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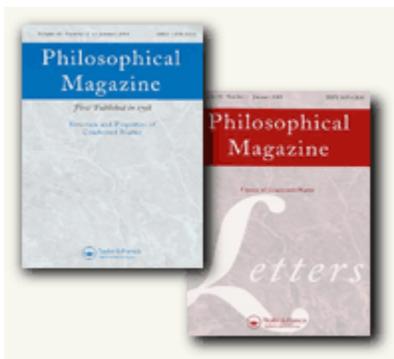
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**Quantitative evaluation of nanotube content in the raw material produced by arc discharge**

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3 **Quantitative evaluation of nanotube content in the raw material produced by**  
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6 **arc discharge**  
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8 **Vittoria Contini, Rita Mancini, Renzo Marazzi, Daniele Mirabile Gattia, Marco Vittori Antisari \***  
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18 **ABSTRACT**  
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20 The amount of carbon nanotube in the raw material grown by electric arc discharge ignited in  
21 different liquid environments has been evaluated by the combined use of X-Ray diffraction,  
22 electron microscopy and TG-DTA in reactive environment. In particular, X-ray diffraction is used  
23 to discriminate among the different carbon microstructures owing to the difference in the lattice  
24 parameter between curved and planar graphite structures. The results are repeatable and in good  
25 agreement with TG-DTA measurements carried out in reactive environment where the relative  
26 amount of carbon nanostructures is evaluated on the basis of the difference in the reaction kinetics  
27 with atmospheric oxygen. In the analysed specimens, SEM and TEM show the presence of just two  
28 allotropic form of carbon, namely nanotubes and globular particles, which relative amount results to  
29 depend on the nature of the liquid surrounding the discharge and on the voltage applied to the  
30 electric arc.  
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49 *Keywords:* Carbon nanotubes, Arc discharge, X-ray diffraction, Thermal analysis, Electron  
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## I. INTRODUCTION

The discovery of carbon nanotubes by Iijima in 1991 [1] has activated a very stimulating research field dealing with the experimental conditions required for the synthesis of this new form of carbon. In the time elapsed since the discovery, it has been shown that carbon nanotubes can be synthesized either by the aggregation of carbon atoms in the gas-solid transformation of carbon, and by solid state reaction in highly defective graphite [2]. Neglecting the last preparation route which is based on different physical-chemical considerations, it has been shown that carbon nanotubes can be obtained from the carbon gas phase generated by laser irradiation of graphite in a laser ablation experiment [3, 4] or by the electric arc discharge method [1]. Moreover multi walled carbon nanotubes, (MWCNT) can result from the condensation, in proper experimental conditions, of carbon atoms resulting from the decomposition of a precursor molecule in a chemical vapour deposition reactor [5]. In all these synthesis routes, the spontaneous aggregation of the carbon atoms gives rise to a large variety of multiwalled nano-structures, while singlewalled carbon nanotubes (SWCNT) can be obtained only with the presence of catalysing particles.

In the electric arc-discharge method, often the carbon evaporating at the anode is condensing at the cathode surface in the form of a hard crust where carbon nanotubes and nanostructured carbon can be found. The electric arc can be ignited in a variety of environments, besides the rarefied inert gas (argon at 100 torr) originally used by Iijima [1] in the pioneering experiments, and the possibility of producing MWCNT by different experimental setups has been ascertained in the recent years. In fact MWCNT have been produced by arc discharge experiments carried out in different gaseous environments having a wide range of pressures up to room pressure. The gas can be either potentially reactive with carbon, like air [6] or hydrogen [7, 9], or inert, like Ar [1] or He [10, 11]. Moreover also liquid environments have been shown to be suitable for the nanotube synthesis. In fact, MWCNT have been synthesized by electric arc ignited under liquid N<sub>2</sub> [12, 14], deionised water [13], and ethanol [15]. It appears so that the synthesis mechanism leading to the formation of MWCNT is operating whichever environment is surrounding the arc and that the role

