

Influence of Exfoliation on Multi-walled Carbon Nanotubes in Their Performance as Electrode Support Material

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ABSTRACT

In this work physical and electrochemical characterization of modified carbon nanotubes are reported. Modification consisted in two different functionalization processes and an exfoliation process. After functionalization, carbon nanotubes (CNT) obtained a better crystalline quality and purity, however, exfoliation granted a high defects density on CNT's surface. After treatment, IR and XPS analysis reveled that exfoliated CNT (*e*-CNT) granted functional groups onto their surface, mainly carbonyl and carboxyl groups. Finally, cyclic voltammetry measurements confirmed that exfoliated CNT have the biggest electrochemical active surface, which together with carbonyl and carboxyl groups, can provide a greater density of nucleation sites to metal nanoparticles than the commercial support material: carbon Vulcan.

Keywords: Carbon nanotubes (CNT), Capacitance, Electrochemical surface area



Introduction

Electrode material based on carbonaceous compounds has been widely applied in electrochemistry since their special properties, remaking their surface chemistry, which make them a proper choice to determine a wide range of substances in electrocatalytic area.

By the other hand, since their discover, carbon nanotubes (CNT) has been intensively studied due to their excellent properties, such as high specific surface area, high electronic conductivity, outstanding chemical and electrochemical stability and so on [1-5].

Recently, CNT have received considerable attention as the supports of noble metal catalysts in heterogeneous catalysis, such as PEM fuel cells. The interaction between noble metal nanoparticles and CNT in nanohybrids induces a peculiar microstructure or modification of the electron density of the noble metal clusters, and enhances the catalytic activity [1].

It is well known that for CNT without surface modification, there are insufficient binding sites for anchoring the precursor of metal ions or metal nanoparticles, which usually leads to poor dispersion and large metal nanoparticles, specially under high loadings conditions. To introduce more binding sites and surface anchoring groups, surface functionalization of CNT is generally carried out [1].

Because of the pore and surface structures of CNT play an important role in electrochemical activity, the understanding of the surface chemistry and the pore structure of CNT are integral for their optimal use.

In this work, the data obtained from Raman spectroscopy, Electron Microscopy and X-Ray diffraction are related with the enhance electrochemical performance of modified CNT.

Experimental

1.1. Functionalization of CNT

Pristine carbon nanotubes (M1) were synthetized by Chemical Vapor Deposition (CVD) technique by research group. Functionalization consisted in two different processes. At the first one, 100mg of M1 were weighed and suspended into a HNO_3 solution (37mL of concentrated HNO_3 /450mL of distilled water at room temperature). They were called M2. At the second treatment, the same quantity of M1 was suspended into a mix of acids (27mL of concentrated H_2SO_4 + 10mL of concentrated HNO_3 /450mL of distilled water at room temperature). They were called M3. Both samples were sonicated at 42kHz at room temperature for 20min. Then samples were washed out with distilled water many times and finally filtrated at vacuum.

1.2. Exfoliation of CNT

250mg of NTC were weighed and dispersed into 15mL of concentrated H_2SO_4 and stirred for 1hr. Then 1.5g of KMnO_4 was added at 50°C . When all KMnO_4 were consume, the solution was



quenched by adding 40mL of deionized water and 30% H₂O₂. Exfoliated NTC (M4) were extracted by centrifugation and vacuum filter, washed out them with distilled water.

1.3. Raman spectroscopy

The Raman spectra were obtained using a Horiba Jobin Yvon Spectrometer HR 800 with a laser of 532 nm in the range of 100-3100 cm⁻¹.

1.4. X-Ray Diffraction

X-ray diffraction (XRD) analyses were carried out with a Bruker D8/Focus X-ray diffractometer with Cu-K α radiation.

1.5. Field Emission Scanning Electron Microscopy

A Field Emission Scanning Electron Microscope (FESEM) JEOL JSM-6701F, coupled with a detector for microanalysis Energy Dispersive Spectroscopy (EDS) was used for morphology study.

