PREPARATION AND CHARACTERIZATION OF CARBON NANOSCROLLS

A. Longo[1], C. Camerlingo[2], S. De Nicola[2], and G. Carotenuto[1*]

[1*] Institute for Polymers, Composites and Biomaterials- National Research Council . IPCBP-CNR - viale Kennedy, 54. Mostra d'Oltremare Pad. 20 - 80125 Naples, Italy. giancaro@unina.it
[2] Institute for Superconductors, oxides and other innovative mateirals and devices, National Research Council. SPIN- CNR Complesso Universitario di M.S. Angelo, Via Cinthia, Naples - 80126, Italy.

Scrolled graphene sheets are very important carbon nanostructures that offer a number of useful physical characteristics (e.g., very high specific surface area, and electrical and thermal conductivity), adequate for applications in different technological fields like, for example, hydrogen storage materials, sorbents, catalyst supports, highly porous electrodes for batteries and supercapacitors, , fillers for high-strength structural composites, etc.

In this work we report a simple approach for the bulk production of carbon nanoscrolls (CNSs) has been recently developped [1] and polarized micro-Raman spectroscopy (μ-RS) scattering measurements on carbon nanoscrolls (CNSs) fabricated by the shear-friction method.

The method to prepare carbon nanoscrolls is based on the application of shear-friction forces to convert graphite nanoplatelets into carbon nanoscrolls using a bi-axially oriented polypropylene (BOPP) surface. The combined action of shear and friction forces causes the exfoliation of graphite nanoplatelets and the simultaneous roll-up of graphite layers.

Evidence of the CNSs formation is given by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM and TEM micrographs are shown in figure 1. These investigations reveal that the CNSs have a long tube-like and fusiform structure with a hollow core surrounded by few layers of graphene. As visible that the produced CNSs are structurally made of continuous graphene sheets rolled up in a hollow tubular form of length ranging from 0.5 to 2.5 μm and diameter *ca*. 100 nm.

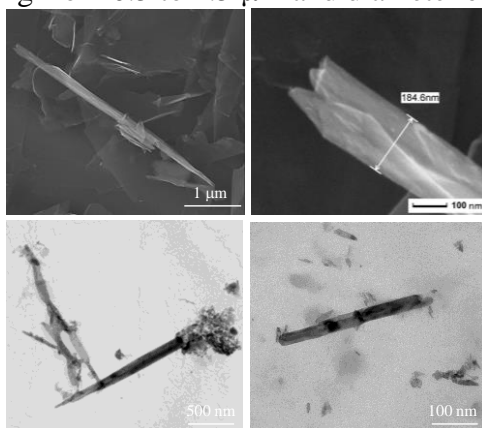
Figure 1: SEM micrograph of (A,B) and TEM images of CNSs (C,D).

The μ-RS spectra were acquired in air at room temperature using a 17 mWatt He-Ne (632.8 nm) laser source. The laser light was focused to a 2-μm spot size on the samples through a confocal microscope with 100x optical objective. In order to gate information of graphene lattice orientation [2], μ-RS was executed with polarized light. The configuration was used with both the excitation and signal light beams polarized along a fixed direction (y-axis) by a polarizing polymer filter . The sample consist of a single nanoscroll . It was rotated under the microscope objective by an angle φ about the optical axis (z-axis) of the incident light.

The carbon based material Raman spectrum is characterized by two main peaks , the so-called D and G modes, positioned at wavenumber of about 1350 cm^{-1} and 1580 cm^{-1}, respectively. The G peak is assigned to the double degenerate E_{2g} phonon mode at the Brillouin-zone center while the D peak is originated by a double resonance process involving phonons near

