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Synthesis of carbon nanowires and nanotubes by plasma ignition in liquid environments

G. COMPAGNINI*, G. PATANÈ, L. D'URSO, O. PUGLISI,
S. SCALESE[a], V. SCUDERI[a], S. BAGIANTE[a], V. PRIVITERA[a]
Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, Catania 95129, Italy
[a]Istituto per la Microelettronica e Microsistemi, Consiglio Nazionale delle Ricerche, Zona Industriale, VIII Strada n. 5, I-95121 Catania, Italy

The synthesis of many carbon nanomaterials is based on the ignition of carbon plasmas during laser ablation or arc discharge phenomena. This paper intends to compare these two methods in the formation of carbon nanotubes and linear carbon chains when a liquid phase is used as the environment for the plasma ignition. We observe similarities in the chemical species (mainly sp hybridized linear carbon chains) trapped in the liquid phase after the processes and we give also details on the properties of multiwall carbon nanotubes deposited at the cathode during arc procedures. It is found that these properties strictly depend on the discharge current and the electrode geometry. Particularly interesting is also the observed formation of tube-chain hybrids during unstable discharge conditions.

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1. Introduction

Since the discovery of fullerene, carbon materials with reduced dimensionality have been considered among the most interesting systems in materials science because of their large implication in nanotechnology. In particular, carbon nanotubes (CNTs) and other one-dimensional carbon systems are considered very promising for their appealing mechanical, optical and electronic properties.

Many CNTs synthesis methods are based on the ignition of hot carbon plasmas[1,2], such as in the case of the laser ablation of carbon targets or in the case of arc discharge processes between two graphite electrodes. These experiments are generally carried out in vacuum or inert atmospheres, while only a limited number of studies have been reported in liquid environments[3]. Despite this, the use of a liquid as an environment during the process has the advantage to skip any vacuum system, leading to a cheaper production way and gives the possibility to study the effect of different chemical species on the growth process. Moreover the analysis of the liquid after the plasma ignition is interesting since the trapped species can be easily analyzed and simply correlated to specific, active components during the nanocarbons formation.

By using both laser ablation and arc discharge approaches, this paper intends to analyze, compare and discuss the species formed during the plasma ignition and trapped in the liquid phase, correlating them with some features of the nanostructures (mainly carbon nanotubes) formed at the cathode during the arcing procedures.

2. Experimental

Details about the experimental setup for laser ablation and arc discharge experiments are reported elsewhere[4,5]. Briefly the ablation of graphite targets has been conducted in water (Millipore grade) and CH_3CN (Analytical grade) using pulses (5 nsec, 532 nm) of a Nd:YAG laser. The irradiation has been performed at room temperature, the optimized laser energy density was found to be around 1 J/cm^2 and the irradiation time was set at 20 min. Regarding the arc discharge setup, we supplied a voltage (25 V) to two graphite rods (electrodes) immersed in liquid nitrogen, setting the current at values up to 80 A. Different experiments have been performed by using (cylindrically shaped) anodes and cathodes with diameters in the range between 5 and 10 mm. The structural characterization of the samples was performed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), while untreated and unfiltered liquids have been analyzed immediately after the processes by performing UV extinction spectra in the range 200-500 nm. Raman spectra have been excited by the 514.5 nm radiation from an Ar ion laser and the scattered light has been confocally collected and analyzed by a Jobin–Yvon 450mm monochromator equipped with a CCD detector cooled at 77 K. In the case of the linear carbon chains (polyynes) found in the liquid phase, the Raman spectra have been taken after the deposition of some drops of liquid onto a silver surface suitable for Surface Enhanced Raman Spectroscopy[6,7].