1.6. Cyclic Voltammetry

Cyclic voltammetry measurements were carried out in a typical three-electrode electrochemical cell, with Hg/HgSO₄ as reference electrode (E=0.680 NHE) and a Pt mesh as the counter electrode. For working electrode, a catalytic ink was prepared by weighing 1 mg of each material under study, which was subsequently mixed with 8 μ L of Nafion® and 60 μ L of absolute ethanol. This mixture was stirred for 15 minutes in an ultrasonic bath to generate a homogeneous suspension. Finally, 8 μ L of said suspension were carefully impregnated on a glassy carbon electrode (geometric area of 0.196 cm²) to form a thin film. A 0.5M H₂SO₄ aqueous solution was used as electrolyte. Finally, the electrochemical cell was bubbled with Ar gas to displace the dissolved oxygen. Corresponding measurements were carried out in a potentiostat-galvanostat GPES AutoLab connected to a PC, evaluating a potential range of 0 to 1.23 V vs. NHE, with scanning speeds from 10 to 100 mV s⁻¹. Note that the potentials obtained were reported compared to NHE. For this technique, commercial carbon Vulcan XC76 (M5) was used as a reference material, because of it is the material support to commercial electrocatalyst.

Results and discussion

3.1 Crystalline quality and purity

Raman Spectra is shown in Fig. 1. All samples presents the characteristic signals of CNT: D (present at about 1300 cm⁻¹), G (1600 cm⁻¹) and G' (near 2650 cm⁻¹) bands [6-14]. By the other hand, in the low frequency range of 140-350 cm⁻¹, there is a signal corresponding to the respiratory mode in the radial direction (RBM), which is characteristic of single-walled CNT [6], suggesting the presence of this type of CNT in all samples.



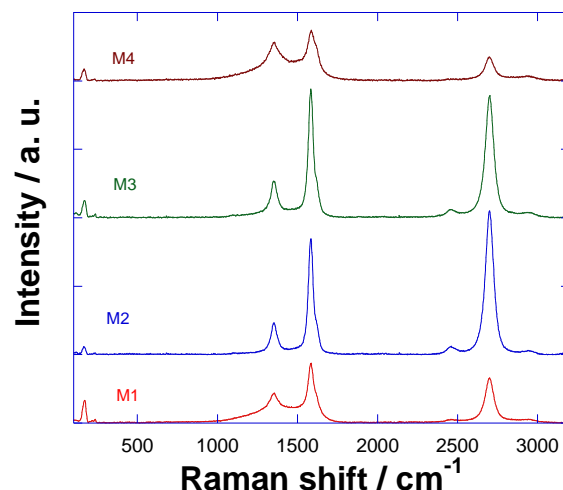


Fig. 1. Raman spectra of M1, M2, M3 and M4

From Fig. 1, the corresponding spectra M1 exposes the existence of impurities such as amorphous carbon and catalyst particles (area under the bands D and G), showing a crystallinity index (I_D/I_G) of 0.50. Subsequently, it is evident that M2 and M3 have increased the crystalline quality significantly, since I_D/I_G has decreased in both cases (0.27 and 0.28, respectively) and the intensity of G' has increased considerably, suggesting a long-range order on CNT's walls [6-8]. Simultaneously, these chemical treatments have removed impurities observed in M1. However, M4 reveled a reduced crystalline quality ($I_D/I_G=0.77$). This decrease could be attributed to a high defects density on the walls of the CNT [6-14] due to the treatment damage strongly the carbon lattice. By the other hand, there is a very high degree of disorder, because the intensity of the band G' has decreased substantially. X-Ray diffraction patterns are reported in Fig.2.

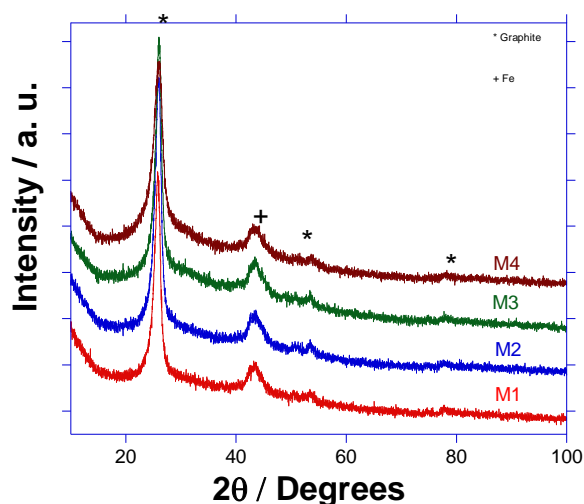


Fig. 2. X-Ray diffraction patterns of M1, M2, M3 and M4

At 26.6° , it is possible to observe the strongest reflection signal of hexagonal graphite, which is associated directly with CNT. Another reflections attributed to graphite from CNT are visible at 54° and 77.5° . In addition, at 43.5° was detected a reflection related with cubic Fe, which its presence was suggested by Raman spectra.