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3 of the coverage gas or of the liquid surrounding the discharge is mainly limited to influence the  
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5 microstructure of the synthesized material and the relative yield among the different phases which  
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7 are generally constituting the raw material.  
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10 The microstructural characterization of the synthesized material, in order to check for the  
11 presence of MWCNT and to discriminate among the present carbon nanostructures, is often carried  
12 out by Transmission Electron Microscopy (TEM) observations, which, even if able to provide  
13 intimate structural details of the analysed specimen, can hardly provide a quantitative evaluation of  
14 the concentration of the different kinds of nanostructures constituting the raw material. In fact it is  
15 well known that TEM observations can be not very reliable when considering the statistical  
16 significance of powder samples, owing to several problems which range from the small analysed  
17 specimen portion to the possible preferential selection of some kinds of nano-particles by the  
18 sample preparation method. On the other hand, owing to the structural similarity of most forms of  
19 nanocarbon, which are all based on modifications of the graphite structure, other experimental  
20 methods fail in discriminating among them in a quantitative way. Consequently, the information  
21 about the relative abundance of the different carbon nanostructures, which is of primary importance  
22 when different synthesis methods are compared and when the effect of the experimental conditions  
23 on the microstructure of the synthesized material is studied, is often difficult to obtain. In most  
24 cases the amount of nanotubes present in the raw material is just estimated, at a first approximation,  
25 on the basis of electron micrographs.  
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48 The purpose of this paper is to test different experimental methods, and in particular X-Ray  
49 diffraction (XRD) and Differential Thermal Analysis (TG-DTA) in order to evaluate the possibility  
50 of discriminating among different forms of carbon aggregation and in particular in order to obtain a  
51 quantitative measurement of the MWCNT fraction in the material synthesized by arc discharge  
52 experiments. The idea of using diffraction as an effective technique to study the average structural  
53 properties of carbon nanotube samples is well consolidated. In 1993 Saito et al., using electron  
54 diffraction [16], pointed out that the  $d_{002}$  layers spacing in nanotubes is wider by a few percent than  
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3 that of the ideal graphite crystal. Only few months later, the same authors [17] showed a X Ray  
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that of the ideal graphite crystal. Only few months later, the same authors [17] showed a X Ray  
Diffraction (XRD) spectrum underlining this peculiar aspect. Nevertheless even if the shift in the  
peak family (00n) has been discussed also by others authors [18], nobody has been using this feature  
to attempt a quantitative analysis. It is worthwhile to mention that Reznik and co-workers [19] by  
studying the shape of the 00n peaks rather than simply the position, supplied interesting discussions  
about particle size.

The experimental method that we have used in this paper is based on the deconvolution of  
the (00n) peaks into the elementary components belonging to MWCNT and to planar graphitic  
structures. The relative intensity ratio is then used as a measurement of the nanotube fraction.  
Complementary information on the structure of the raw material can be obtained by TG-DTA  
experiments, carried out in oxidizing conditions. In this case the various carbon phases present in  
the sample are differentiated from each other on the basis of the onset temperature of the reaction  
with air. In fact, the burning temperature is expected to increase from the less perfect structures, like  
amorphous carbon, to the more perfect ones, where the density of dangling bonds is progressively  
reduced.

The experiments have been carried out on material synthesized by arc discharge performed  
in liquid environments as in a previous report [13]. In order to investigate how the synthesis  
parameters could modify the MWCNT content in the sample, arc discharge experiments were  
performed in different environments and with different values of the applied voltage.

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## II EXPERIMENTAL RESULTS AND DISCUSSION

The carbon material to be characterized has been synthesized by arc discharge ignited in a home designed experimental device able to stabilize and homogenize the electric arc. These conditions are achieved by axially rotating the two electrodes with respect to each-other and by a constant speed advancement of the anode toward the cathode. The equipment operates in an open vessel which can be filled by the chosen liquid phase. Liquid nitrogen, deionised water and different concentrations of hydrogen peroxide (10, 20, 30 % in volume) in deionised water were used to insulate the discharge from the atmosphere.

A 6 mm diameter anode and a 30 mm diameter cathode, both made of pure graphite (99,99%, Aldrich, low density) have been arched by applying a DC voltage from a power supply able to provide up to 100 A. The experiments were carried out with the anode approaching the cathode at the constant speed of 11 mm min<sup>-1</sup> while the cathode was rotating around its own axis at the speed of 30 rpm. In these conditions a stable and continuous discharge can be obtained in a voltage range from 25 V to 28 V, the corresponding currents being in the range from 50 A to 80 A. In these experimental conditions the anode was consumed by the arc and the sublimated material was condensing at the cathode as nanostructured carbon. This deposit (a hard crust of cylindrical shape with roughly the same diameter of the anode) was hand ground in an agate mortar to produce powder suitable for the subsequent characterizations.

