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Determining the structure of graphene-based flakes from their morphotype

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ABSTRACT

Graphene-based flakes of various origins were investigated by transmission electron microscopy. For each of them, the morphotype was described, and then both the related structure (stacking type) and nanotexture (degree of perfection of the graphene layers) were described as well. Two kinds of clearly discriminated morphotypes were found ('crumpled' and 'folded'), for objects with similar overall dimensions (in the range of several micrometers large) and similar multi-graphene nature (with the number of stacked graphene layers in the range of 2–15, sometimes more). It is found that the morphological discrepancies relate to the structural discrepancies. Typically, whether the structure is either turbostratic or graphitic makes the flake morphotype be either crumpled or folded, as a consequence of preferred folding directions related to lattice periodicities. In this regard, structure prevails over nanotexture. This strict relationship implies that the 2D (turbostratic) or 3D (graphitic) nature of the stacking in graphene-based flakes whose determination usually requires diffraction studies may be merely deduced from low magnification images of their morphotypes.

1. Introduction

Defining carbon as a versatile material is a trivial statement. However, this versatility covers distinct characteristics whose discrimination is not always well understood. Carbon objects made of several graphenes piled-up, including the multi-graphene flakes which are studied here, may exhibit a large variety of morphologies. On the other hand, two types of thermodynamically-favored crystallographic structure exist as soon as a minimum of two graphene layers pile up, i.e., the turbostratic structure (corresponding to random rotational stacking), and the graphite structure (2H hexagonal, corresponding to the well-known ABA stacking sequence of graphite, first identified by Bernal in 1924 [1]). Other stacking possibilities such as ABC (3R rhombohedral structure) and AA (simple hexagonal structure) are incidental only, as they are usually found as stacking faults in genuine hexagonal graphite [2]. Actually, only a single example of isolated, rhombohedral graphite crystal has been found in the literature [3] since this peculiar stacking sequence has been identified, back in the forties [4,5]. In this paper, whether the structural and/or nanotextural characteristics of graphene-based flakes may somehow reflect on their morphotype was investigated by studying multi-graphene flakes originating from three kinds of preparation route.

2. Experimental

2.1. Synthesis and analytical procedure

Three different graphene-based materials were compared:

Material #1: a solution of few-graphene flakes was prepared by the intercalation of natural graphite (with gaseous potassium) and then spontaneous exfoliation of the resulting KC_8 graphite intercalation compound in an organic solvent (dimethylsulfoxide) [6].
Material #2: is a graphene-based material originating from the synthesis and/or deposition process of the amorphous lacey carbon films onto the transmission electron microscopy (TEM) copper grids, hence those objects were naturally present on the TEM grids as contaminants [7].
Material #3: is a pyrolytic carbon material obtained by a proprietary Chemical Vapor Deposition process. A chunk of the

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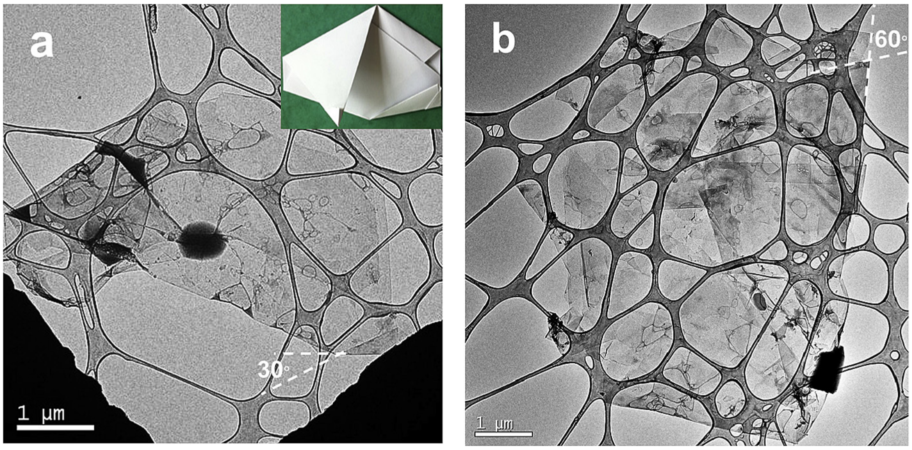

Fig. 1. Two examples of multi-graphene flakes from the exfoliated graphite material (Material #1) exhibiting the so-called ’folded’ morphology (referring to the folded paper model shown in the inset in (a). (A colour version of this figure can be viewed online.)

material was wet-ground in a boron carbide mortar in presence of a bit of ethanol, and the resulting powder was dispersed and sonicated for 10 min in a large amount of ethanol in order to make a somewhat stable suspension.

