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RESEARCH PAPER

Microstructures of carbon nanoscrolls characterized by polarized micro–Raman spectroscopy

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Abstract: Carbon nanoscrolls (CNSs) are produced by rolling up the graphite layer in graphite nanoplatelets on a nanofibrous bi-axially oriented polypropylene surface by a shear-friction mechanism. Microstructures of the CNSs are characterized by optical and scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy and micro-Raman spectroscopy. Results indicate that the CNSs have a long tubular and fusiform structure with a hollow core surrounded by few graphene layers. The orientation of the graphite lattice with respect to the scroll axis is accurately determined from the split of the vibrational *G* mode by polarized micro-Raman spectroscopy. Morphological changes produced by the rolling are also described.

Key Words: Carbon nanoscrolls; Shear stress; Bi-axially oriented polypropylene; GNP; Micro-Raman spectroscopy

1 Introduction

Carbon nanoscrolls (CNSs) are novel carbon nanomaterials that have many useful graphene properties without the disadvantages of stacking phenomena that are observed with graphene. Already in 1960, Bacon[1] described a graphite whisker in which a graphene sheet is rolled into a scroll. However, the scrolled structures have been available in a high purity and large quantities only recently. These carbon nanostructures are generated by wrapping a graphene sheet into a helical structure [2–9]. Because of the scroll topology their properties differ from those of either single or multi-walled carbon nanotubes. In contrast to carbon nanotubes, CNSs contain interlayer galleries. CNSs offer a number of useful physical characteristics (e.g., very high specific surface area, and electrical-thermal conductivity) adequate for applications in different technological fields like, for examples, biomedical (drug-delivery, image contrast agents, hyperthermie, et al.) [10], electrical (high-porous electrodes) and hydrogen storage applications [11–13]. A variety of synthetic approaches have been widely explored to produce large amounts of carbon nanoscrolls and to realize their applications [14–29]. Lithography had been used to synthesize wide ribbons from graphene sheets, but the quality was limited by the lithographic resolution [14]. Chemical and sonochemical methods have been developed to produce narrow carbon nanoscrolls, but with a low yield [15–22]. Nanoscrolls have also been produced by unzipping carbon nanotubes, but the resultant quality and yield also need to be improved [23–25]. Scrolled structures have been obtained by direct rolling up of the graphene monolayers by ball milling [26]. Little amount and low quality CNSs were obtained at the end of the graphite grinding process, and the diameter of these scrolls was quite large (ca. 400 nm) [27]. Tunable graphene nanoscrolls were produced by using Fe_3O_4 nanoparticles as the catalyst precursor based on a chemical vapor deposition method [28]. Recently, we have developed a simple approach for the production of CNSs [29]. This method is based on the application of shear-friction forces to convert graphite nanoplatelets to carbon nanoscrolls using a biaxially oriented polypropylene (BOPP) surface. An important aspect for the assessment of the technique is the morphological investigation of these produced rolled structures. One of the most commonly used techniques to characterize carbon related materials is Raman spectroscopy. It plays a very important role in acquiring information not only on morphological properties but also on physical, chemical properties of graphene and graphene based structures [30, 31]. Herein we report on a polarized micro-Raman spectroscopic technique, which allows to determine the chirality, hence the crystal orientation of the graphite lattice with respect to the scroll axis of the structures produced by the micromechanial method. The technique allows to obtain both qualitative and quantitative

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information of the graphite lattice orientation by using the split of the vibrational G mode.

2 Experimental

An alcoholic (ethanol, Sigma-Aldrich 99.9%) dispersion of nanographite (graphite nanoplatelets, GNP), was slowly rubbed against on the surface of a BOPP (Manucor S.p.a., film thickness = 40 μm) film using a low-density polyethylene (LDPE) piece. The alcoholic suspension was allowed to dry during the rubbing down process. After drying the concentrated liquid suspension was removed from the BOPP film by pouring pure ethanol on it. The resulting black suspension contained a large amount of nanoscrolls. Nanoscrolls were separated from the un-rolled and/or partially rolled graphene-based material by sedimentation in ethanol since their Stokes coefficient value is significantly higher than that for graphene sheets. The high roughness of the BOPP due to the nano-fibers on BOPP surface is able to induce a rolling up process in the graphene sheet. Indeed, the dimension of the nano-fibers is 4.20 Å [32], which is comparable to the graphite interlayer spacing (3.35 Å), thus leading to enhanced mechanical grip between the two sliding surface. The mechanism involved in the CNS formation is schematically depicted in Fig. 1.