XRD patterns were obtained using Cu K<sub>α</sub> radiation in a Bragg-Brentano powder diffractometer equipped with a graphite monochromator positioned in the diffracted beam. Considering the low absorbing power of the material under examination and with the purpose of reducing the contribution of the background signal, the powder sample was placed on top of a cubic Si (n00) single crystal support in order to avoid Bragg reflections in symmetrical conditions. In fact, in this configuration, the supporting material does not display any Bragg reflection in the angular range of interest here, showing only a very weak (2 0 0) peak, which effect can be easily accounted

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3 for. This configuration keeps the background radiation particularly low for a better reliability of the  
4 spectrum elaboration procedure.  
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8 The analysis of the peak profiles and the deconvolution of the different contributions to the  
9 XRD reflections were carried out using PANalytical PC-APD (PW 1877) diffraction software. The  
10 experimental diffraction profile is fitted using a Marquardt non-linear least squares algorithm. In  
11 order to evaluate the reliability of this kind of analysis, the reproducibility of the whole  
12 experimental procedure was tested. In fact, even if carried out always with the same procedure as  
13 reported above, an arc discharge synthesis can be affected by uncontrolled parameters. To this  
14 purpose we have prepared four samples in the same experimental conditions (deionised water  
15 environment, 26V and 15s of synthesis time) and we have compared the corresponding XRD  
16 patterns. The results confirmed the accuracy of the experimental method, since the XRD line profile  
17 of all these samples was the same within the statistical uncertainty of the X-Ray counting statistics.  
18 In particular the ratio between the two elementary components of the (004) peak, as it will be  
19 described later, was the same within an error of about 1%.  
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36 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in reactive  
37 environment were carried out simultaneously by a Netzsch STA 409 instruments. Preliminary test  
38 were necessary to identify the appropriate mass of samples, heating rate and air flow required to  
39 maintain the oxidation reaction under kinetic control. On the basis of these measurements it was  
40 chosen to use samples with a constant weight of 5.8 mg, a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in the  
41 temperature region from 30 to  $1200\text{ }^{\circ}\text{C}$  under a dynamic air flow of  $100\text{ ml min}^{-1}$ . A empty pan was  
42 always used as a reference.  
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53 The powder morphology was analysed by high resolution Scanning Electron Microscopy  
54 (SEM) in a Leo 1530 microscope equipped with a high brightness field emission source, while the  
55 powder microstructure was characterized with a FEI TECNAI G<sup>2</sup> 30F Transmission Electron  
56 Microscope (TEM) operated at 300 kV. In both cases the sample under investigation was sonicated  
57 in ethanol and a drop of the suspension was allowed to dry on the specimen support, which was a  
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3 polished Si wafer in the case of SEM and the usual holey carbon support grid for the TEM  
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5 observation.  
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8 In figure 1 a typical XRD pattern of the carbonaceous material from the cathode deposit is  
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10 compared with the spectrum of the hexagonal graphite parent material. It is possible to notice that  
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12 the spectra show several differences evidencing the different nature of the analysed structures. In  
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14 particular, the deposit reflection indexed as (10) is broad and asymmetric, probably because of the  
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16 turbostratic nature of the graphene layers packaging, while its  $2\theta$  position is just the same of the  
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18 (100) reflection in three-dimensional graphite. These features, even if evidencing structural  
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20 differences between the two samples, can hardly be used to evaluate the relative fractions of  
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22 MWCNT and planar graphitic structures. The (00n) family of diffraction lines, on the contrary,  
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24 appear to be more suitable to this purpose. In fact, in this case, the lines belonging to the deposit,  
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26 have a structure similar to pure planar graphite, with differences in the angular position and in a  
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28 broader profile. The (00n) line profile of the parent graphite comprises a single contribution, while  
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30 in the case of the deposited material the line structure has to be interpreted considering the presence  
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32 of two contributions, as it can be seen in figure 2, where an enlarged view of a (004) peak is  
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34 reported. The result of the line profile analysis, evidencing the presence of two contributions, is also  
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36 reported in the figure. On the basis of the angular position reported in the literature [17], we can  
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38 assign the peak at smaller scattering angle to the MWCNT component and the higher angle  
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40 contribution to the planar graphitic structure. The analysis has been carried out on the (004) line  
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42 because it represents the best compromise between the spectral peak separation and line intensity.  
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44 In fact, as it is expected, the angular shift between the elementary components is larger with respect  
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46 to the (002) line improving so the reliability of the line profile analysis, while the intensity is still  
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48 large enough to avoid problems related to the statistical noise. Moreover there are no overlapping  
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50 peaks in the interested range of scattering angles.  
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60 '[Insert figures 1 and 2 about here]'