3. Results and discussion

a) Analysis of the residue after the plasma ignition

Fig.1a compares the UV absorption spectra of the residual species found in the liquid immediately after the ignition of carbon plasmas by the ablation of a graphite target in water or acetonitrile and by arcing between two graphite electrodes in liquid nitrogen (after Cataldo[8]). All the spectra are representative of the absoption of polyynes. These intriguing molecules with alternating single and triple bonds (general formula C_nH_2) are considered precursors for the formation of nanotubes and fullerenes[9] and possess 'per se' intriguing nonlinear optical properties[10] as well as a π-electron system suitable for the application in nanoelectronics for conductance switching and negative differential resistance at single molecule levels[11].

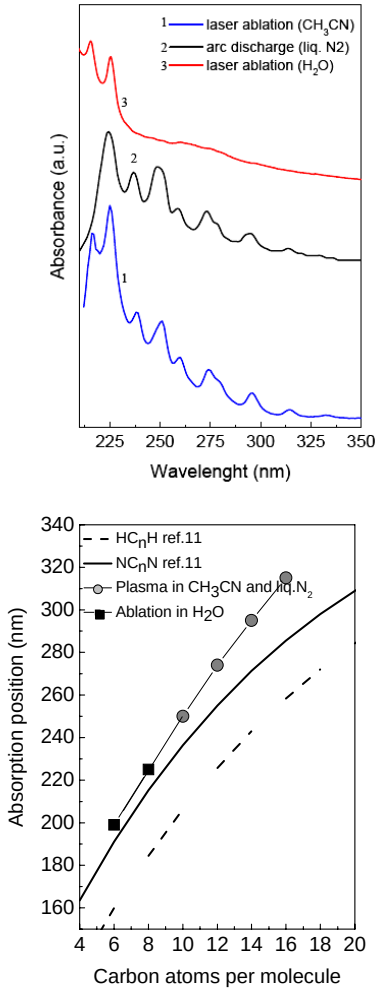


Fig. 1. Comparison between the UV absorption spectra (a) of the residual species found in the liquid immediately after the ignition of carbon plasmas by the ablation of a graphite target in water or acetonitrile and by arcing between two graphite electrodes in liquid nitrogen (after Cataldo[7]). Part (b) reports the results of the absorption behavior as a function of the polyyne length as obtained by semi-empirical calculations[10].

Coming back to the absorption spectra reported in fig.1, it is interesting to observe that while in the case of the ablation in water the spectrum is very simple and provides two signals located at 215 and 225 nm (belonging to C_8H_2 species), the absorption data found for the ablation in CH_3CN and for the discharge in liquid nitrogen is much more rich. Moreover the spectral pattern in these two last cases indicates that the species formed and trapped in the liquid are the same: the structures located between 220 nm and 340 nm are indicative of the presence of polyynes with a length up to $C_{16}H_2$. The same figure (fig.1b) reports the results of the absorption behavior as a function of the polyyne length as obtained by semi-empirical calculations [12] for the electronic absorption of hydrogen terminated polyynes and cyano-polyynes. The allowed low energy electronic transition $^1\Sigma^+ \leftarrow {}^1\Sigma^+$ of monocyano-polyynes and $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ of polyynes and dicyano-polyynes give contributions at increasing wavelengths as the linear carbon chain length increases.

After laser ablation or arc discharge processes at low or moderate currents (below 20 A) some carbon material is either suspended in the liquid or slightly deposited on the targets (electrodes). Fig.2 reports a SEM image of this carbon stuff, showing an amorphous matrix without evidence of any ordered carbon structures (e.g carbon nanotubes). The absence of carbon nanotubes is ascribed to the absence of a suitable driving force which induces the species formed into the plasma to interact directly and evolve towards ordered sp^2 features (see further discussion).

