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## Describing carbons

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### ABSTRACT

Carbon materials are unique materials for their diversity, owing to three possible hybridisation states ( $sp$ ,  $sp^2$ ,  $sp^3$ ), their ability to switch from one phase to another upon various external stresses (thermal, mechanical, pressure...), and the tolerance of graphene ( $sp^2C$ ) to defects of many kinds. This makes their description difficult, due to the lack of standardised vocabulary and misuses or ignorance of the existing ones. A common language is needed so that every word has the same meaning to everyone and that carbon scientists understand each other as accurately as possible. This paper aims to clarify the basic terminology to be used on this matter, by reminding some important definitions or terms, e.g. allotrope, polymorphism, molecular form, crystallite, graphitic, graphene, graphene layer, graphenic, graphitisation, graphitisation treatment..., based on authoritative publications when available. In addition, as  $sp^2C$ -based carbon materials exhibit the largest variability, a four-term description scheme (namely: morphology, texture, nanotexture, structure) is proposed and argued, which is believed to be sufficient (and necessary) to describe any kind of carbons, but molecular forms. Applying the recommendations proposed is expected to bring more consistency, clarity, and understandability to the forthcoming literature dealing with carbon materials.

### 1. Introduction

Carbon and humankind share a millennium-long common history. However, at a time where science was barely born, identifying some natural phases as carbon or, even more, discriminating between carbon phases was a job left to alchemists, that is to say, identification criteria were based on experiments where empiricism disputed with magics. The poor accuracy of the identification criteria mostly based on visual observations and biased interpretations had made that graphite was confused with lead for a long while, making it named “plumbago” (from latin “*plumbum*”). Then chemistry came to help, and plumbago was identified as actually being carbon, though as tardily as in 1779, thanks to C. W. Scheele. It was then proposed to be named “graphite” instead of plumbago 10 years later by A. G. Werner, to refer to its main application at that time, as pencil... lead. It was the same for diamond, even once proposed to be made of water (by L.-B. Guyton de Morveau [1]), until the joint efforts of chemists such as A. L. Lavoisier and L.-B. Guyton de Morveau in France and S. Tennant in UK finally acknowledged diamond to be pure carbon, in mid-18th Century. Then, the question regarding what could make diamond and graphite so different from each other raised up. Mineralogy came to the rescue, and the serious description of phases started, based on external, eye-visible aspects such as morphology, brightness, colour, and geometry measurement (angle

between faces, and symmetries). But the methodology was lacking the appropriate tools, and was unfortunately mostly limited to the macroscopic scale. It was not so much different, though, that the methodology which was used in Antiquity by Plato to propose some relationship between 5 different geometrical solid forms (that he could find in minerals) and the elemental components (namely: fire, air, water, earth, and universe). But progress was made, and A. Bravais (in 1848, books say) was able to propose his famous system of 32 symmetry classes dispatched into 7 different main crystal systems. But at that time, it was more an intuition, which appeared to be right and is still valid today, than a demonstration. This limitation has made materials to be tentatively discriminated by their properties, as an indirect characterisation of structure differences, since the identification of the atomic configurations was lacking. This was the approach based on which Berzelius proposed the term “allotropy” in 1841 [2] to discriminate between the different phases made of a single type of atoms but exhibiting different properties and multi-atom phases (compounds) of similar compositions. In the latter case, the term “polymorphs” was preferred in case the discrimination was based on physical behaviour, or “isomers” in case the discrimination was based on chemical behaviour [3,4]. As the terminology was depending on which property was considered, confusion and debates kept going on until the principle of X-ray diffraction (XRD) was discovered, understood, and exploited by the cumulated work

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performed by W. Röntgen, then M. von Laue, then W. H. and W. L. Bragg in the early 20th century [5]. From this moment, discriminating between phases was able to be made through the positions of their constituting atoms.

Since then, the problem of discriminating between phases from their crystallographic structures instead of properties was solved, but it was not sufficient for carbon. Carbon is the only element of the Mendeleev Table able of a tremendous versatility regarding its solid forms thanks to (i) a choice of three electronic structures ( $sp$ ,  $sp^2$ ,  $sp^3$ ); (ii) the possibility to exist as molecular forms as well as allotropic crystals; (iii) the existence of metastable forms which allow carbon to exist either as two-dimensional crystals or three-dimensional crystals while being able to adopt all the intermediate structural compositions; (iv) and most of all, the extraordinary flexibility and adaptability of the graphene sheet which allows building an infinity of possible graphene arrangements, the same way a paper sheet has in the art of origami.