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3 More accurate results could be probably obtained by neutron diffraction since the absence  
4 of the atomic form factor gives rise to strong high order reflections where wide peak separation and  
5 good counting accuracy can be simultaneously obtained. This technique is however limited by the  
6 small absolute value of the scattering factors and a larger amount of sample material, is requested.  
7 Even if the high flux provided by the modern neutron sources mitigates this requirement, a  
8 minimum amount of sample of the order of 500mg has been estimated ( 20 ). In this paper we have  
9 used XRD although the atomic form factor reduces the coherent intensity at high angle, by selecting  
10 an experimental strategy in which statistical accuracy is built up by counting for a longer time with  
11 a diffractometer available in the laboratory. It will be of high interest to compare, in future  
12 experiments, diffraction patterns obtained with different radiations.  
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27 From figure 2, relative to the sample synthesized in water with an applied voltage of 26V, it  
28 is possible to notice also that the numerical line analysis fits very well the experimental results. The  
29 two resulting line profiles, once separated from each-other, are ready for further elaborations based  
30 on the ratio between the relative integral areas, related to the fraction of nanotubes in the sample, on  
31 the angular position, marking the nature of the graphitic compounds (nanotubes or planar  
32 structures), and on the angular width, related, as usual, to the size of the coherently scattering  
33 crystallites.  
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43 The value of  $d_{002}^{CNT}$  is larger by about 0.007 nm (2 %) than that for the ideal graphite crystal  
44 (0.3354 nm). This value, in good agreement with the literature results [17], is the same for all the  
45 samples within the experimental uncertainty. A more refined analysis reported by Kiang et al. [21]  
46 relates the lattice parameter to the inner tube diameter of the MWCNT according to the following  
47 empirical equation:  
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$$d_{002} = 0.344 + 0.1e^{-D/2}$$

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3 where D is the inner tube diameter and all the constants are in nm. From this equation we can derive  
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5 that our nanotubes have an average value for D of 5 nm in all samples, in good agreement with the  
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7 TEM results (figure 9) as it will be reported later.  
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10 In order to evaluate the relative concentration of the phases constituting the raw material, all  
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12 the samples have been analysed with the procedure previously described and the fraction of  
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14 nanotubes was determined as the ratio between the integral areas of the two peaks constituting the  
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16 (004) reflection. The results are reported in figure 3, where the concentration of MWCNT in the raw  
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18 material is reported versus the voltage applied to the electric arc for the different environments  
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20 explored. Without entering into the mechanism of nanotube formation in these experimental  
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22 conditions we can just notice that the amount of nanotubes in the raw material appears to depend on  
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24 the nature of the liquid environment for all the values of the applied voltage, even if no relevant  
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26 differences have been observed on samples synthesized in solutions with different concentrations of  
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28 H<sub>2</sub>O<sub>2</sub>. Deionised water appears to be the most suitable synthesis environment followed by the H<sub>2</sub>O-  
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30 H<sub>2</sub>O<sub>2</sub> solution and the liquid nitrogen. Moreover also the applied voltage appears to have a strong  
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32 influence on the structure of the synthesized material. In fact, when the discharge is carried out in  
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34 deionised water both pure and with the addition of H<sub>2</sub>O<sub>2</sub>, the nanotube concentration increases  
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36 almost linearly with the applied voltage. On the contrary, when the discharge is performed under  
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38 liquid N<sub>2</sub> we observe a broad maximum in the nanotube concentration located at about 26 V.  
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40 Optimum condition in our experimental set is obtained by applying 28 V to the electrodes  
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42 submerged in deionised water; the corresponding MWCNT concentration results higher than 80%.  
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50 ‘[Insert figure 3 about here]’  
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53 Further information on the structure of the synthesized material can be obtained from the  
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55 analysis of the X-Ray diffraction peak profile other than the angular position. From the full width at  
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57 half-maximum intensity of the two separated contributions, using the Scherrer equation [22], we  
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59 obtained the mean size of the coherent zones composing the powders which result of about 9 nm  
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for MWCNT and 16 nm for the planar graphite. We did not observe differences among the analysed