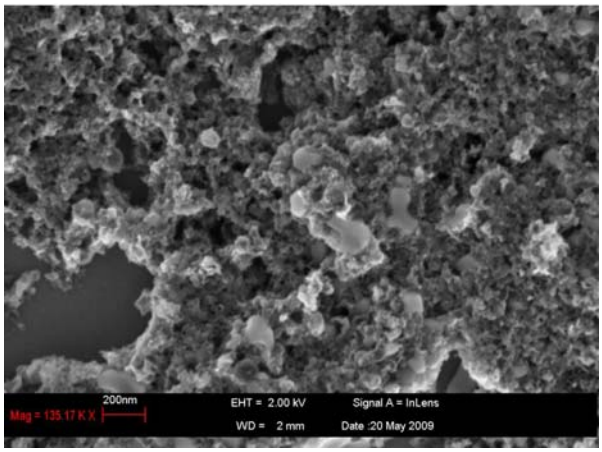
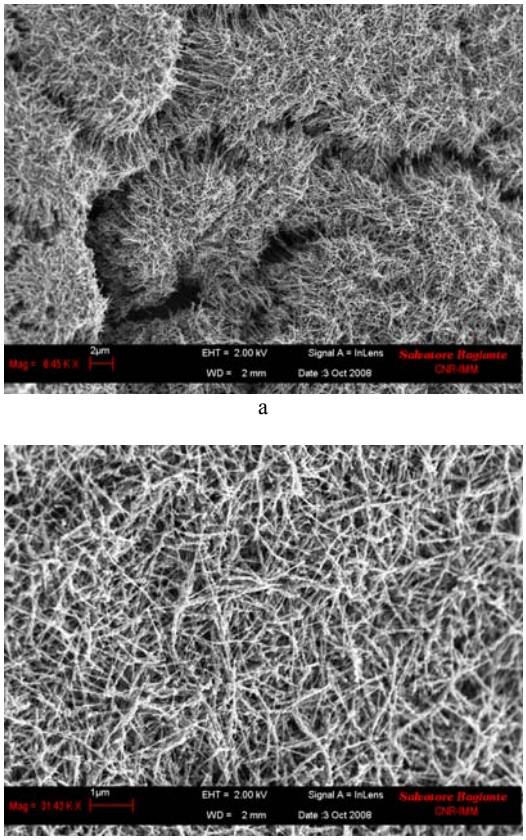


Fig. 2. SEM image of the deposit after laser ablation of a graphite target in pure water

b) Deposition and analysis of carbon nanostructures at the cathode during arc discharge

When the arc discharge experiment is conducted at moderate or high current values (above 20 A) a short time (10 s – 30 s) is sufficient to get a considerable carbonaceous deposit at the cathode. As an example, fig.3a

shows a SEM image of the deposit after arcing between two graphite electrodes in liquid nitrogen: it appears a sponge-like surface containing a great amount of thin nanotubes, as evidenced in the higher magnification image shown in fig.3b. At a macroscopic scale, the deposits have size and shape which mimic the anode geometry. Moreover other experimental evidences indicate that the growth rate of the nanotubes is related to the geometry of the setup as well as to the specific discharge conditions [13].



a

b

Fig.3. SEM image of the deposit after arcing between two graphite electrodes in liquid nitrogen at low (a) and high (b) magnifications.

Even though literature presents a large number of experiments in which the arc discharge method is used, a direct correlation between discharge parameters (current, voltage, electrode geometry) and the properties of the carbon deposit is hard to be achieved because of several differences in the various approaches. In order to gain information on a specific set of experiments and correlate them to the properties of the nanotube grown, we report in fig.4a some Raman spectra for the carbon deposits as a function of the discharge current. The spectra are taken on samples produced by using electrodes with a 6 mm diameter. In each spectrum typical D and G signals appears at around 1360 and 1580 cm^{-1} respectively. As widely known the intensity ratio (I_D/I_G) between these two signals is an indication of the structural order of the carbon structure [14-16]. Fig.4b also reports the I_D/I_G values as a function of the discharge current, for different electrode diameters (anode/cathode: 5mm/6mm, 6mm/6mm, 10mm/10mm) and definitely confirms that the quality of the produced nanotubes as well as the materials growth rate are strictly correlated either to the current and to the electrode geometry.