The displayed time sequence (from top to bottom) illustrates the formation of a rolled nanostructure. The sliding and separation of graphene sheets take place under the weak shear forces acting along the BOPP surface. GNP and CNSs were morphologically characterized by SEM (a FEI quanta 200 FEg equipped whit an Oxford Inca Energy system 250) and TEM (a FEI Tecnai G2 Spirit TWIN whit LaB6 source). The powder containing CNSs was diluted in ethanol (98.8%) and sonicated for 10 minutes. A drop of the liquid was placed on a microscope glass and left in air until the solvent was completely evaporated. Single CNS was identified by optical microscope and analysed by micro-Raman spectroscopy (μ-RS). For the measurements a Jobin-Yvon system from Horiba ISA was used, with a TriAx 180 monochromator, equipped with a liquid nitrogen-cooled charge-coupled detector. The grating of 1800 grooves/mm allows a final spectral resolution of 4 cm^{-1}. The spectra were recorded in air at room temperature using a 17 mW He-Ne laser source (wavelength 632.8 nm). The spectrum accumulation time was 300 s. The laser light was focused to a 2 μm spot size on the samples through an Olympus confocal microscope with a 100 × optical objective. The laser light beam was polarized along a fixed direction (Y–axis) by a polarizing polymer filter. The same filter was used for polarize the Raman signal. By rotating the sample under the microscope objective by an angle φ about the optical axis (Z–axis), μ-RS was performed at different incidence angles φ of the polarized light with respect to the CNS orientation. The CNS axis was aligned to the Y–axis for $\varphi = 90°$. In order to determine the basic vibrational modes that contribute to the Raman signal, the spectra were analyzed in terms of convoluted Lorentzian functions by using a best-fit peak-fitting routine of a GRAMS/AI (2001, Thermo Electron) program, which is based on the Levenberg-Marquardt nonlinear least-square method. Peaks constituting the spectrum were manually selected in order to define the starting conditions for the best-fit procedure. The best-fit was then performed to determine convolution peaks with an optimized intensity, position and width. Its performance was evaluated by means of the χ^2 parameter. Fourier Transform Infrared (FT-IR) spectroscopy of the CNS samples was performed in the mid infrared range of energy (4000-400 cm^{-1}). A FT/IR–6000 spectrometer from JASCO Inc (USA) has been used in transmission mode. An ethanol solution of CNS was dropped on the surface of a thin (thinner than 1 mm) fresh prepared pellet of KBr and left in dry air until the solvent was completely evaporated. The FT-IR spectrum was acquired in transmission mode on a surface area of about 5 mm^2. A 100 scan acquisition process has been used with a spectral resolution of 1 cm^{-1}.

3 Results and discussion

The nano-fibrous structure of the BOPP film surface was analyzed by atomic force microscopy (AFM) as shown in Fig. 2a. It can be seen that the BOPP surface is made of nanosized polypropylene fibers capable of inducing the opening of the graphite nanocrystal edges, thus causing a scrolling-up process under the effect of the applied shear stress.

Fig. 2b shows the morphology of the GNP precursor. Flat graphite nano-platelets with sharp edges can be clearly seen. The average size and thickness of the GNP precursor was of a few microns and ca. 20 nm, respectively. After the mechanical treatment the material morphology was completely modified. SEM and TEM analysis of the scrolled structures are shown in Fig. 3. Fig. 3a shows a large amount of tubular structures produced by the rolling-up of carbon sheets. They appear to be distributed all over the examined surface in presence of nanoplatelets of varying size and orientation. The reaction yield was about 14%. The produced CNSs are structurally made of continuous graphene sheets rolled up into a hollow tubular form of length ranging from 0.5 to 2.5 μm and diameter ca. 100 nm.

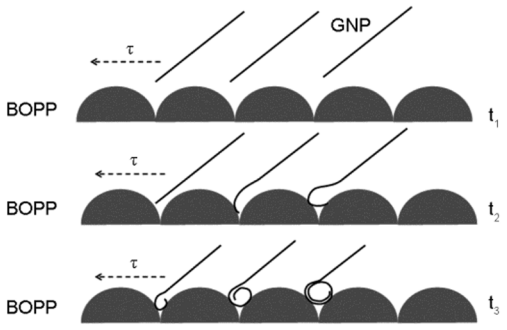

Fig.1 Scheme of the micromechanical method for transform GNPs to carbon nanoscrolls.