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3 sample within the experimental error. These values are in good agreement with the results obtained  
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6 from TEM and reported in figure 7.  
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8 In order to investigate the potentialities of the thermal analysis for the characterization of  
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10 this kind of material, and with the aim of providing a support to the X-Ray diffraction results,  
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12 thermo gravimetry (TG) and differential thermal analysis (DTA) runs were performed up to the  
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14 temperature of 1200 °C under flowing air, as previously described. Figure 4 shows TG, DTA and  
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16 DTG (differential thermo gravimetry) curves for samples synthesized in deionised H<sub>2</sub>O and in H<sub>2</sub>O  
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18 + 20% H<sub>2</sub>O<sub>2</sub> with an applied voltage of 28V. The DTG curve performed on the parent crystalline  
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20 graphite is also reported for comparison. The TG signal displays a small mass loss (of the order of  
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22 1%) at temperatures lower than 160°C (not shown in the figure), that can be ascribed to the  
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24 desorption of water and CO<sub>2</sub> absorbed from the environment before the test. A well-defined mass  
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26 loss was found to occur between 570°C and 970°C accompanied by an exothermal effect showed by  
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28 the DTA curves. This was due to the reaction of the carbon material with the atmospheric oxygen  
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30 and the reaction proceeded for all samples until the whole specimen mass was consumed.  
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36 ‘[Insert figures 4 and 5 about here]’  
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38 By analyzing the experimental results it is possible to observe that both the DTA and the  
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40 differential TG curves show a double peak, which can be ascribed to the differences in the reaction  
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42 kinetics of the different carbon structure in the sample.  
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46 The nanocarbon material appears to be more reactive with oxygen than the crystalline parent  
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48 graphite. In fact while the DTG of parent graphite shows an asymmetric profile peaked at about  
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50 923°C, the curves relative to the raw material show clearly a well defined double peaked structure.  
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52 The two peaks are found at T = 895.7°C and T = 805.2°C (onset at about T = 640°C) for the  
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54 sample synthesized at 28 V in deionised H<sub>2</sub>O, and at T = 913°C and T = 826°C (onset at about  
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56 644°C) for the sample synthesized at the same voltage in 20% H<sub>2</sub>O-H<sub>2</sub>O<sub>2</sub> solution. A similar  
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58 findings result from the analysis of the DTA curves.  
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3 The absence of any appreciable reaction below 600°C excludes an important contribution  
4 from amorphous carbon, which oxidation temperature is reported to be even below 370°C [23]. The  
5 DTG and DTA curves are generally analysed using multiple Gaussian profiles. In our case the  
6 results of this kind of fitting are quite satisfactory since with fit indexes of  $R^2=0.999$  and  $R^2=0.998$   
7 for the samples synthesized in deionised in  $H_2O$  and in  $H_2O + 20\%H_2O_2$  respectively. The profile  
8 analyses evidencing the single contributions to the experimental curves are shown in figure 5. We  
9 associate the individual contribution to the two allotropic forms of carbon so that their integral ratio  
10 can be a measurement of the relative concentrations. Under this hypothesis we obtain 84% and 76%  
11 of MWCNT in the sample synthesized in deionised  $H_2O$  and in  $H_2O + 20\%H_2O_2$  respectively, in  
12 excellent agreement with the X-Ray results.  
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27 The morphological analysis of the particles present in the raw material, carried out by high  
28 resolution SEM, evidences the presence of nanotubes, displayed as thin elongated structures and of  
29 globular particles as it can be observed in figure 6. The small size of the synthesized particles does  
30 not allow to derive further information by SEM; we can only notice that the whole sample is  
31 constituted by a mixture of these small scale units, whichever are the synthesis conditions.  
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38 ‘[Insert figure 6 about here]’  
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41 To obtain a more detailed information on the sample structure, the specimens have been  
42 observed by TEM. Lattice resolved images have been used to identify the nature of the different  
43 structures present in the samples. As stated in the introduction, also in this case, the purpose of the  
44 observation was mainly related to the identification of the present structures without any attempt of  
45 evaluating their relative abundance. In agreement with the SEM observation, all the samples show  
46 the presence of similar particles independently of the synthesis environment and of the applied  
47 voltage. In particular two kinds of particles, namely nanotubes and globular particles, can be  
48 noticed. A typical example of the observed microstructures is reported in figure 7 where an image  
49 taken on the sample synthesized in deionised water at 26 V is reported. It is possible to observe how  
50 the globular particles, an example of which, taken from the top-left corner of figure 7, is enlarged in  
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3 figure 8, have a polygonalized structure and appears to be made of grains comprising relatively  
4 large volumes constituted by planar graphite separated by relatively sharp boundaries where the  
5 strong bending of the graphite basal planes is localized. Since we did not observe any other particle  
6 having a planar graphitic structure, we are ascribing to this kind of particles the contribution at high  
7 scattering angle observed in the (00n) X-Ray diffraction peaks.  
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15 ‘[Insert figures 7, 8 and 9 about here]’  
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17 As far as the nanotube structure is concerned, we notice the contemporary presence of units  
18 with different structural perfection as evidenced in figure 9 where the images of two nanotubes are  
19 compared. While the MWCNT displayed in the section a) shows high structural perfection, so that  
20 the high resolution image can displays the carbon atomic columns, the one displayed in the part b)  
21 has a more distorted structure with the presence of strongly oscillating lattice planes. Even if it is  
22 known that MWCNT can be damaged by electron irradiation in the microscope, what displayed in  
23 the figure has to be considered as a true effect since both images are enlargements of figure 7 and  
24 have experienced the same electron dose. From figure 9 it is possible also to notice that the structure  
25 of the MWCNT is not perfect at the surface also in the nanotubes of high structural quality. In fact  
26 the outer graphene layer appears often incomplete and not planar, evidencing a high density of  
27 structural defects.  
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43 Summarizing, it is possible to say that the experimental results obtained in the present work  
44 confirm that the X-Ray diffraction represent an extremely powerful method to investigate the  
45 structural properties of nanocarbon material produced by arc discharge. In fact the details of the  
46 diffraction profile provide information on the amount of MWCNT and on their size. The  
47 experimental results are supported by the complementary analyses carried out by TG-DTA and  
48 electron microscopy. In particular, the thermal analyses, both DTA and TG evidence the presence  
49 of two well separated contribution which can be ascribed to planar graphite and MWCNT  
50 respectively. It is interesting to notice that the two experimental methods, which are based on  
51 completely different physic-chemical effects, provide the same information on two important  
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3 features of this material. On one side both method agree in estimating in a quantitative way the  
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5 relative fraction of MWCNT in the raw material, while on the other both support the experimental  
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7 evidence that the samples are constituted by the mixture of just two kind of particles. It appears that  
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9 the particles with larger lattice parameter, MWCNT, are more reactive with oxygen than the  
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11 particles constituted by planar graphite. The higher reactivity of MWCNT finds a support from the  
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13 TEM analysis which shows the presence of damaged outer wall also in nanotubes otherwise  
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15 showing high structural perfection which can enhance the kinetics of the reaction with oxygen.  
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20 The result of both methods seems to suggest that the transition from one family to the other  
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22 is quite abrupt since neither analysis evidences the presence of intermediate structures. The particles  
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24 appear so to belong to two well defined phases showing different properties.  
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28 As far as the structure of the material deposited by liquid submerged arc discharge is  
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30 concerned, this finding can be considered one of the main results of this work. The reliability of this  
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32 conclusion and, more generally of the whole analysis is supported also by crossed results of X-Ray  
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34 diffraction and thermal analysis assuring that these two phases constitute the whole sample and no  
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36 spurious phases, both crystalline or amorphous are present in the synthesized samples. In fact the  
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38 former should be detected by X Ray diffraction which is very sensitive to the presence of crystalline  
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40 phases, and the latter should give rise to a detectable signal in the DTA-TG curves, since  
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42 amorphous carbon is known to react with oxygen at a lower temperature. TEM results supports the  
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44 above findings, showing, beside MWCNT constituted by the stacking of curved graphene layers,  
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46 only the presence of globular particles with a polygonalized structure.  
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### III CONCLUSIONS

