Self-Assembling of Graphitic Nanoplatelets

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ABSTRACT

Low dimensional carbon based materials are strictly dependent from the intrinsic property of self-assembling. Three simple and fast methods to unzip Single Wall Carbon Nanotubes (SWCNTs) have provided different structural organization of graphite layers, observed by electron microscopy investigations. Our structural studies reveal the presence of a deviation from perfect crystal of the graphite aggregations, called turbostratic graphite, because of the presence of rotational and/or translational stacking faults of its hexagonal basal planes. Furthermore, one more different crystallographic phase of graphite with an orthorhombic cell and symmetry Cmma has been experimentally detected by Selected Area Electron Diffraction (SAED) analysis.

INTRODUCTION

Chemical approaches and self-assembling processes may produce graphitic nanostructures with desired shape and dimension for fundamental and practical application. One of the most feasible methods to produce graphitic layered materials is by CNT unzipping, which is a processes intentionally used to control the self-assembling aggregation of nanoribbons graphitized.

The interesting properties of low-dimensional carbon based materials have led to the exploration of numerous applications such as electronic applications due to the potential use that these light, stiff and flexible materials can offer for designing building block components in nanoelectromechanical systems (NEMS). Moreover, there have been numerous investigations on the potential use of such materials as conducting channel in CMOS transistors. Unzipping process of CNTs produces 2D nanostructures, reported in the literature as nanostrips [1], nanoplatelets [2] and also as graphene nanoribbons (GNR) [3], that are of great interest, in particular for the nature of edge dislocations and the appearance of defective dangling bonds in carbon networks. The electronic structure of such nanostructures depends sensitively on the crystallographic orientation of the edges.

EXPERIMENTAL

The graphitic nanoplatelets were obtained from disruption of Single Wall Carbon Nanotubes (SWCNTs) by using high-shear mixing and/or treatments in sulfonitric mixtures either at room or high temperatures. Depending on the process procedures, different kinds of re-organization are found to occur, as evidenced by
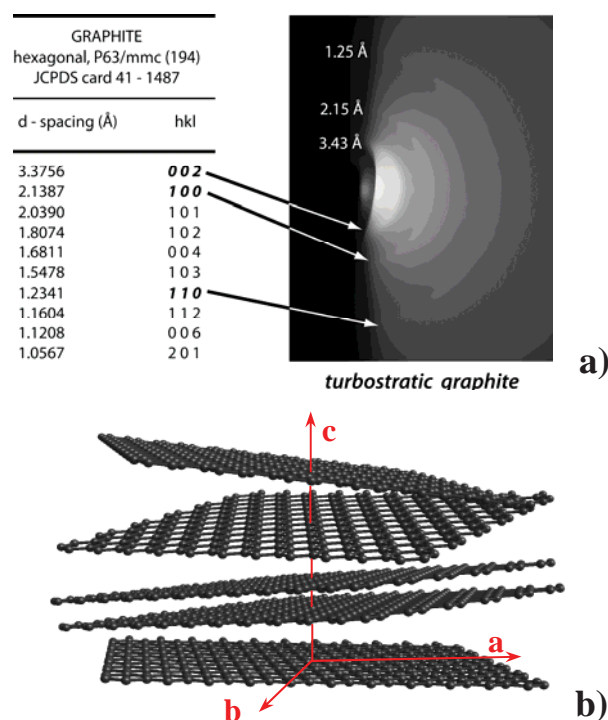

Figure 1. *a) crystal structural parameters and experimental diffraction pattern of unzipped SWCNTs graphitized.*
b) structural model of the graphene planes in a turbostratic stacked arrangement not perfectly oriented along the c-axis.

different and complementary electron diffraction and microscopy techniques.

The adopted disruption methodology allows indeed to obtain samples characterized by very different interactions between proximal units.

Here, we focus our investigation on the structural characterization of self-assembling graphitic layers that it has been and it is a long-standing scientific problem. Unlike crystalline system, where long-range ordering is established by periodic stacking of fundamental building blocks, known as unit cells, rolled open SWCNTs process produces graphitic flakes, having no long-range translational or orientational order, although some degrees of short- and medium-range order do exist. We used transmission electron microscopy (TEM), selected area electron diffraction (SAED), scanning electron microscopy (SEM), and Reflection High Energy Electron Diffraction (RHEED) to image graphitic structures

produced from SWCNTs [4]. The samples were deposited by drop casting on a Si substrate for SEM and RHEED analyses and by dipping, for a very short time, holey carbon grids in the sulfonitric mixture for TEM and SAED analysis.

