SYNTHESIS AND CHARACTERIZATION OF SINGLE WALL CARBON NANOHORNS PRODUCED BY DIRECT VAPORIZATION OF GRAPHITE

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ABSTRACT

A new method is described for large-scale production of Single Wall Carbon Nanohorns (SWCNH). In a prototype reactor (a 30 kW plant for an estimated production of about 100 g/h of soot) optimal thermodynamic conditions that favour nanohorn formation were determined. The characterization of collected soot was performed by several techniques: thermogravimetric analyses (TGA), Raman spectroscopy, and transmission/secondary electron microscopies (HRTEM - SEM). The soot analyses revealed conspicuous presence of good-quality carbon nanostructure, mainly SWCNHs, with small amounts of graphene foils and amorphous phase material.

The first results demonstrated the excellent capability of the new approach that can be easily scaled up to tens the present scale, potentially becoming a powerful method to bring SWCNHs into every day applications

Keywords: carbon, nanotubes, nanohorns, graphene

INTRODUCTION

Single Wall Carbon Nanohorns [1,2] (SWCNH) represent one of the most interesting carbon nanostructures belonging to the thrived nanotube family.

A key characteristic is their tendency to group together and form aggregates (spherical clusters or bundles) like dahlia flowers or buds, with overall diameters of tens/hundreds nm. Advantage of this “self assembling” characteristic is not only the very large surface area, but also an easy permeation of gases and liquids inside their structure.

In spite their tiny tubular structure, SWCNHs maintain many of the typical properties of carbon nanotubes: easiness of functionalization and good electrical and thermal conductivities. Nowadays, SWCNHs therefore represent more than a promise for a very wide range of possible uses, e.g.: methanol fuel cells support; efficient hydrogen storage; super-capacitors; generation of hydrogen by decomposition or steam-reforming of methane; composites for lubrication. Moreover, recent literature [3,4] focussed the important role of SWCNH for photovoltaic applications, since they are considered to be ideal for electron-acceptors hybrid systems.

In addition, many applications in life science were recently reported, e.g. ranging from drug delivery to NIR laser-driven functional CNH complexes used as antiviral materials. Regarding SWCNH toxicity, a very important issue for social sustainability of nanotechnologies, it is widely confirmed that, in experiments using mice and rats, the cytotoxicity was negligibly small [5,6]. Also SWCNH-based hybrid materials and nanofluids with promising properties were reported [7,8].

Not still commercially available, SWCNHs can be produced in laboratory-scale quantities without catalysts, a key feature since they are very difficult to remove, and with high purity starting from graphite by laser ablation/vaporization processes [1,9] or by AC or DC arc discharge [10,11].

For relevant amount, the only known industrial-scale process uses an advanced graphite vaporization method, consisting in spotting a powerful CO_2 laser on a rotating cylindrical rod [12].

With all the foreseen potential market applications, an enormous impact is expected if SWCNHs could become a low-cost raw material thanks to diffusion of methods for massive production.

In this framework, a new method, based on heating of graphite rods by induction of very intense, high frequency, eddy currents (a patented method already tested successfully for fullerenes and carbon nanotubes production [13]) was tailored for mass production of SWCNHs and presented here.

EXPERIMENTAL

To produce carbon nanostructures like fullerenes, nanotubes or nanohorns starting from solid precursors (graphite), a very high specific energy (~60 kJ/g) supply is necessary for the vaporization/atomization of precursor. Arc discharge and laser ablation reach such critical energy density, but discharge methods, being limited in the maximum current compatible with a controlled arc current, cannot be easily scaled up and the laser ablation technique requires a very high power and costly CO_2 laser for real mass productions (hg/h of soot), although it is the only actually used.

The process of heating a conductors by electromagnetic induction, where eddy currents are generated within the

object itself giving rise to Joule heating, is well known and consolidated for industrial application. One of the most interesting properties of heating by eddy currents is the relevant power density that is possible to concentrate on workpieces, that can reach several $kW \cdot cm^{-2}$, sufficient to reach the temperature (3000-3200°C) necessary to sustain the evaporation of graphite and permits the successive condensation of carbon nanostructures. Moreover, this kind of plant can be scaled up till to MW scale, even increasing the overall efficiency.