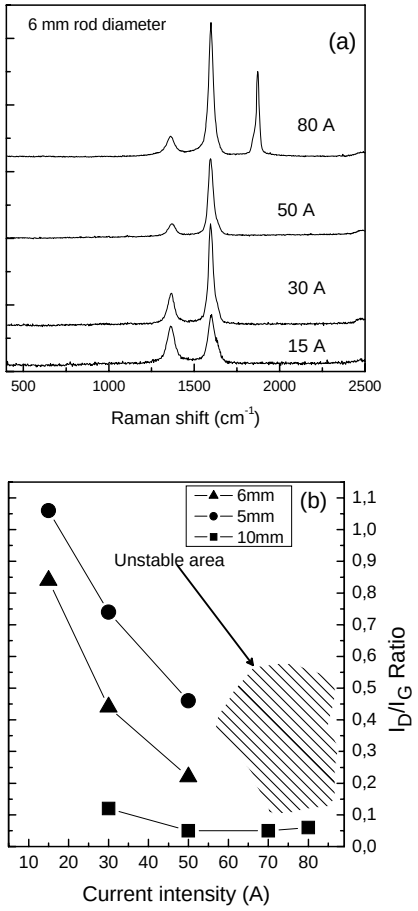


Fig.4. Raman spectra (a) of different deposits obtained at different currents with a 6 mm electrode configuration. In particular the spectrum at 80 A is obtained with unstable arc discharge conditions. The I_D/I_G integrated ratios are reported in pat (b) as a function of the discharge current.

The behaviour quantitatively described in fig.4 can be interpreted on the base of the Gamaly model [17] for the nanotube growth. Following this approach, the CNT formation in an electric discharge is driven by the ratio between two velocity distributions (anisotropic and isotropic or Maxwellian) for the C^+ species formed in the plasma. The anisotropic distribution is due to the strong potential drop, at around 12 μm far from the cathode surface, which accelerates the C^+ ions towards the cathode itself, while the isotropic one is related to the carbon atoms/ions expelled from the cathode surface for thermal

effect. It is supposed that the formation of carbon nanotubes and other carbon nanostructures occurs when these two groups of ions impact.

The anisotropic travelling species are then involved in building up a nanotube in length, while Maxwellian carbons are responsible for the nanotube growth in width. At high current values the first group predominates and, consequently, we get the formation of longer low-defective nanotubes, while at low currents it is outnumbered by the isotropic species, leading to shorter and more disordered products (like the carbon onions, horns or beanpod structures), that contribute to the increase in the I_D/I_G ratio.

The same fig.4 reports a discharge instability region, observed at high discharge current values (70 A- 80 A) in the case of both anode and cathode with 6 mm diameter. In such conditions, Raman spectra performed in different regions of a carbon deposit show very different I_D/I_G ratios, therefore having a nearly complete lack of homogeneity. Nothing similar is found for the samples produced with the 10 mm rods, where the I_D/I_G values are very low and do not even show any considerable variation for different discharge current values. We argue that, if a sudden current interruption occurs, like in the case of an unstable arc, the anisotropic component immediately disappears and the isotropic velocity distribution dominates the process.

From the spectroscopic point of view, carbon deposits produced under unstable discharge conditions reveal additional Raman signals like those reported in fig.4a (80 A) at around 1850 cm^{-1}. Raman features in this spectral range generally belong to sp-hybridized carbon systems[18] thus confirming the presence of polyynes in the solid deposit. It has been recently argued that such linear carbon chains can be arranged into the inner walls of the carbon nanotube[19]. Some of them have been also directly observed by TEM (see fig.5), evidencing a peculiar bottle-neck shape for the inner CNTs.