Analysis of the peak detected at 44° is shown in Fig. 3. It is well known that Fe characteristic reflection signal appears at 44.6° , therefore, this shift suggests the formation of a solid solution C/Fe or the presence of a semi-stoichiometric iron carbide, since carbon is introducing at iron cubic lattice.

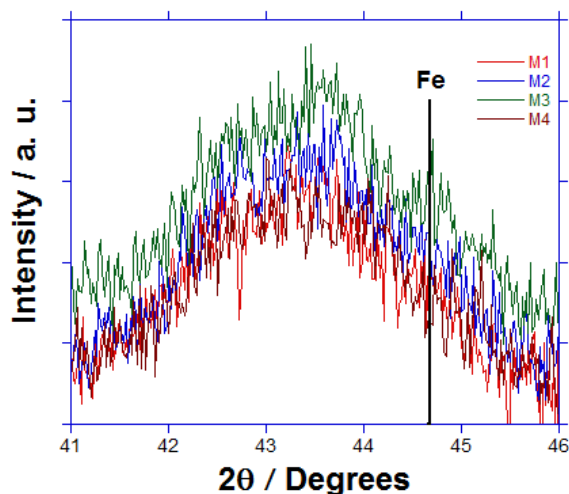


Fig. 3. Fe peak analysis of M1, M2, M3 and M4

3.2 Morphology

Fig. 4 shows the FESEM micrographs of the samples under study. In M1 exists the characteristic tubular morphology, observing a preferential orientation growth, however, it is evident the presence of several defects onto surface, being consistent with Raman measurement. CNT's size is relatively long, because of their average length is on micrometers order. The M2 micrographs show a tubular structure with pronounced curvatures, respecting the oriented growth. Removal of defects onto surface is remarkable, following up with the I_D/I_G increment and elimination of area under D and G bands of Raman spectra. The length in this sample is very similar to that observed in M1. Analyzing the M3 micrographs, the tubular structure is very similar to that seen in M1, with the small difference that the density of defects was reduced significantly, which was predicted from the Raman spectra. Concerning the length, it can be seen that some tubes have a few micrometers because exit broken tubes. Finally, M4 micrographs reveal conservation of aligned tubular structure and defects have mostly disappeared, however, CNT's walls are irregular because of the damage that exfoliation caused.