RESULTS AND DISCUSSIONS

RHEED technique conditions have been used to probe the samples achieved from SWCNTs unzipping by high-shear mixing method (Fig. 1). The electron diffraction pattern (EDP) evidences that the number of rings detected is much lower than the expected for graphite. No diffraction lines were observed from the planes *hkl* with $l \neq 0$, with the exception of (002) planes having a slightly broadened ring. Diffraction broadening of the (002) ring and absence of the second-order diffraction (004)
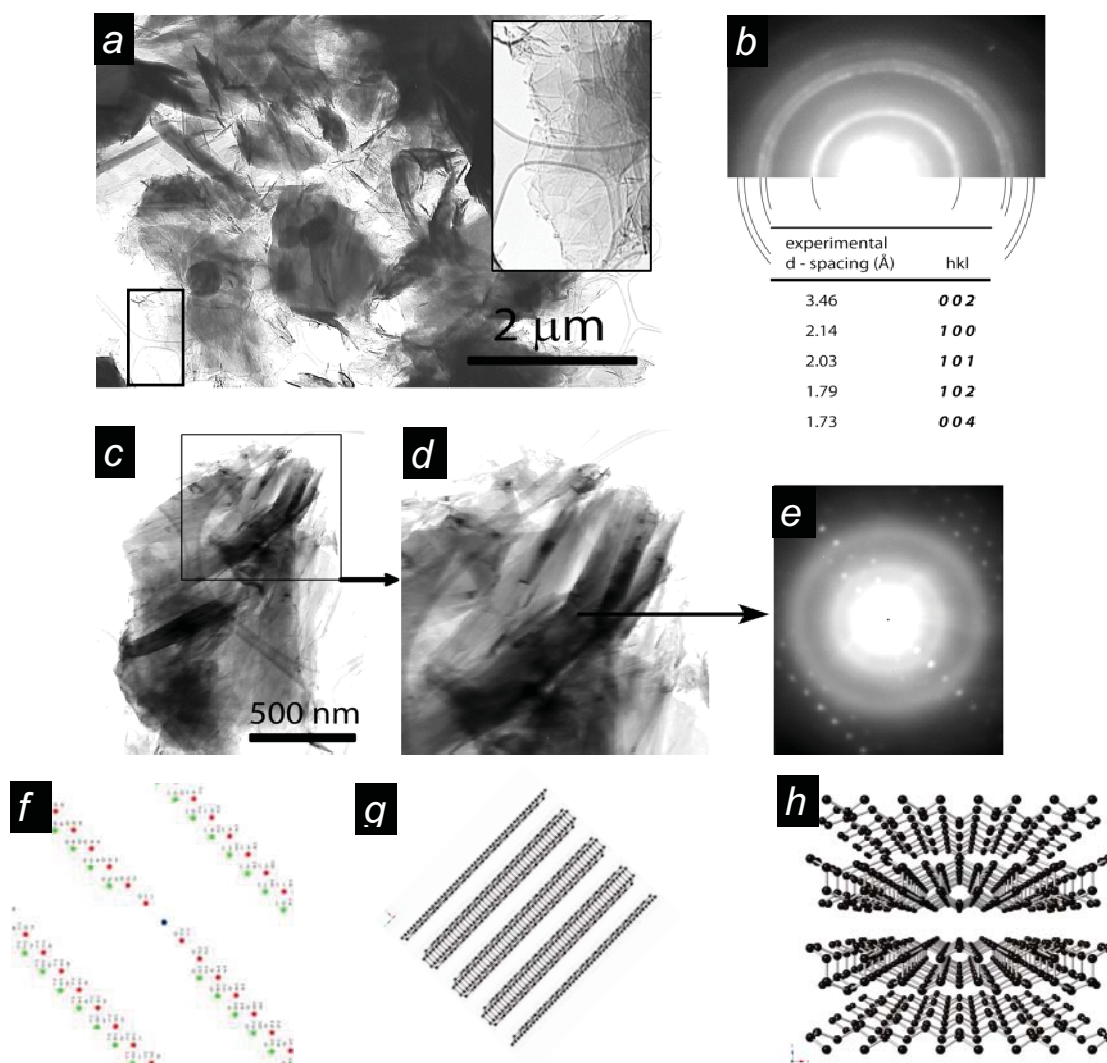

Figure 2.

a) TEM image of unzipped SWCNTs after sulfonitric mixture treatment at room temperature, and b) corresponding ED pattern. c) and d) bright field TEM image of a folding graphene layers. e) electron diffraction pattern taken from image a). f) theoretical electron diffraction pattern into reciprocal space and g) corresponding structural model of orthorhombic graphite with the electron beam along [9-11] zone axis into real space. h) perspective structural model of bilayer graphite stacking along the c crystallographic axis.

graphite ring, let us to consider a loss of periodicity along the *c*-axis crystallographic direction of the hexagonal lattice (Fig. 1a). The deviations from perfect single crystal is probably conditioned (*i*) by an interlayers distance not perfectly constant between the hexagonal planes, (*ii*) by rotational and/or translational stacking faults of the hexagonal basal planes, and (*iii*) by bending of layers planes.

