TEM investigation of the crystal lattice registration of carbon nanotubes over graphene membranes

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Summary

We investigated the adhesion of single-walled carbon nanotubes to the surface of graphene membranes using aberration-corrected transmission electron microscopy. We mixed nanotubes of different chiralities with a solution of dispersed graphene flakes. The spontaneous atomic match of the two lattices was directly imaged using high-resolution transmission electron microscopy, and we found evidences of a chirality dependent grafting of the tubes to the surface of the graphene membranes.

Key words: graphene, SWCNTs, chirality selection, lattice registration, surface adhesion.

Introduction

Chirality dramatically affects the physical and electronic properties of Single-Walled Carbon Nanotubes (SWCNTs) determining whether the SWCNTs are metallic or semiconducting (Odom *et al.*, 1998; Widem *et al.*, 1998). Current growth methods result in SWCNTs of mixed chiral indices, and an atomic level control during the growth is far from being achieved. Finding a simple and effective way to discriminate and sort chiral from achiral SWCNTs will be an important step toward their practical exploitation. Chirality control and selection are commonly addressed in post-grown processes, and among them, two main strategies can be identified: the elimination (partial or total) of tubes with specific chirality, or the selection of only one family of tubes from a solution (Chen *et al.*, 2007; Sato *et al.*, 2008). Within the frame of this second approach, the specific surface interaction between SWCNT and poly-aromatic molecule has been recently investigated (Ju *et al.*, 2008). Under specific relative orientations between the lattice of SWCNTs and of the poly-aromatic molecules, the selective locking of certain tubes matching the lattice orientation of the underlying molecules has been shown. The unlocked SWCNTs were then removed by means of different further treatments. Following the above method, using graphene membranes as large poly-aromatic molecule, we investigated the structural relationships between the two lattices at their contact area. We used aberration-corrected transmission electron microscopy high-resolution imaging to determine the atomic structure of both carbon nanotubes and of the supporting graphene membrane, and we found a systematic registration of the tubes with the underlying honeycomb lattice. Moreover, results suggest a preferential grafting of aligned zig-zag tubes to the surface of the membranes, providing evidences for graphene membranes to act as tangential nanosieves to select the chirality of supported nanotubes.
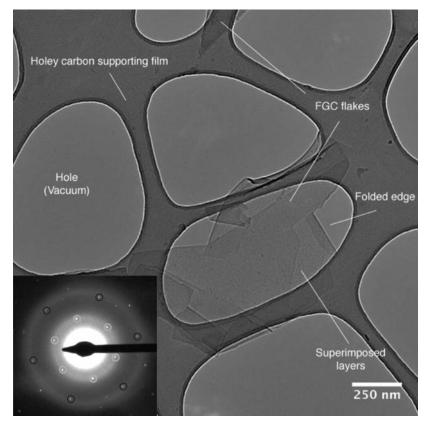
Materials and Methods

Commercial arc-discharge grown SWCNTs of different chiralities were dispersed in isopropanol and sonicated for 10 hours to separate tubes bun-

dles and to reduce their length. The solution was then centrifugated to sediment larger aggregates and bundles of tubes, and the spernatant has been separated. Natural Madagascar's graphite microcrystals have been mechanically exfoliated by means of gentle grinding in a mortar, to reduce the grain sizes avoiding excessive flakes fragmentation. The ground graphite was then mixed in the solution of SWCNTs previously prepared, and sonicated for 15 minutes to provide additional exfoliation of the flakes. Finally the mixture of SWCNTs and graphite flakes has been centrifuged to obtain the sedimentation of the residual graphite crystals, leaving a suspension of large FGCs, suitable for the Transmission Electron Microscope (TEM) characterization.

TEM samples were prepared by drop casting the solution of SWCNTs and FGCs on standard 3 mm copper grids covered by a perforated amorphous carbon film. TEM observations and electron diffraction experiments have been performed using a Tecnai F20 TEM microscope, equipped with a CEOS aberration corrector, available at the CNRS-CEMES Laboratory in Toulouse. A customized electro-optical set-up was devel-

oped to allow the microscope to be operated at an accelerating voltage of 80 keV to reduce beam damage to the sample (Molhave *et al.*, 2007; Girit *et al.*, 2009).