K points and its intensity strongly depends on the disorder degree and on defect presence [3]. A further broad peak, the 2D mode, is observed at about 2650 cm^{-1}.
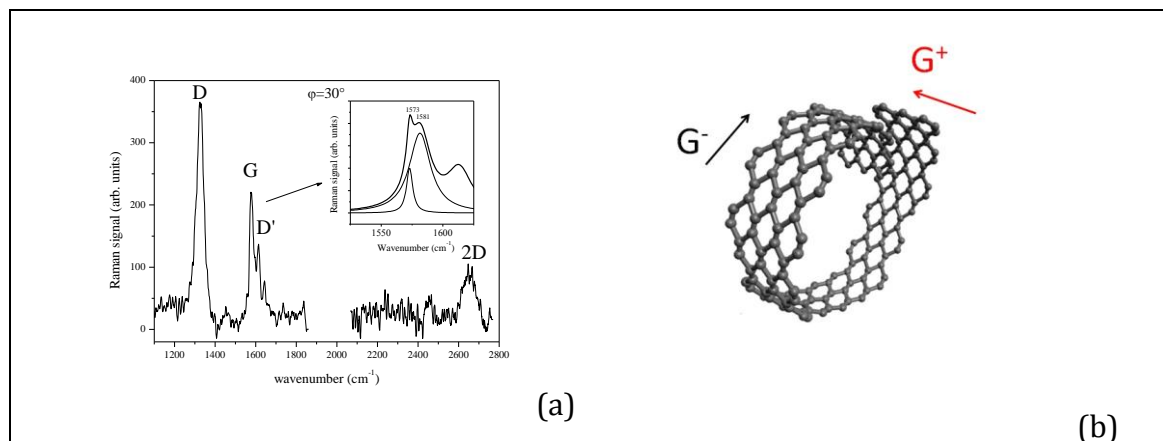

Figure 2: Raman spectrum of an insulated CNS. Both the excitation light and Raman signal were polarized along a fixed direction (Y-axis). The CNS is rotated by an angle φ =30° with respect to the strain x-axis. The enlarged view of the G peak is reported into the inset: The peak can be deconvolved in terms of two Lorentzian components, because of the energy split of the G mode induced by strain.

This peak is the second order of the D mode, but, differently from this one, it does not require the presence of disorder for its activation. A strong polarization dependence of the 2D mode intensity in graphene has been experimentally reported [4-5], while not changes with polarization is expected for the G mode intensity because corresponds to phonons with E_{2g} symmetry. However, the E_{2g} symmetry is lowered when graphene is stretched out of equilibrium and strain is induced. This is also the case of CNS and carbon nanotubes because the curvature of the graphene foil induces a deformation of the C-C bonds that are expected to lengthen and soften in the direction perpendicular to the axis of curvature. The unaxial strain induces a split of the G mode in two components G$^-$ and G$^+$ with different energy, corresponding to fixed orientation of the vibration with respect to the strain axis [6]. The lower energy subband G$^-$ is generated by phonons directed longitudinally to the strain axis, while G$^+$ is related to phonon mode transverse to the strain axis. In the case of CNS, the strain axis is directed perpendicular to the main scroll axis.

This energy split is clearly observed in the CNS. When the G peak is analyzed in terms of convolution of Lorentzian functions, two different components have been evinced (see inset of Fig.2a) centered at 1573 cm^{-1} and 1581 cm^{-1}, and assigned to the G$^-$ and G$^+$ modes respectively. The lower energy subband G$^-$ is generated by phonons directed longitudinally to the strain axis, while G$^+$ is related to phonon mode transverse to the strain axis (see Fig. 2b).

The axis orientation of the graphene sheet with respect to the direction normal of CNS axis has been determined by the analysis of the dependence of the intensity of the G$^-$ and G$^+$ Raman modes with polarization angle φ.

References
[1]   G. Carotenuto, et al., Nanoscale Research Letters 8 (2013) 403.
[2]   V. Zólyomi, et al., Physica Status Solidi B 248 (2011) 2435.
[3]   R. J. Nemanich, et al Physical Review B 20 (1979) 392.
[4]   D. Yoon, et al., Nano Letters 8 (2008) 4270.
[5]   S. Sahoo, et al., Journal Applied Physics 110 (2011) 044320.
[6]   T.M.G. Mohiuddin, et al., Physical Review B 79 (2009) 205433.
[7]   This work has been financially supported by the ENAM project (Rif: 2011-S116-00100).