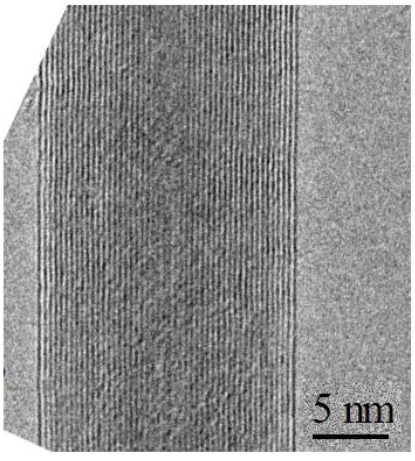


Fig.5. Linear carbon chains inserted into a MWCNT observed by TEM. Its is also evident a peculiar bottle-neck shape for the inner CNTs at the end of the chain.

The micrograph shows also that the diameter of the innermost tube suddenly changes from 0.9 to 0.7 when the linear carbon chain appears (see arrow in fig.5). This means that the distance between the linear chain and the nanotube inner wall is just the typical distance between two graphene sheets, in agreement with the findings by Zhao et al. The data are also confirmed by the study of the radial breathing modes as reported elsewhere[5].

c) Comparison of the observed carbon nanonanostructures

The experimental findings discussed up to now suggest that during the discharge a complex series of reactions between carbon radicals and ions (mainly C_2 and C_2^+) produce a variety of sp-hybridized carbon molecules[20]. Some of them remain trapped in the liquid environment, while other contribute to the formation of the carbon nanostructures if a suitable driving force (the electric field in the case of a discharge) is able to collect them, for instance at the cathode.

Moreover, we have already discussed that in a laser ablation experiments, we never observe the formation of carbon nanotubes, while a plenty of nanowires (polyynes) are obtained. We noticed the same result in arc discharge experiments with currents below 20 A. From these considerations, it is our opinion that the formation of nanotubes is related either to the possible formation of long linear carbon chains and to the presence of a (strong enough) driving force which leads these chains to interact each other, as in the case of arc discharge experiments at high currents. In the case of the nanotube formation at the electrode, if the growth process is not completed or it is frequently interrupted (like in the case in which strong current instabilities are present), some carbon nanowires can remain trapped inside the nanotube, thus forming the observed nanotube-nanowire hybrids.

We have already shown that Raman spectroscopy readily indicates the occurrence of the presence of sp-hybridized carbon systems. For this reason we compare in fig.6 the spectra as taken in the carbon deposit and in the collected liquid residue.

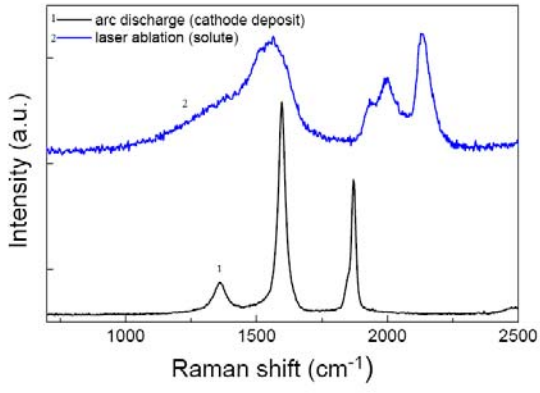


Fig.6. Comparison between the Raman spectra of the deposit collected onto the cathode (in the case of the formation of the hybrids) and the material left into the liquid after an ablation process.

Apart from the differences observed in the D and G line region due to different graphitization processes, we observe that the nanowires inserted into the nanotubes have stretching signals which are strongly red shifted with respect to free polyynes.

This can be understood considering that the position of the -C≡C- stretching is inversely proportional to the chain length [21] and that the chains inserted into the nanotubes are certainly much longer than 20 carbon atoms. Furthermore it has been recently observed that a moderate contribution to the red shift could come from an interaction between the linear carbon chain and the nanotube walls which soften the carbon bonds [22]. Finally it has been observed that carbon nanowires inserted into the nanotubes are much more stable with respect to free linear chains. Then the understanding and the control of the formation processes can be useful for specific applications of these 1D carbon materials with intriguing properties.