Raw materials, synthesized by electric arc ignited in different liquid environments (deionised water, liquid nitrogen and different concentrations of hydrogen peroxide in deionised water), containing MWCNT have been characterized by different experimental methods with the purpose of ascertaining the structure of the present carbon nanostructures and their relative amount.

TEM observations show that all the samples are constituted by two kinds of particles, nanotubes and globular particles independently of the synthesis environment and conditions.

The thermal analysis shows that the nanotubes are more easily oxidized with respect to planar structures and the TEM analysis evidenced a possible explanation based on the not complete rolling up of the outer graphene layer of the nanotubes.

The relative amount of nanotubes, constituted by the pile-up of curved graphitic layers relative to globular structures constituted by polygonalized planar graphite, has been measured by X-Ray diffraction taking advantage of the difference in the lattice parameter of the two structures. Experimental results showed that the contribution of a careful X-Ray diffraction analysis can strongly contribute to the study of the structural characteristic of this kind of carbon nanomaterial. In particular the reproducibility of the method has been successfully ascertained and the relative amount of the carbon allotropic forms present in the samples has been quantitatively measured. The experimental data, supported by the good agreement with other independent methods and in particular by thermal analysis in reactive environment, provide a sound set of results which can be useful for the analysis of different synthesis routes. In particular we have shown that the synthesis environment and the voltage applied to sustain the electric arc influence the structure of the raw material and in particular the amount of MWCNT. We want to stress that a detailed analysis of the nanotube synthesis mechanisms by this method is beyond the purpose of the present paper.

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## ACKNOWLEDGMENTS

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**FIGURE CAPTIONS**

Figure 1. X-ray diffraction profiles of: (a) the graphite used as electrode and (b) the deposit grown after arc discharge synthesized in water with an applied voltage of 26 V.

Figure 2. Enlarged view of the (004) peak (figure 1) of the deposit grown and the separated contributions after the deconvolution algorithm for the sample synthesized in water with an applied voltage of 26 V.

Figure 3. Amount of MWCNT formed respect to planar graphitic structures synthesized in different environments and for different values of applied voltage.

Figure 4. TG\DTA\DTG curves, resulting from oxidation of: (a) - sample synthesized in H<sub>2</sub>O and (b) - sample synthesized in H<sub>2</sub>O + 20%H<sub>2</sub>O<sub>2</sub> both with an applied voltage of 28 V. The dash lines correspond to DTG of pure graphite in dynamic air atmosphere (100 ml min<sup>-1</sup>) at a heating rate of 10 °C min<sup>-1</sup>.