Recently, the patented reactor [13] was realized to demonstrate feasibility of induction heating for CNTs production, where a synergic heating of both solid and plasma phases reaches the necessary thermodynamic conditions for the NTs synthesis. A new 30 kW power plant was specifically set up for SWCNH fabrication for soot production rates around 0.1 Kg/h. A detailed description of the apparatus and typical operational conditions is given in the cited patent.

The reactor chamber, cooled by water circulation, is pumped down by primary and turbomolecular vacuum pumps (Edwards and Pfeiffer Vacuum), equipped with a (Air Liquide) gas streaming inlet, controlled by a mass flow controller (MKS). A cooled finger acts as collector to harvest soot production. Since production occurs in dynamic gas flow condition, an exit port drain the excess gas, that is filtered (0.1 micron mesh, Donaldson) and recycled in the process. A quartz window allows the process to be observed externally. No direct temperature control is possible in the process, but off-line measures by an optical pyrometer through the quartz window assured that temperatures over 3000°C on graphite surface were reached during heating.

Soots were produced under diverse experimental conditions and with different kind of commercial graphite (SGL Carbon Gbmh). Experiments to optimize the flux and the fluidodynamic behavior in presence of extreme temperature gradient are still in progress.

RESULTS

All the mentioned SWCNH production methods tends to produce some quantities of wrapped or unwrapped graphene foils, amorphous carbon and graphite sub-micron particles, aka "giant graphite balls" (GGBs) [14]. Thermo-Gravimetric Analysis (TGA) in air or in oxygen flux is a very efficient tool for determining the overall quality of soot material, providing information on the different carbon structures, due to differences in their decomposition temperatures.

Fig.1 (red lines) represents typical TGA curves (800°C max, in air flux, 5°C/min ramp, performed with a SDT Q600 - TA Instruments) of a production batch of soot "as prepared". In accord with literature ([7,14]), in the derivative curves different phases are well observable: an amorphous phase peak at 400°C, followed by peaks related to SWCNHs, and almost two peaks ascribable to residual graphitic structures as in [7] (GGBs and graphene). The residual is quite low, below 4%, compatible with the purity of graphite used in these experiments. For comparison, neat TGA curves of used graphite are reported (blue lines) in the same figure.

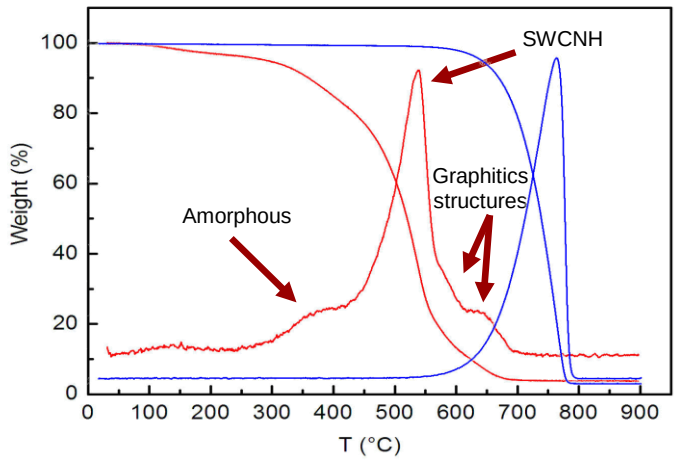

Figure 1: TGA curves of untreated soot (red) and pure graphite (blu).

TEM is the most accredited technique to evaluate the soot, even if, visualizing less than few pg of sample, cannot be assertive for overall production quality. Fig. 2 shows TEM images of single particles found in the soot produced by the reported method: both typical assemblies of nanohorns (bud-like and dhalia-like) are present. Fig.3 represents a direct comparison of HR-TEM and SEM images, showing agglomerates of dhalia- and bud-like nanohorns.