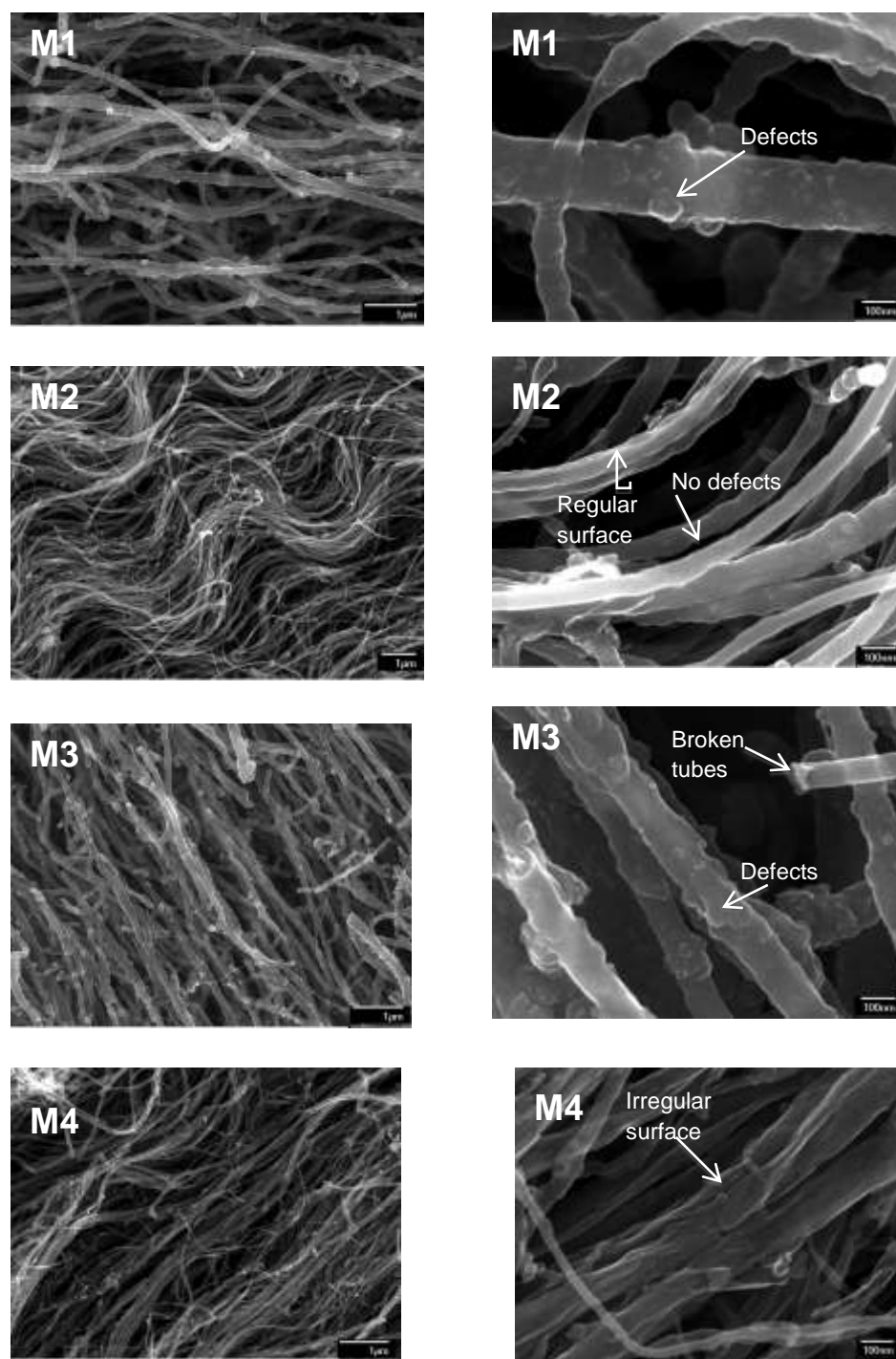


Fig. 4. FESEM micrographs of M1, M2, M3 and M4



This observation has a relationship with Raman results. Despite carbon defects have mostly disappeared, exist a higher amorphous carbon quantity, therefore, area under D and G bands in Raman spectra of M4 rose considerably, and I_D/I_G increased substantially. Since G' band intensity results from a two-phonon process it is plausible that its intensity should decrease as the sample becomes less ordered (i.e., more impurities present) not allowing for the coupling effect which is necessary for the two-phonon process [7]. Then, microanalysis by EDS (see Table 1) revealed the composition of samples, demonstrating existence of Fe, catalyst used to CNT growth, and predicted by XRD measurements. As may be evident, M2 is the one who has fewer quantity of Fe and lower crystallinity index, concluding that treatment with HNO_3 , which is allowed to have the best crystalline quality in CNT, however, there is considerable quantity of oxygen in M4, as there is a small amount of sulfur. These two elements were not found in the other samples using this technique.

Table 1. EDS results (%w)

	C	O	Fe	S
M1	97.56	--	2.44	--
M2	98.21	--	1.79	--
M3	97.60	--	2.40	--
M4	87.62	11.05	0.38	0.95

3.3 Electrochemical characterization

Fig. 5 presents cyclic voltammograms of all samples. These graphics were obtained at 100mV s^{-1} , by reporting the last one of 10 applied cyclics, noting minimum waste current density. By observing M1, its evident the presence of an electroactive specie, because of there is an reversible redox process between 0.2 and 0.4 V, where current density intensities, in both directions, are similar (approximately 0.2 mA cm^{-2}). According to X-Ray diffraction patterns and EDS results, these signals can be attributed to agglomerated Fe particles. By analyzing the rest of the profile, exists an electrochemical stability, since there is no considerable increases in current density and the whole signal possess an almost rectangular shape, as expected for a carbon electrode material showing a capacitance characteristic of a steady state behavior [12-18].