From the experimental RHEED patterns, the measured interplanar distance of the basal planes has been determined to have a value of about 0.343±0.003 nm. This value is larger than the interplanar distance along the *c*-axis of the graphite, but it is similar to the disordered form called "*turbostratic graphite*" [5-7], schematically drawn in Fig. 1b.

SWCNTs sample were rolled open using sulfonitric mixtures at room temperature. TEM bright field image observation shows self-aggregation of graphite nanoribbons with anisotropic bending layers on the edges depending on the extension area of the flakes graphitized (Fig. 2a). Inset exhibits evident boundary lines between nanoribbons of graphite, forming a nano-mosaic arrangement with single pieces of several shapes because of the different etching directions of the unzipped process. Transmission electron microscopy also reveals the formation of high-contrast platelets, probably due to the graphene layers stacking self-aggregation, that can be rationalized in terms of a minimization of the pristine surface energy (Figs. 2c,d).

Mesoscale EDP of these self-assembled platelets, obtained from RHEED analysis, evidences the presence of polycrystalline material with *P63/mmc* hexagonal symmetry (Fig. 2b). The analysis of the fine structure is characterized by perfect superposition of diffraction spots coming from different crystallites randomly oriented. Since the RHEED resolution in the reciprocal space is better than in the case of SAED method in transmission conditions, accurate observation displayed one more internal weak ring pattern closer to the direct beam. The diffraction ring measures a distance spacing of about 5.65 Å, indicating the existence of anomalous different carbon phase because of the self-assembling evolution of graphite nanoribbons.

Selected Area-ED analysis probed on wrinkles and folded area display evidences of the presence of highly ordered (single-crystal) flakes with a relatively large (some thousands of nm^2) surface (Fig. 2e). Single-crystal, belongs to the diffraction spots pattern, has been characterized by EDP simulation. At the start of this study, we believe a hexagonal superstructure existed in the sample and we tried to determine it according to the EDP. The large discrepancy of the position of the diffraction spots between the experimental and theoretical patterns led us to attempt another phase of graphite with an orthorhombic cell and symmetry *Cmma* (amcsd 0013979) (Fig. 2f). The ideal crystal-structure, oriented with [9-11] zone axis, has the same lattice parameters (Fig. 2g) proposed by J. Fayos et al. [8], except the *c* stacking lattice parameter increased of 0.2 Å. Furthermore, this phase of graphite is recognized by the higher intensity peak of the interplanar spacing of $d_{002} = 5.64$ Å, that it has been observed and measured into