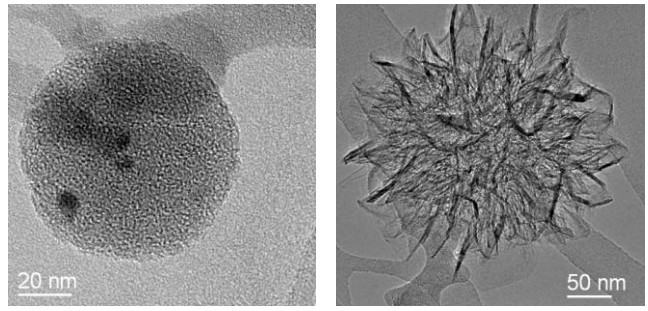

Figure 2: TEM images of single nanohorn particles in the untreated soot: both bud-like and typical Dhalia-like structures are present

The other acknowledged technique able to evidence the presence of SWCNHs is the Raman spectroscopy. Raman spectrum in fig. 4 shows typical bands observed for SWCNH, from two samples of soot respectively collected from the cool finger inside the reactor and from the residual dust from the chamber walls, with a high intensity D band

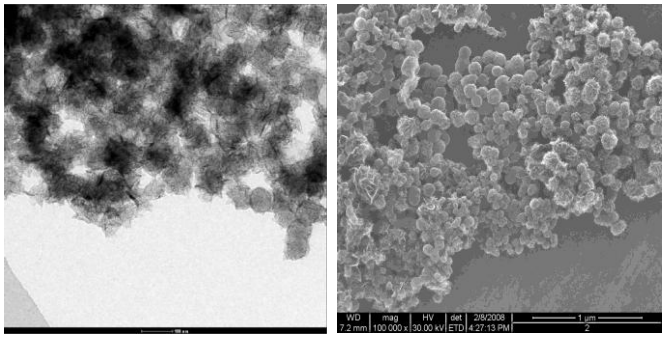

Figure 3: Comparison of TEM (left) and SEM (right) images of SWCNH

at 1314 cm^{-1} and the G band at 1594 cm^{-1} with intensity comparable to that of the D band. The spectrum also shows the G' band (overtone of the D band) at 2620 cm^{-1} and a characteristic band at 2895 cm^{-1}.

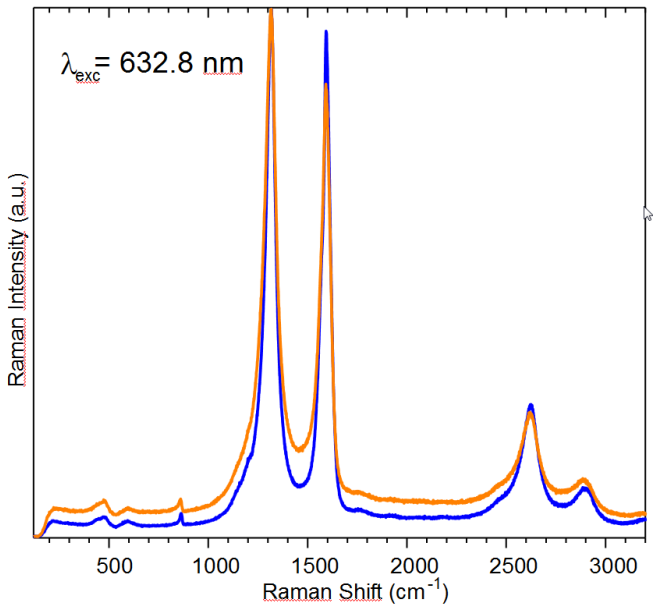

Figure 4: Raman spectra of soot sampled in two zones of rector chamber. Typical bands for SWCNH are observed in both samples

CONCLUSION

The presented method demonstrated its remarkable potentiality in large-scale production of SWCNHs with good purity. The plant can be scaled up to tens the present scale. Furthermore, by changing the reactor parameters and injecting suitable catalyst (Fe or Co organometallic compounds) or adding other gases to carrier gas (like nitrogen or diborane), the same plant could be able to produce N-doped or B-doped SWCNHs or different kind of carbon nanomaterial, i.e. single wall nanotubes.

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