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A facile method to oxidize carbon nanotubes in controlled flow of oxygen at 350 °C

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Abstract

The functionalization of carbon nanotubes (CNTs) is a very important step in many applications but it is still a very complex and variable task. This work shows an efficient, easily reproducible and optimal method to introduce oxygenated functional groups to CNTs by treating them for 60' at 350 °C with a mixture of 2% oxygen in argon. The oxidized nanotubes were characterized through FT-IR, Raman and TGA to verify the quality of the oxidation and the lattice integrity of the treated CNTs. The results demonstrate that the treated nanotubes are not damaged even after introducing a significant number of new groups. This methodology could be easily tuned to functionalize other types of graphitic materials.

Keywords: Carbon Nanotubes; Functionalization; Oxidation; Dispersion

Introduction

Since carbon nanotubes (CNTs) have been rediscovered in 1991 [1] the scientific community has started a thorough investigation regarding the use of this materials in several scientific and technological applications. CNTs have extraordinary physical and chemical properties and innumerable potential applications [2]. For what concerns the use of carbon nanotubes as fillers in composite materials, the studies primarily focused on the enhancement of the mechanical and electrical properties of matrices. However, the use of CNTs in nanocomposites can be problematic. Their chemical structure leads to aggregates and bundles thus making uniform dispersion of CNTs very difficult. Moreover, interaction (adhesion) between matrix and CNTs is also badly affected [3]. To achieve a good dispersion and interaction in polar media it is necessary to functionalize the surface of CNTs with polar groups. Currently the possible functionalizations are physical coating, wet chemistry and plasma treatment. The physical coating consists in the use of surfactants to coat the surface of CNTs. Unfortunately, this method decreases the interaction between CNTs and matrix, hence worsening the final properties of the composite[4,5]. Wet chemistry consists in the use of reagents in liquid phase (e.g. acid, base or oxidants)[6–8]**.** The use of wet chemistry has different drawbacks: firstly, the crystalline structure of CNTs can be severely damaged, secondly the use of chemicals in liquid phase is not environmental friendly and a high cost can be expected in order to scale-up this method for industrial production of oxidized CNTs. Another possibility is the oxidation of CNTs using an oxidant in gas phase [9]. Oxidant gases such as O_3, CO and CO_2 are used principally to purify CNTs from metal catalysts particles used during the synthesis. The plasma treatment allows nanotubes to be functionalized with complex molecules [10], guaranteeing a good surface functionalization. Main disadvantages are the low stability of the grafted functional groups over time, and the inhomogeneous functionalization of the sample's surface [11]. The latter occurs because only the face of the sample exposed to the plasma is functionalized, unless the powder sample is uniformly stirred during the treatment [12].

This work proposes a new idea to overcome environmental problems (principally due to the use of strong acid) and to functionalize CNTs in an easy, efficient and up-scalable way. Moreover, with this method guarantees a stable and uniform functionalization. We analyzed the treated CNTs with several characterization methods and we proved the successful dispersion in a polar solvent by monitoring a suspension of treated CNTs in water. The methodology shown in this work could easily be tuned to oxidize and disperse other types of graphitic materials such as other carbon nanofibers, graphene and other commercial CNTs.

Materials and methods

Commercial carbon nanotubes Nanocyl 7000 were thermally degraded using thermal gravimetric analysis (TGA) Mettler Toledo model 1600 with a heating ramp of 5°C/min, with a mixture of 2% oxygen in argon. The gas mixtures were monitored with Mass Flow Meters Bronkhorst®. The oxidation was carried out in isotherm for 1 hour at 350, 400 and 450°C. The CNTs, before and after oxidation, were evaluated with Raman spectroscopy (Invictus 785 nm DIODE LASER, spectra acquired at 20 mW, 10 seconds, 3 accumulations). A Bruker Tensor 27 Fourier Transform Infrared (FT-IR) Spectrometer was employed to investigate the presence of the functional groups formed on the surface of the CNTs after oxidation. The CNTs were mixed with KBr in order to prepare the pellets to be analyzed, the analysis was conducted at frequencies ranging from 500 cm^{-1} to 4000 cm^{-1}. The dispersion evaluation was carried out by sonicating the nanotubes in water with an ultrasonic tip (Vibra-cell^{TM}) for 10 minutes (70 W, 35% amplitude). To better evaluate the dispersion some of the solutions were diluted with water 1:10. Electrical resistivity was evaluated using a multimeter with 2 electrodes on CNTs pellets.