For Materials #1 and #3 above, droplets of each solution or suspension obtained were deposited onto lacey amorphous carbon film-coated TEM copper-grids. Obviously, no specific TEM preparation procedure was needed for Material #2. The resulting graphene-based objects were studied by means of medium-range magnification (see scale bars in the micrograph shown) then high resolution TEM, and selected area electron diffraction. All objects exhibited similar overall dimensions (in the range of half to several micrometers large, but a variable number of stacked graphenes, ranging from 2 to ~30 depending on the materials). The TEM used were a Philips CM30 (LaB$_6$ source) operated at 150 kV or a Cs-corrected Tecnai F20 operated at 100 kV. Electron doses were adjusted in order to limit irradiation damages (this means that illumination on the specimen was set at values able to provide an acceptable signal/noise ratio while the nanotexture remains visibly not affected during the time of exposure).

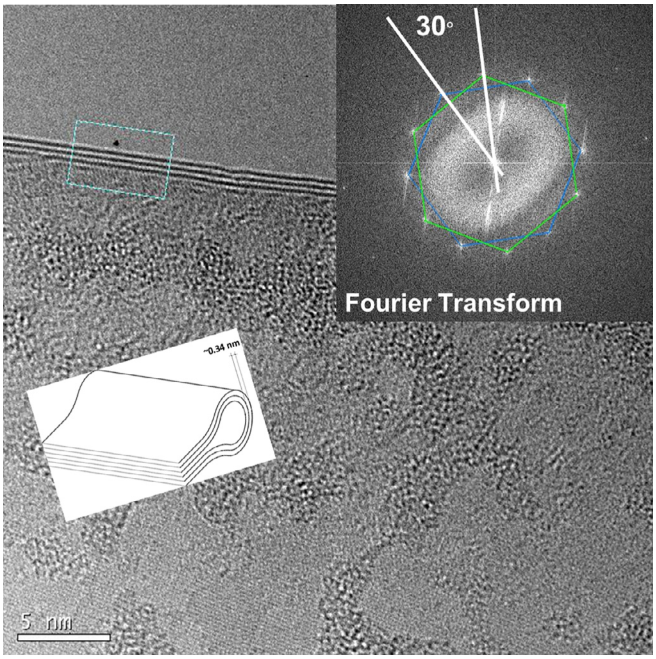

Fig. 2. High-resolution TEM image as an example of a single 3-graphene crystal with graphite structure (ABAB Bernal stacking) folded on itself, generating a second set of six*110* spots with a 30° misalignment. The bottom inset is a sketch illustrating how the flake is folded. The top right inset is a Fourier Transform of the lattice image (the resolution was indeed high enough for revealing the lattices of both the superposed flake parts, although they do not show up in the published image because of the low magnification). (A colour version of this figure can be viewed online.)

2.2. *Definitions*

The paper discusses the results while using a multi-scale nomenclature (namely: structure, nanotexture, texture, morphology) which is not consensual (yet) and which is specific to carbon materials in some aspects. It is therefore necessary to define the terms in the way they are used in the paper:

- *Morphology* describes features affecting the overall aspect of any kind of carbon objects, whether it is external or internal regardless of the actual presence of graphenes (for instance, the object can be made with amorphous carbon) and their orientation. Flake, filament, nanoparticle, are terms related to morphology.
- *Texture* is a feature which is common to all kinds of polyaromatic solids, as soon as they involve graphene stacking. It describes the inner arrangement of the graphene layers (or the graphene stacks) with respect to each other and/or to a specific direction, hence it includes any description related to isotropy/anisotropy. Concentric, random, aligned, are terms related to texture.
- *Nanotexture* is also a feature which is common to all kinds of polyaromatic solids, as soon as they involve graphene layer stacks. Thanks to high resolution lattice fringe mode TEM images, it describes the quality of face-to-face stacking and side-to-side association of graphene layers within areas of overall similar graphene orientation (SGO), whatever the texture. In most of polyaromatic solids, such SGO areas are spatially limited and separated from each other by grain boundaries in which structural defects concentrate upon thermal annealing, resulting in large, non-healable disorientations between neighboring SGO areas [8]. The average length of the straight parts of the graphene layers relates to the average width L_a of the coherent domains as seen by X-ray diffraction, and the average number of graphene layers stacked strictly parallel relates to the average height L_c of the coherent domains.
- Finally, *structure* relates to the various ways graphenes can pile up within a coherent stack, hence relates to crystallinity and coherence. There are several remarkable stacking configurations, the prevalent ones being turbostratic and graphitic, as reminded in the Introduction section.