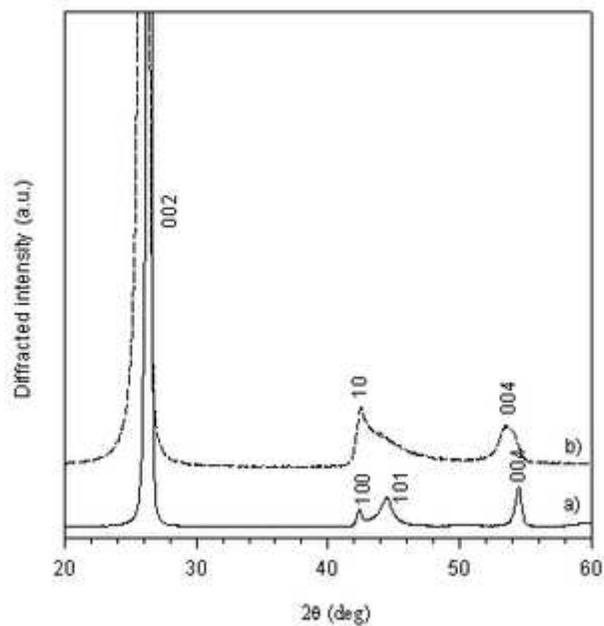
Figure 5. DTG and Gaussian fit of DTG curves, of (a) - sample synthesized in H<sub>2</sub>O and (b) - sample synthesized in H<sub>2</sub>O + 20%H<sub>2</sub>O<sub>2</sub> with an applied voltage of 28 V .

Figure 6. SEM image of the sample synthesized in water at 26 V.

Figure 7. TEM image of the sample synthesized in water at 26 V.

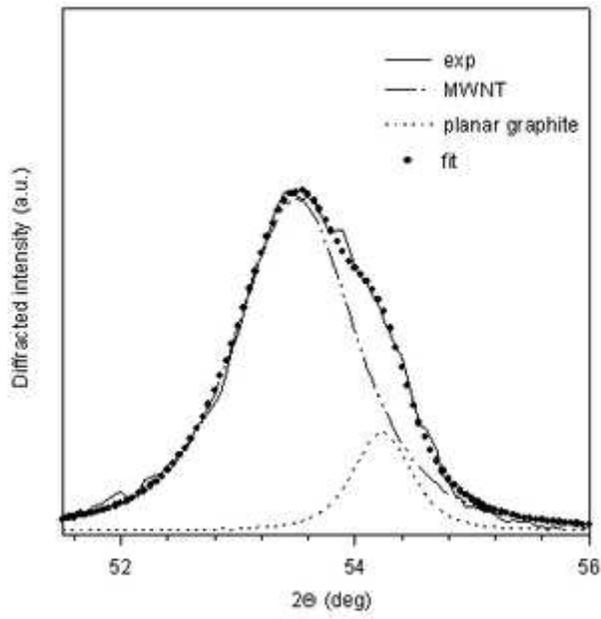
Figure 8. Enlargement taken from the top-left of figure 7. The picture shows a globular particle.

Figure 9. The figures (enlargements of figure 7) compare two nanotubes and shows the contemporary presence in the same sample of different degrees of structural perfection.