Regarding M2, the signals corresponding to Fe disappeared, showing a steady-state in both directions. It is noteworthy that the current density from 0.6 to 1.23 V increases discretely. Finally, it can be seen that M3 signals related to contamination by Fe disappeared, despite EDS results revel almost the same quantity of Fe than M1. This phenomenon could be attributed to the leaching of Fe onto CNT's surface. According to XRD patterns, there is a solid solution C/Fe, probably the treatment which was used for M3 was not enough strong to eliminate such contamination, as well as current density across the profile moderately increased compared to the previous ones. However,



the most important thing to mention here is the presence of two shoulders near 0.8 V. These signals can be associated with pseudo-capacitive contributions of oxygenated functional groups present in the walls of the CNT [13-17].

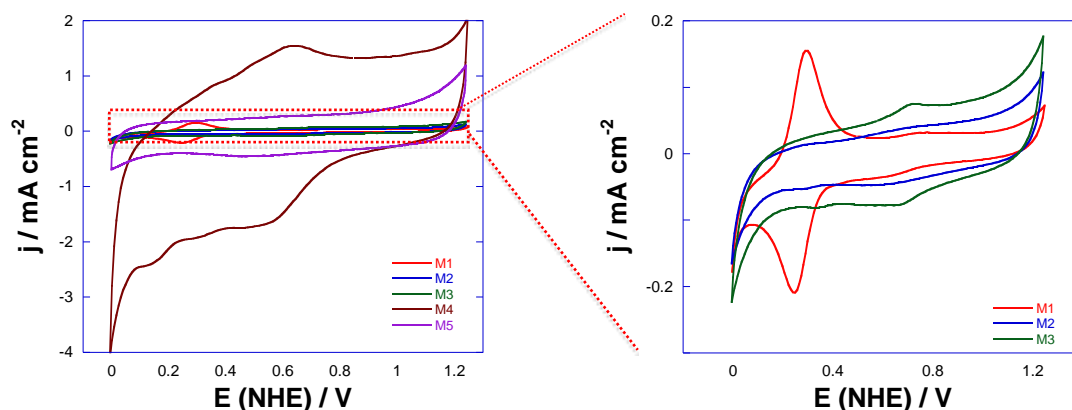


Fig. 5. Cyclic voltammograms of M1, M2, M3, M4 & M5

The increase in the current density in j vs. E profiles is an indicator that the available electrochemical area has increased [12-18]. Finally, the "shoulders" observed in M3 have a pseudo-capacitive contribution, as the oxygen-containing functional groups may react faradaic manner, increasing the current density [14-16].

By observing carefully Fig. 5, signals obtained by the three samples analyzed above practically disappear, because the registered current densities of M4 and M5 increases by one order of magnitude. For M5 it is visible the stability that comes in the range of applied potential, showing a steady state, however, about 0.5 V a very light signal related to irreversible pseudo-capacitive contributions were markedly reduced, as suggesting that this material has small amounts of oxygen-containing functional groups at their surface, in which there is an irreversible reduction. The maximum current density for this material is slightly larger 1 mA cm^{-2} in the anodic direction, while the maximum cathodic direction is greater than -1 mA cm^{-2} . Finally, the registered signals by M4 represent a very marked increase of current density respect to its precursors, having a maximum in the anodic direction of 2 mA cm^{-2} and a maximum in cathodic direction slightly lower than -4 mA cm^{-2} . The signals observed at about 0.6 V represent pseudo-capacitive contributions from the oxygen-containing functional groups on the nanotubes' walls. The current density profile suggests that the electrochemically available area of this material far exceeds the materials discussed above, by adding the oxygen-containing functional groups present on the surface of nanotube. This analysis corresponds to the detected by EDS, since the amount of oxygen detected in M1 was zero,



while the quantity of the same element to M4 is substantially increased, peaking at 11.05 %w. Qualitatively, the capacitance of the electric double layer (DLC, area under the curve j vs. E profiles, excluding pseudo-capacitive contributions) is directly proportional to the surface area and the area of the material available electrochemically [12-18]. Fig. 6 shows DLC determination for all samples.