Results and discussion:

The TGA results (Figure 1A) show that the degradation of the nanotubes started above 450°C. Since the thermal degradation in presence of oxygen was usually preceded by a phenomenon of surface oxidation, it was decided to investigate, in such conditions, at what temperature the highest ratio of oxidation versus degradation can be achieved. In order to do so we chose to investigate the isothermal oxidation treatment at three temperatures: 350, 400 and 450°C. By plotting the isothermal results as % weight loss vs treatment time (Figure 1B), it is evident that at 450°C there was a significant weight loss likely caused by the formation of CO and CO_2 (hence structural damage is to be expected).On the other hand, at 350 °C and 400 °C a negligible weight loss was observed. We assume that in these two cases only graphitic defects and amorphous carbon were being oxidized. As shown in Figure 1C, we tested the dispersion in water of the nanotubes oxidized in isothermal conditions and we found the best results for those treated at 350 °C. In fact, in this case the nanotubes are individually dispersed making the solution uniformly dark regardless of the dilution. The dispersion of CNTs treated at 450 °C might seem good because the concentrated solution is uniformly black, however, once the solution was diluted 1:10 it was clear that CNTs were aggregated and not well dispersed. For what concern the nanotubes treated at 400 °C, is evident the presence of aggregates and no dispersion in water. These results are probably due to a different kinetic reaction explained by Singh et al. [13]: at temperature below 350 °C the oxidation reaction is slow and controlled. Whereas at 400 °C the reaction follows a diffusion mechanism of oxygen on the surface with the opening of the tube, finally at 450 °C CNTs are broken into smaller parts (thus thermal degradation of CNTs occurs). The isothermal TGA curves reported in Figure 1B do not show a significant difference between the 350°C and the 400°C probably because the technique is not sensitive enough to detect a small, but significant for dispersion purposes, variation in the number of functionalities. Given the dispersion results, in the rest of the article we focused only on the CNTs isothermally oxidized at 350°C.