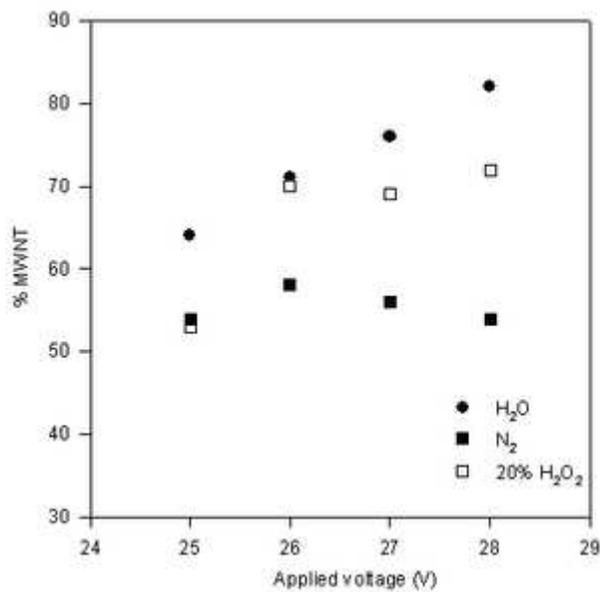
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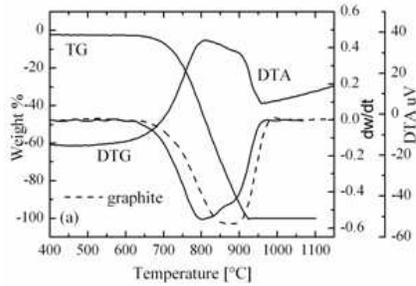
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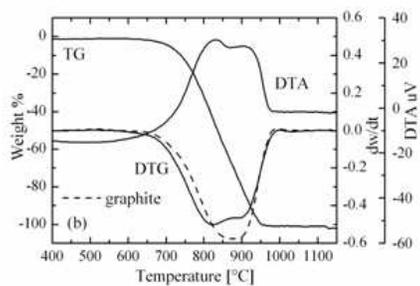
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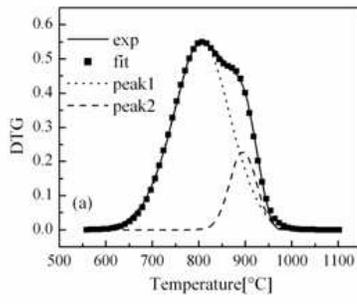
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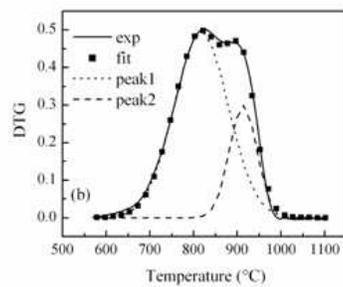
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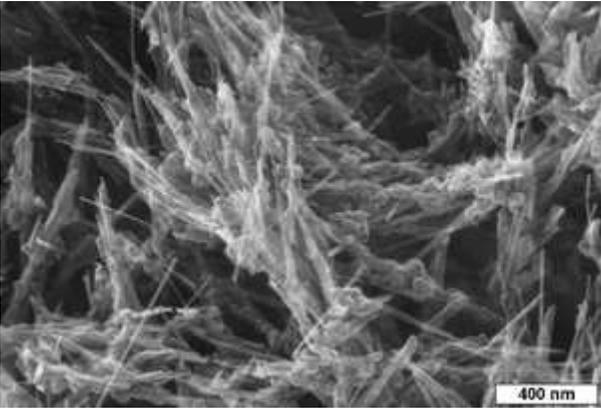
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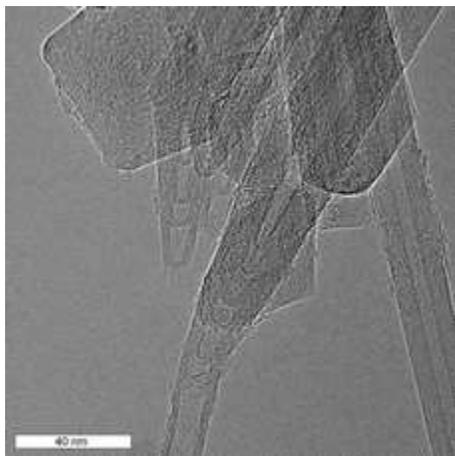
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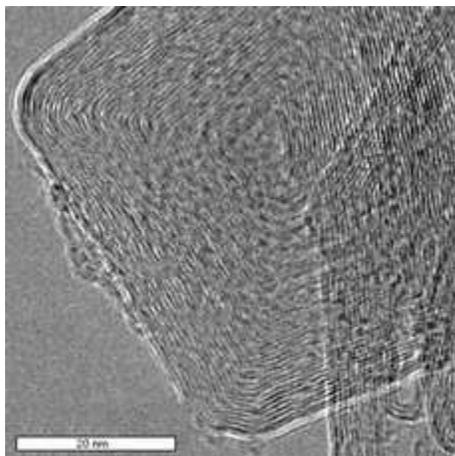
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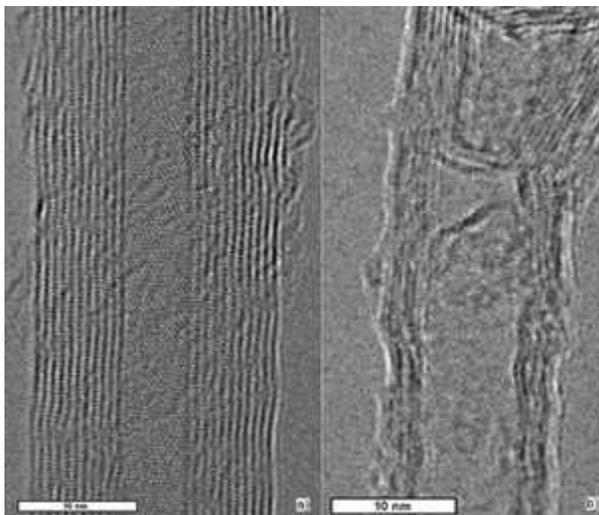
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