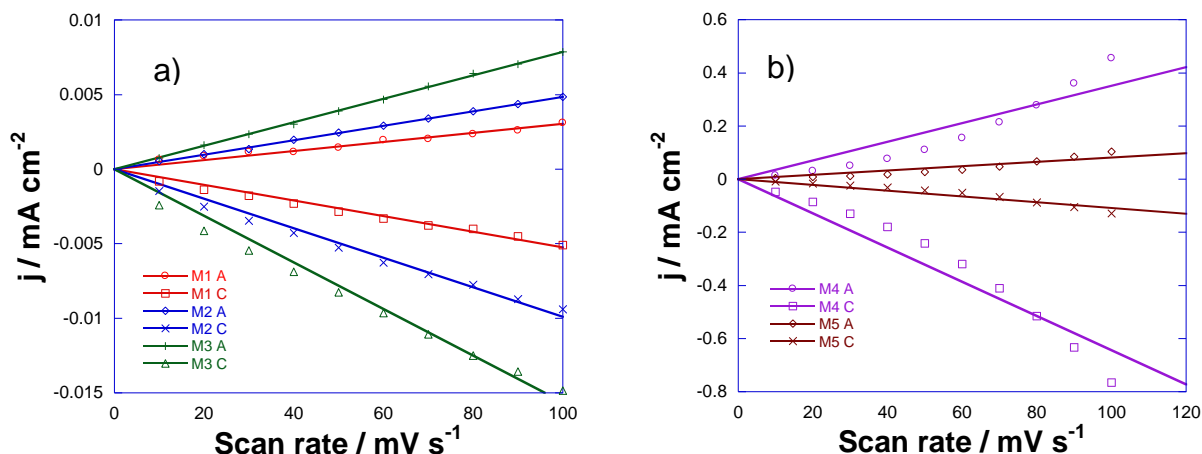


Fig. 6. DLC determination, in both directions, of: a) M1, M2 & M3; and b) M4 & M5

DLC was determined at a potential of 0.66V, reporting the response obtained in the anodic and cathodic direction. According to Fig. 6 it is evident that the value of DLC increased after chemical treatments. The increase in value of DLC from chemical treatments can be attributed to the presence of oxygenated functional groups, placing greater emphasis to the carbonyl group ($\text{C}=\text{O}$) [13]. In addition, for the particular case of M4, DLC can also be attributed to the substantial increase in the effective surface area by the increased defect density of the tubular structure exfoliated [16] having detected tracking with SEM micrographs and Raman spectra. Table 2 reports DLC values for all samples.

Table 2. DLC values ($\mu\text{F cm}^{-2}$)

	Anodic direction	Cathodic direction
M1	2.632×10^{-5}	4.323×10^{-5}
M2	4.825×10^{-5}	8.825×10^{-5}
M3	7.919×10^{-5}	1.376×10^{-4}
M4	4.770×10^{-3}	7.865×10^{-3}
M5	1.099×10^{-3}	1.299×10^{-3}



Conclusion

After functionalization treatments, CNT obtained better crystallinity, that means, less density of agglomerates and amorphous carbon onto their surface, however, exfoliation treatment granted a higher defects density onto CNT walls. By XRD measurements emerged a hypothesis that agglomerates could be a (Fe,C) solid solution. EDS results reveled the presence of Fe particles, which were almost eradicated by exfoliation treatment, however, functionalization couldn't be efficient to remove Fe particles. In addition, a high quantity of oxygen was found onto exfoliated CNT's walls, suggesting the formation of oxygenated functional groups on this sample.

Electrochemical measurements confirmed the capacitance's development while chemical treatments were applied. Moreover, exfoliated CNT showed the highest capacitance, therefore, they have the highest electrochemical surface area (beating carbon Vulcan), where there are pseudo-capacitive contributions that belongs to oxygenated functional groups onto their surface. This result suggest a possible application of this material as support material electrode for PEM fuel cells and electrolizers.

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