ -Fe₂O₃. From these results we can conclude that there was a high efficiency of the functionalization methodology applied. The synthesized CNF/ γ -Fe₂O₃ material shows improved dispersion in aqueous media and magnetic properties at room temperature, which make it

a promising candidate for fabrication of composite structures with improved characteristics, high temperature conductive coatings, or biosensors.

The morphology obtained by SEM and TEM indicates formation of maghemite nanoparticles with an average size of 10 ± 0.5 nm homogeneously distributed on the inner and outer surfaces of the functionalized carbon nanofibers. The EDS analysis performed on the cumulus areas gave the highest mass percentage of iron. XPS results support the formation of γ -Fe₂O₃ in the carbon nanohybrid material, showing the characteristics peaks for Fe 2p_{1/2} and Fe 2p_{3/2} at 725 and 711 eV BE, respectively. XRD results indicate single symmetric 5 1 1 and 4 0 0 peaks with maximums at 57.3° and 62.8°, respectively, supporting the formation of

FIGURE 7: (a) Carbon nanomaterials just dispersed and (b) carbon nanomaterials after 24 h.

FIGURE 8: (a) CNF specimen, (b) oxidized CNF, and (c) maghemite carbon nanofiber (CNF/ γ -Fe₂O₃).

γ -Fe₂O₃. Raman spectroscopy showed essential differences between the CNF, CNF-COOH, and CNF/ γ -Fe₂O₃ samples. The characteristic peaks of graphite (G) band and disorder induced (D) band were observed in the spectra of all samples. However, the CNF/ γ -Fe₂O₃ spectrum showed five additional peaks in the range of 200–600 cm⁻¹; two of them, at 485 and 598 cm⁻¹, may be attributed to maghemite nanocrystallites with size of ~10 nm, the average size of the nanoparticles in this study.

One of the important physical properties of γ -Fe₂O₃ is its high magnetic permeability. The results of the magnetism experiment showed that only the nanohybrid material reacted to a magnetic field, which is another indication for γ -Fe₂O₃ formation. From these results we can conclude that there was a high efficiency of the functionalization methodology applied. The synthesized CNF/ γ -Fe₂O₃ material shows improved dispersion in aqueous media and

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Conflicts of Interest

The authors declare no conflicts of interest.

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