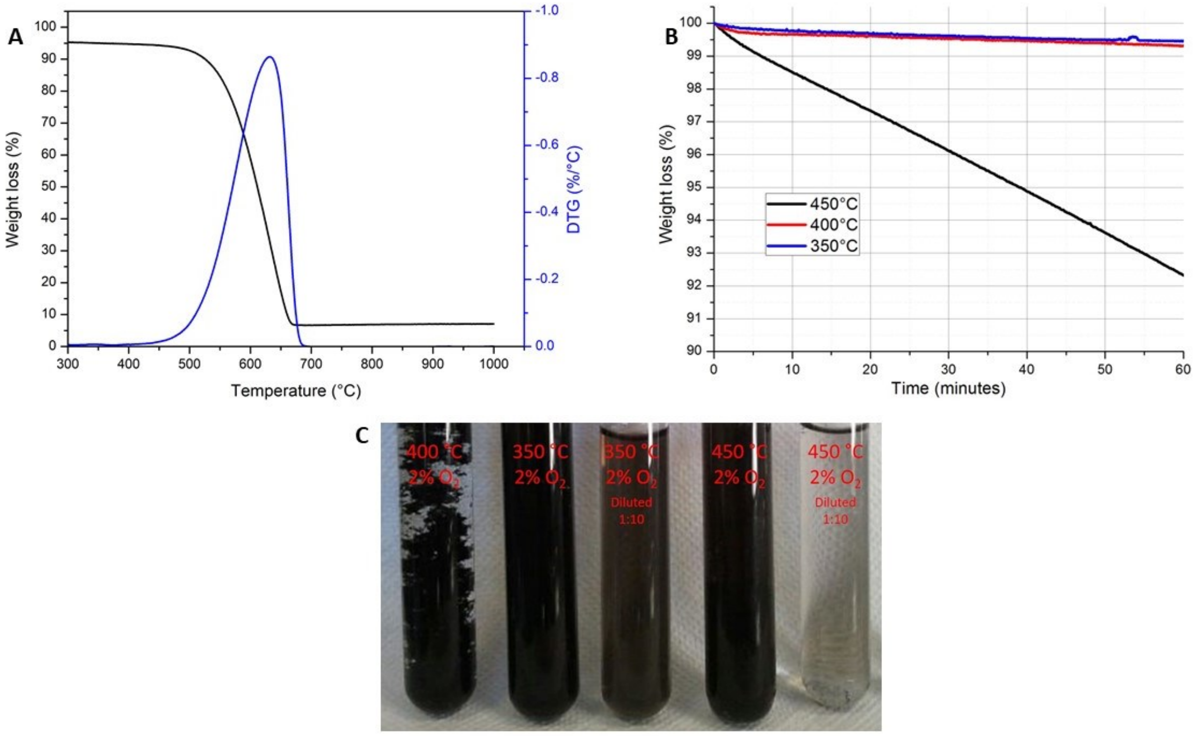

Figure 1: A) TGA curves and derivative curves (DTG) of CNTs with a ramp of 5°C/min flux of 2% O_2 98% Ar; B) Isothermal thermal gravimetric analyses at different temperatures (350°C, 400°C and 450°C); C) Dispersion of CNTs in water after isothermal treatment (some of the solutions are diluted 1:10 to better observe the degree of dispersion)

FT-IR analyses of both pristine and oxidized CNTs at 350°C are reported in Figure 2A. Regarding the oxidized CNTs, the large band around 3400 cm^{-1} is due to the introduction of –OH functional groups. At lower wavenumber the peak at 1427 cm^{-1} is generated by the stretching of C-O bond and deformation of O-H bond of carboxylic acid; while the high peak at 1224 cm^{-1} is likely due to stretching of acidic dimer or asymmetric stretching of saturated aliphatic ester. For the pristine CNTs, the two band between 2000 and 2300 cm^{-1} are due to aromatic stretching C=C. Even though we cannot determine the type of oxygenated groups we have introduced on the CNTs, the FT-IR spectra prove that oxygen containing groups have been produced on the surface of the treated CNTs, and their presence explains the successful dispersion of the treated CNTs in water. To compare the amount of lattice defects present in the CNT samples (before and after isothermal oxidation treatment), Raman spectroscopy was used (Figure 2B). No main differences can be seen comparing the two Raman spectra, except for a negligible reduction of the I_D/I_G ratio after oxidation. This reduction might indicate that, given the relatively low temperature treatment (350 °C), oxygen reacted only with the traces of amorphous carbon present on the surface of the pristine CNTs, hence producing a slight decrease in the overall number of lattice defects present in the pristine CNTs. In any case these results suggest that CNTs were not damaged by the isothermal oxidation treatment at 350°C.