4. Conclusions

We have shown that 1D carbon nanomaterials can be obtained either by using laser ablation or arc discharge processes in liquid environments. A comparison between these two strategies has shown that linear carbon chains are one of the most important products of any experimental condition either in the case of laser ablation or arc discharge. On the other hand, the formation of carbon nanotubes is mostly due to the presence of a strong driving force during the discharge at high current values. In some particular cases the formation of these nanotubes is accompanied by the presence of tube-chain hybrids, during unstable discharge conditions.

References

[1] "Carbon Nanomaterials", Y.Gogotsi edt, Taylor and Francis (London, 2006).
[2] "Carbon Nanotubes", M. S. Dresselhaus, G. Dresselhaus, Ph. Avouris Edts, Topics in Applied Physics 80, Springer (London, 2001).
[3] I. Alexandrou, H. Wang, N. Sano, G. A. J. Amaratunga, J. Chem.Phys **120**, 1055 (2004).
[4] A.Scalisi, G.Compagnini, O.Puglisi, J.Appl.Phys. **94**, 7874 (2003).
[5] V. Scuderi, S. Scalese, S. Bagiante, G. Compagnini, L. D'Urso, V. Privitera Carbon **47**, 2134 (2009).
[6] G. Compagnini, B. Pignataro, B. Pelligra, Chem. Phys. Lett. **272**, 453 (1997).
[7] G. Compagnini, M. E. Fragala, L. D'Urso, C. Spinella, O. Puglisi, J. Mater. Res. **16**, 2934 (2001).
[8] F. Cataldo, Tetrahedron, **60**, 4265 (2004).
[9] J. R. Heath, Q. L. Zhang, S. C. O'Brien, R. F. Curl, H. W. Kroto, R. E. Smalley, J. Am. Chem. Soc. **109**, 359 (1987).
[10] A. D.Slepkov, F. A. Hegmann, S. Eisler, E. Elliott, R. R. Tykwinski, J. Chem. Phys. **120**, 6807 (2004).
[11] Z. Crljen, G. Baranovic, Phys Rev Lett **98**, 116801 (2007).
[12] A.Scemama, P.Chaquin, M.C.Gazeau, Y.Benilan, Chem.Phys.Lett. **361**, 520 (2002).
[13] A.Shashurin, M.Keidar, Carbon **46**, 1792 (2008).
[14] G. Compagnini, G. Baratta, Appl. Phys. Lett., **61**, 1796 (1992).
[15] A. C. Ferrari, J.Robertson Phys. Rev. B **61**, 14095 (2000).
[16] L. Calcagno, G. Compagnini, G. Foti, M. G. Grimaldi, P.Musumeci, Nucl.Instr.Meth. B **120**, 121 (1996).
[17] E. G. Gamaly, T. W. Ebbesen, Phys Rev B **52**, 2083 (1995).
[18] L. D'Urso, G. Compagnini, O. Puglisi, Carbon, **44**, 2093 (2006).
[19] X. Zhao, Y. Ando,Y. Liu, M. Jinno, T. Suzuki, Phys. Rev. Lett. **90**, 187401 (2003).
[20] T. Sakka, K. Saito, Y. H. Ogata, Appl. Surf. Sci. **197-198**, 246 (2002).
[21] L. Kavan, J. Kastner, Raman and infrared spectroscopy. In Carbyne and Carbynoid Structures. Kluwer Academic Publisher, Dordrecht, 1999.
[22] D. Nishide, T. Wakabayashi, T. Sugai, R. Kitaura, H. Kataura, Y. Achiba, H. Shinohara, J. Phys. Chem. C **111**, 5178 (2007).

*Corresponding author: gcompagnini@unict.it