Results and Discussion

Figure 1 shows a dispersed FGCs flake from the prepared solution over the carbon support of the TEM grid, while the inset shows the diffraction pattern from the central part of the flake, where the hexagonal pattern from the honeycomb lattice of graphite is clearly visible. It is worth noting that the proposed method is not effective to the synthesis of large monolayer graphene flakes, as also reported elsewhere (Hernandez *et al.*, 2008). Nevertheless, deposits from the solution contain mainly thin FGCs flakes few microns in size, as shown in Figure 1, which are usually composed of tens of graphene layers, as can be determined by a careful analysis of the border of the flakes. Since SWCNTs will interact only with the surfaces of the FGCs flakes, we did not need individual
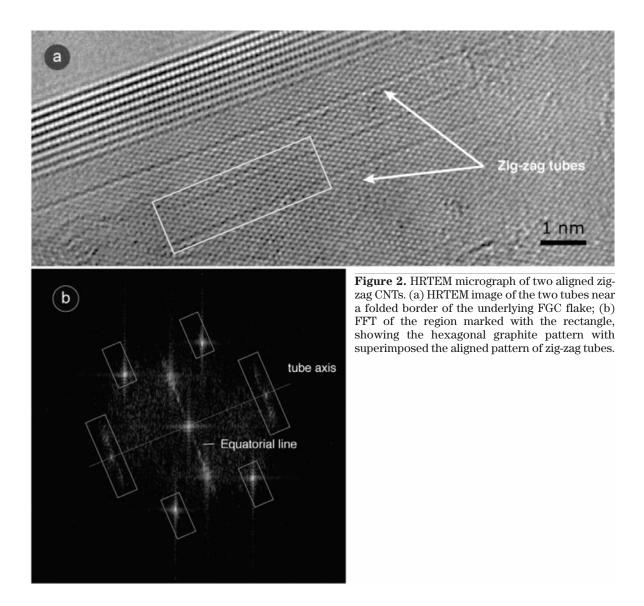

Figure 1. TEM image of the produced thin FGC flakes. In the image a flake is suspended over the amorphous carbon support of the TEM grid. (Inset) Electron diffraction pattern from the central area of the flake, showing graphite hexagonal symmetry, highlighted by black and gray circles.

graphenes, and the produced samples fulfill simply the essential requirement of obtaining electron transparent flakes for TEM investigation. TEM analyses also confirmed the absence of large ropes and bundles of SWCNTs in the solution, therefore effectively removed with the centrifugation process.
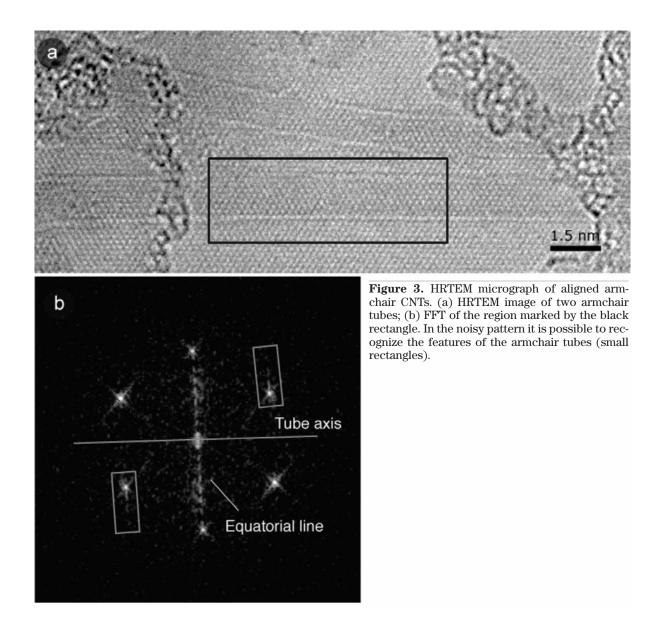
Nonetheless shorter, individual SWCNTs were effectively dispersed over the surface of the FGCs. Using HREM, a direct determination of the atomic structure, and of the lattice orientation, of individual SWCNTs and of the underlying FGC is possible. Figure 2a shows the HRTEM image of two tubes over a FGC flake. The tubes run parallel to the folded border of the FGC flake, which exposes the (0002) fringes, and both are perfectly

aligned along the direction of the underlying honeycomb lattice. Figure 2b) shows the Fast Fourier Transform (FFT) of the region highlighted with the rectangle. In the image, both the hexagonal pattern from the honeycomb lattice of the flake, and the elongated features with modulated intensity of the SWCNT are superimposed and perfectly aligned. From the geometry of the pattern in the FFT, and the diameter of the tube measured in the HRTEM image, it has been possible to determine the precise chiral structure of both tubes (Qin, 2006). The upper one was a (17,0), while the lower one was determined to be (14,0), therefore both zig-zag.