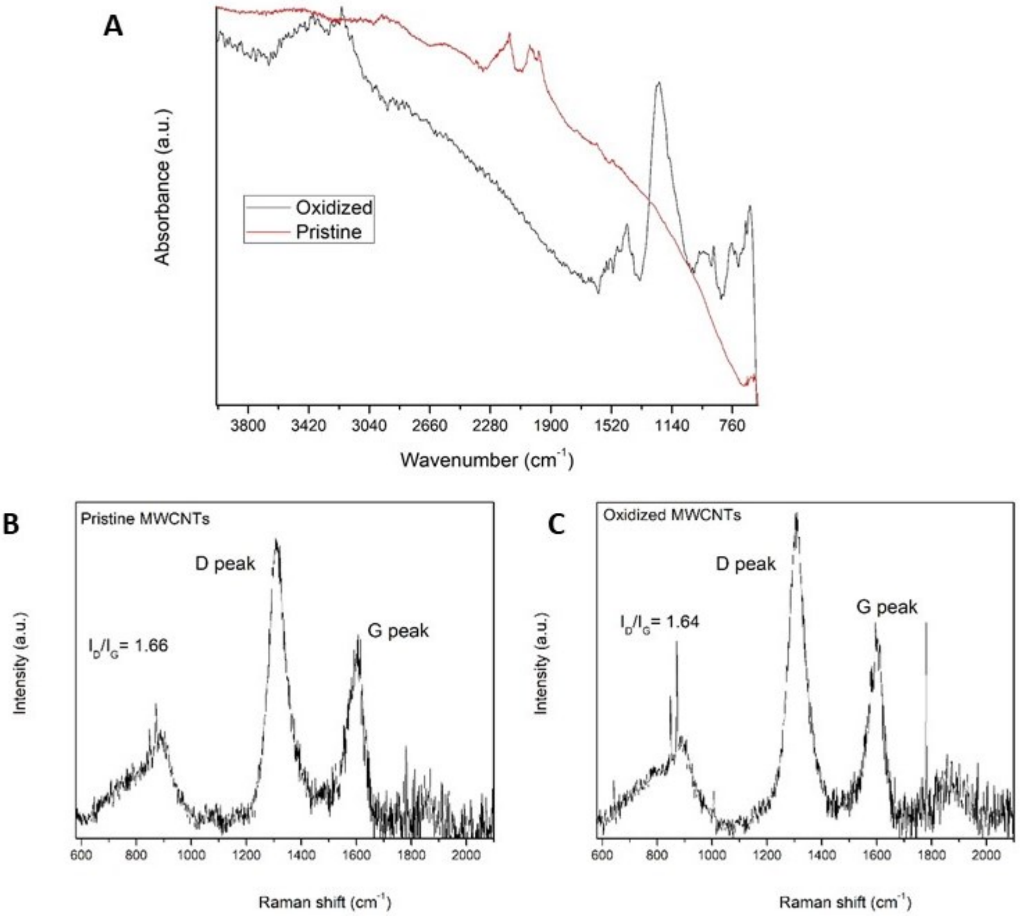

Figure 2: A) FT-IR spectrum of pristine and oxidized CNTs; C) Raman spectra and average ID/IG of the pristine MWCNTs and oxidized CNTs.

To support this hypothesis, it has been tested the oxidation, at 350°C, of CNTs which have been previously annealed at 1700°C in vacuum for 7 hours. After annealing of the CNTs the amorphous carbon is totally graphitized, consequently no sites should be available for oxidation at 350°C. As shown in Figure 3A, after oxidative treatment the CNTs are not dispersed since they aggregate in large bundles that precipitate in the water. This result confirms our theory that only the amorphous carbon present in these commercial CNTs reacts with oxygen in this oxidizing condition.