previously EDP (Fig. 2b). The crystal packing is constituted of graphite bilayers covalently bounded with the hexagonal benzene deformed into a chair conformational shape and the bilayers are shifted and
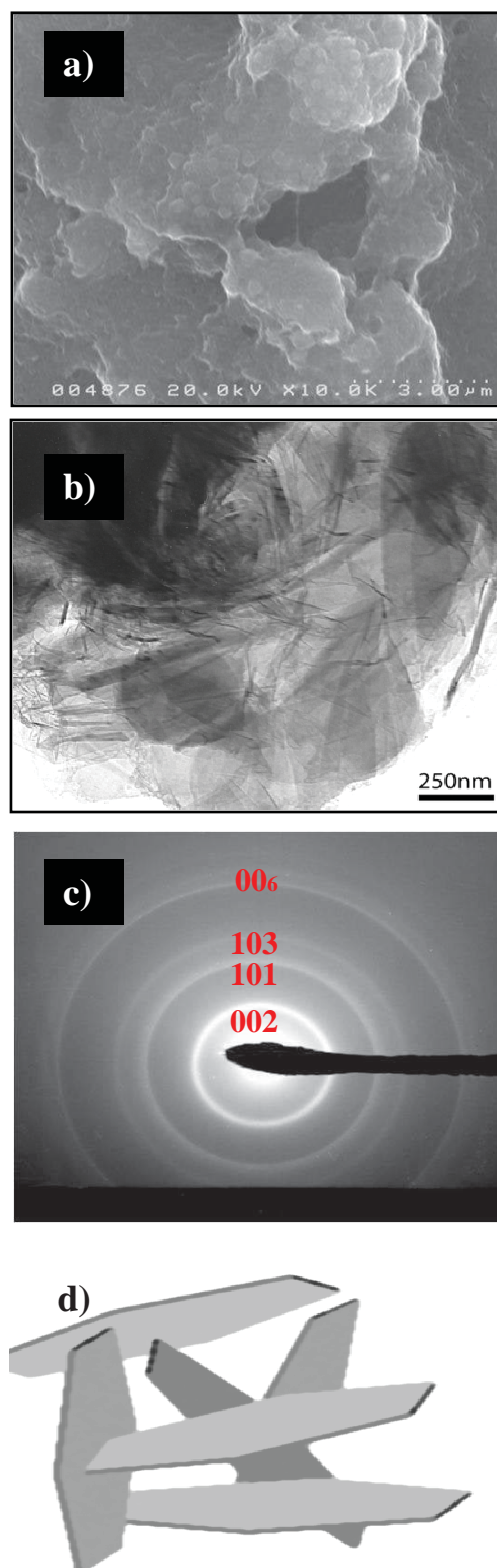
Figure 3.
a) SEM image of unzipped SWCNTs after sulfonitric mixture treatment at high temperature,
b) bright field TEM image of a folded graphene layers and multilayer turbostratic graphite.
c) electron diffraction pattern taken from image a), d) three dimensional model of graphite layers randomly orientated.

with an inter-biplanar distances of about 3.20 Å (Fig. 2h). Two experimental broad rings overlapping the single-crystal diffraction spots have an interplanar spacing of a very large distances of $d_{002} \sim 3.42$ Å and of $d_{103} \sim 1.56$ Å, corresponding to the presence of graphite with real missed orientations and increased interplanar distance of the hexagonal graphene layers. In addition, we examined the state of the reassembled unzipped SWCNTs obtained after sulfonitric mixtures treatment with the same above procedures, but at high temperature. SEM studies show compact graphite powder with particles clustered on a roughly surface, without evidence of the typical graphite platelets aggregations (Fig. 3a). TEM analysis probed on a large nano-area shows a high degree of nanotube opening in multilayers nanoribbons and forming graphite platelets turbostratically stacked with several edges scrolled up or folded slightly (Fig. 3b).

The use of thermal treatment in annealing steps show smooth surfaces of graphitic clusters compared to the room temperature treatment. This treatment leads more uniform graphite layers, decreasing the formation/size of wrinkles around the step edges and defect line of graphite nanoribbons and increasing the growth surface of the graphite islands.

Structural characterization has been performed by RHEED analysis on a relatively large thickness of the platelet-clusters. EDP shown in Fig. 3c undoubtedly confirms the presence of polycrystalline graphite, with lattice parameters practically coincident with those ones of 'reference' graphite reported in Fig. 1a. Hypothetical 3D-view of a disordered self-assembling of graphitic nanoribbons is sketched in Fig. 3d.

As a result of the thermal-stress induced process, the bilayer of orthorhombic graphite phases was regarded as a structural phase transition into the classical hexagonal graphite phase, during annealing and recrystallization treatments

Overall, the analysis of the EDPs indicates that the platelets are 'expanded' graphite, with a larger interplanar distance between successive graphene layers and coherent slightly reduced interplanar distances for the transversal planes. It is worth to noticing that the signal of un-processed SWCNTs has not been detected into any electron diffraction pattern collected with the appearances of equatorial oscillation or lines, or short diffraction lines located in the vertical or horizontal direction, or diffraction lines with arc shapes.

In all examined samples we were able to detect the different layer form of conventional graphite and bilayers of orthorhombic graphite. One most important finding is derived from the electron diffraction technique by reflection and transmission methods. The last case study clearly confirms that EDPs are very sensitive to small variations in periodic structure or lattice imperfection and to investigate phase transition phenomena. In order to resolve the fundamental problem of how is thick the bi-dimensional structures, TEM analysis of the flake-edges must be coupled with electron diffraction pattern studies.

The results show that the assembly processes can be tailored by modulating the disruption treatments and choosing a suitable dispersion medium, in order to produce selectively different forms of self-assembling, from polycrystalline aggregates to highly self-oriented mosaic-like structures, evidencing the possibility to achieve single-crystal platelets. It is expected that the identification of cooperative mechanisms acting in such systems could help in opening innovative crystallization pathways and give a relevant contribution for nanotechnologies.

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CONLUSIONS