Another example of aligned SWCNTs is shown in Figure 3. In this case two armchair tubes are

Figure 2. HRTEM micrograph of two aligned zig-zag CNTs. (a) HRTEM image of the two tubes near a folded border of the underlying FGC flake; (b) FFT of the region marked with the rectangle, showing the hexagonal graphite pattern with superimposed the aligned pattern of zig-zag tubes.
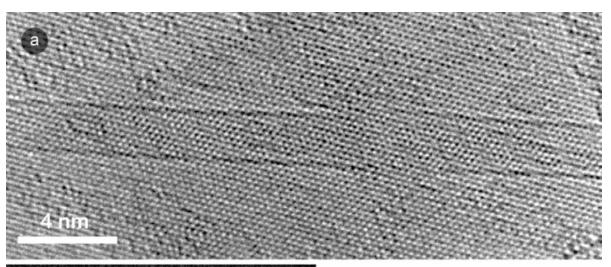
visible over the FGC flake surface. Figure 3b) reports the FFT of the region marked by the black rectangle. Notwithstanding the pattern is rather noisy, the characteristics features of the graphite lattice as well as of the armchair tube are still visible. Again a perfect alignment between the two lattices is observed, with the axis of the tube exactly oriented with respect to the underlying FGC flakes structure.
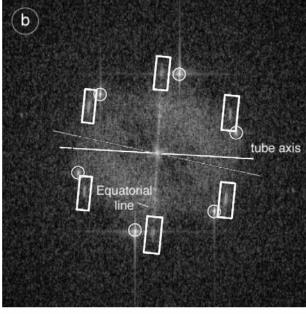
Figure 4a reports the HRTEM image of one of the few armchair CNTs lying over the surface of a FGC flake without a perfect match of the two lattices. Figure 5b shows the FFT of the region of

the carbon nanotube where it is evident the superposition between the tube and the FGC membrane. It is possible to clearly distinguish the features corresponding to the graphene lattice (small circles) as well as the ones of the armchair tube (rectangles). It is worth noting that the HRTEM image of Figure 4a demonstrates that both the lattices of the CNT and of the underlying membrane are simultaneously but individually imaged. When the two lattices do not match, as in the case of Figure 4a, moiré effects (e.g. the modulated intensity variation noticeable along the imaged tube) are clearly visible, while when there is a perfect

Figure 3. HRTEM micrograph of aligned armchair CNTs. (a) HRTEM image of two armchair tubes; (b) FFT of the region marked by the black rectangle. In the noisy pattern it is possible to recognize the features of the armchair tubes (small rectangles).

alignment of the two crystal structures, as in the previously shown images, a single lattice is observed. This confirms the capability of the experimental approach to distinguish between aligned and not aligned tubes as well as the reliability of the previously shown results.

The results of the HREM investigation suggest hypothesis of the capability of graphene membranes to graft on their surfaces SWCNTs of specific chiralities. More in details, this retaining property seems to act preferentially on achiral tubes and depends strongly on the relative orientations between the graphene and the CNTs lat-

tices. To confirm these achievements an extensive investigation of the samples has been performed with HRTEM. More than 30 tubes lying on the surfaces of FGCs were investigated. Unfortunately, on the one hand, in most of the cases the tubes were superimposed over thick portions of the flakes and it was impossible to distinguish the lattice image of the tube from that of the different graphene layers of the FGC. On the other hand, frequently the flakes were folded and scrolled several times, originating in the FFT of the images several graphene hexagonal patterns with different orientations, making actually
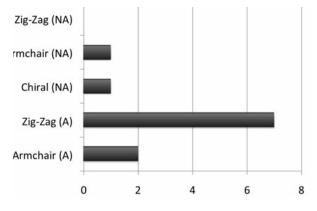

Figure 4. (a) HRTEM image of an armchair CNT over a FGC flake, showing moiré effects along the tube due to the superposition of the two lattices; (b) FFT of the region of the tube showing the superposition of graphene honeycomb lattice reflections, highlighted by the small circles, and misaligned elongated features of the armchair tube, indicated by the rectangles.

impossible to determine the relative orientation of the CNTs lattice. Therefore, only few tubes were lying on single crystal domains, and only for those it was possible to complete the analysis. The results are summarized in Figure 5.