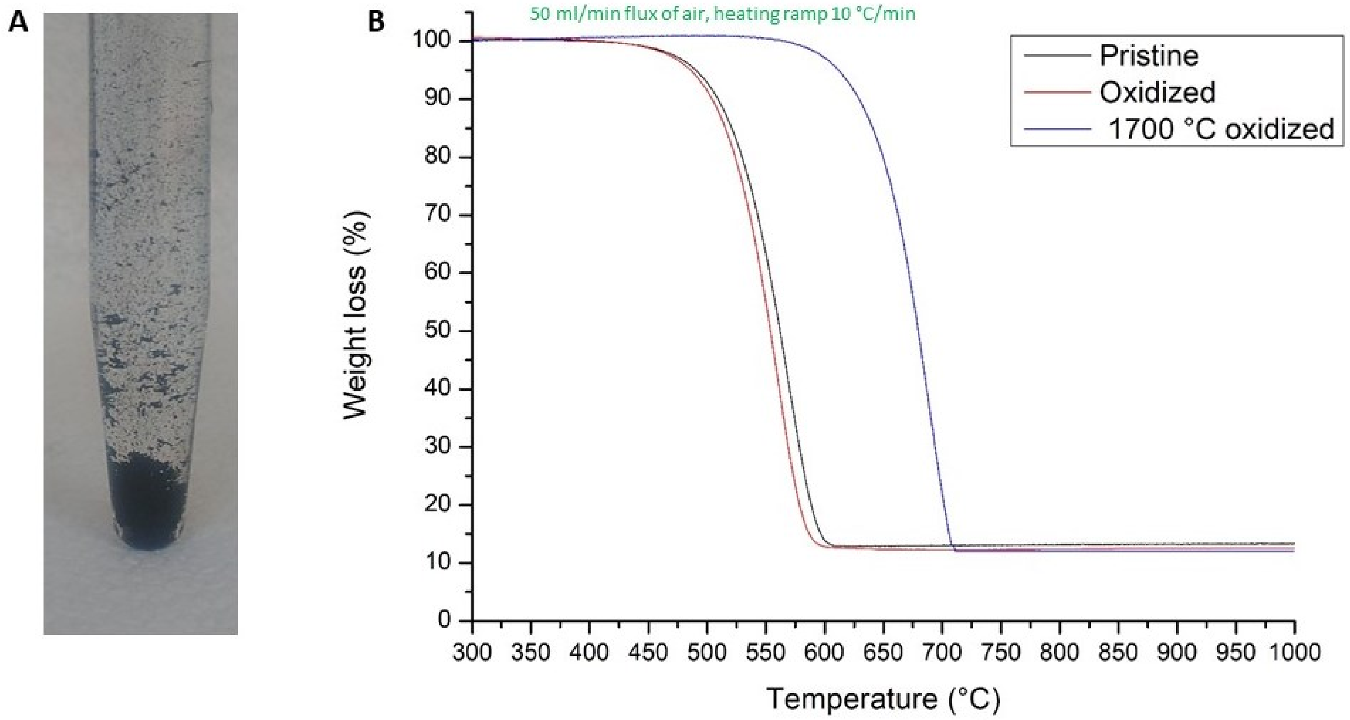

Figure 3: A) Dispersion of annealed CNTs in water after isothermal treatment at 350°C; B) TGA analysis of pristine CNTs, oxidized, and annealed/oxidized CNTs.

Finally, a thermal gravimetric analysis (50 ml/min flux of air, heating ramp 10°C/min) was performed to compare the thermal stability of pristine CNTs, oxidized CNTs, and annealed/oxidized CNTs. The TGA results shown in figure 3B, reveals that oxidized CNTs start degrading at temperature slightly lower than pristine CNTs, suggesting that a low content of oxygen containing groups was effectively grafted on the surface of the oxidized nanotubes, thus accelerating the thermal degradation of the treated CNTs. On the other hand, annealed/oxidized CNTs are extremely more thermally stable than pristine CNTs. As explained in the previous section, this is to be expected because after annealing the CNTs did not contain any more amorphous carbon and the isothermal oxidation at 350°C could not introduce any oxygenated group. Hence, the annealed/oxidized CNTs did not have any weak point that could potentially with oxygen during the TGA showed in Figure 3B. Finally, a measurement of the electrical resistivity was performed on CNTs before and after functionalization. The electrical resistivity was for both the samples of about 2.5 Ω*m, confirming that the graphitic lattice was not damage.

Conclusion

An oxidation under conditions of low oxygen content and at low temperature was carried out. The effective oxidation was assessed through FT-IR, Raman and TGA. No damage was observed on the graphitic lattice of CNTs. However, the oxidation allowed to obtain an optimal dispersion of CNTs in water. The optimal dispersion of nanotubes enables an effective use in nanocomposite materials where the dispersion of the nanofiller plays a key role. This new methodology not only opens a new route for green oxidation of CNTs, but given how easily the process parameters can be investigated and optimized, it could also be simply tailored to effectively oxidize and disperse other types of graphitic materials where traces of amorphous carbon are present.

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