In spite of the weak statistics it is evident that almost all the SWCNTs were found to be zig-zag and aligned with the underlying FGC structure, with essentially no evidence of chiral or not aligned tubes, as if they were effectively eliminated from the graphene surfaces during the sonication and centrifugation processes. This singular interaction between graphite surfaces and CNTs has been previously studied experimentally (Yanagi *et al.*, 2001; Rettig *et al.*, 2003) and theoretically (Buldum and Lu, 1999). From the experimental point of view, Atomic Force Microscopy (AFM) at low temperature demonstrated that carbon nanotubes could be easily manipulated over graphite layer (Yanagi *et al.*, 2001). Moreover the authors reported that the lateral force applied to the cantilever of the AFM to rotate in-plane a CNT is not continuous, presenting peaks at specific orientation of the tubes: the CNT locks at minima of the interaction energy every 60o. Subsequent high-resolution Scanning Tunneling Microscopy (STM) studies demonstrated the atomic alignment between the CNTs and the graphite lattices in those locking positions (Rettig *et al.*, 2003). These results confirmed previous theoretical calculations concerning the simulation of the frictional energy between CNTs and graphene (Buldum and Lu, 1999). The simulations, performed for SWCNTs of different chiralities (see Figure 1 in Buldum and Lu, 1999), show that each nanotube has a specific equilibrium minimum, depending on its chirality, and with a periodicity of 60o, which reflects the symmetry of the underlying graphene lattice.

Outside the equilibrium positions, the potential energy corresponding to different orientations is nearly flat, confirming the low friction expected out of the locking positions. Only for zigzag tubes the minima have a clearly visible "cup" shape, suggesting a more stable retaining of zigzag nanotubes on the graphite surface towards small rotations around the equilibrium value. Notwithstanding all the differences between the reported calculations and the systems studied in this paper, this last result gives us an encouraging suggestion in the explanation of the observed preferential locking of the shortened zigzag SWCNTs over the FGCs surfaces.

Figure 5. Histograms showing the number of Aligned (A) and Not-Aligned (NA) tubes of different chiralities among the few CNTs that were lying on a single crystal domain orientation and therefore it was possible to analyze completely.

Conclusions

By means of aberration-corrected high-resolution transmission electron microscopy, the spontaneous interaction between single wall carbon nanotubes of different chiralities and few graphene crystals membranes has been carefully investigated. The experimental results show evidences for the surface of the flakes to act as an effective selector for zig-zag tubes perfectly aligned over the graphene lattice, as chiral or not aligned tubes were eliminated from the FGCs surface with sonication and centrifugation processes.

This achievement is in good agreement with previously published results concerning the frictional energy between SWCNTs and graphite. The statistics of the performed analyses is quite weak, mainly due to a low control in the sample preparation, resulting in a low rate of details fulfilling the requirements for a reliable HRTEM investigation. A better control on the quality of the FGCs in terms of dimensions of the flakes as well as number of layers, will allow us to improve significantly the statistics.

Nevertheless the proposed approach resulted capable to completely analyze the observed systems, to determine the chirality of the tubes as well as their alignment over the FGCs surfaces, and to distinguish between aligned and not aligned tubes, and therefore the evidence of the preferential sticking of zig-zag CNTs over the graphene surface is solid. On the one hand, these achievements suggest that, for a more complete understanding of the

problem, the effect of different honeycomb substrates, such as individual graphene and FGCs with a different stacking, has to be done. Nonetheless, on the other hand, these results envisage the exploitation of the graphene and FGC surface as an effective tangential nano-sieve to select SWCNTs as a function of their chiralities.

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