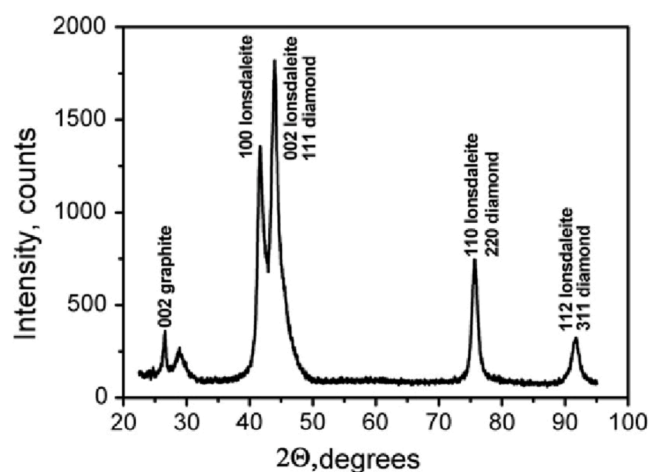
Obviously, then, XRD is not enough to describe a carbon material accurately. This means that giving a specific name to each of the carbon crystal structures identified so far (graphite, diamond, lonsdaleite...) thanks to XRD is not enough, a more comprehensive terminology is needed to describe whatever makes a carbon material different from another. And this is where confusion and misunderstanding take place. Because of the lack of standardised nomenclature, or the ignorance of those which exist [6,7], words such as **allotrope**, **phase**, **structure**, **microstructure**, **microtexture**, **graphitic**, **amorphous**, **graphite** and so on are largely misused in scientific papers dealing with carbon materials or used with different meanings. Even worse, they may be used willingly as words which the meaning is fuzzy enough to cover various aspects and features of the materials studied within the same paper, precisely because there is no normalised vocabulary available.

A contemporary French scientist and philosopher, Etienne Klein, once said: “*Si on dit mal les choses, on risque de mal les penser*” (“*With saying things wrong, comes the risk of thinking them wrong*”). This paper is here to focus on this problem, and aims to introduce a simple semantic guide to carbon scientists so that each of them may speak the same language and understand each other with no ambiguity, not by introducing new words, but by giving each of them a unique meaning and a unique, not-overlapping lexical field. Consequently, this paper does not intend to describe all kinds of carbon materials (they are too many for this). Excellent textbooks and monographs doing this can be found in the literature [8–12]. However, reading such textbooks evidences the lack of consistency regarding the terminology and vocabulary used, and reading them while keeping in mind the definitions and descriptors proposed here is advised.

## 2. What is a carbon allotrope?

Because carbon **phases** are made of a single type of atom, the term “**allotropes**” is the one to use for them, preferably to “**polymorphs**”. However, since the advent of XRD methods, Berzelius’s definition may be revised and completed, say upgraded, and carbon **allotropes** are actually those which discriminate by their atomic configurations, no longer by their difference in properties, in particular because the latter might not be discriminating enough. For instance, no significant difference in properties experimentally measured discriminates two crystallised forms of  $sp^3$  carbon such as diamond and lonsdaleite (although calculations predicted the latter being 58 % harder than the former [13]), but they clearly discriminate by their crystallographic systems, cubic and hexagonal, respectively (Fig. 1).

Therefore, a modern and more accurate definition of **allotropy** (yet already 60 years old) is “*the phenomenon of the existence of an element in a crystalline solid state in at least two distinct forms that differ from each other by the spatial arrangement of their atoms*”, as stated by Addison [15]. Attention has to be paid, though, that the diffraction patterns have to be obtained in powder mode, *i.e.* where the sample subjected to the incoming X-ray beam (or electron beam, eventually) is made of a



**Fig. 1.** X-ray diffractogram (Cu radiation) of the diamond and lonsdaleite structures. The specimen is a polycrystalline material in which diamond-lonsdaleite polytypes developed, obtained by a high pressure, high temperature treatment of **graphite** (reprinted from Ref. [14] by permission of Elsevier).

sufficient amount of randomly oriented **crystallites** so that no diffraction peak can be missed or altered in intensity. In other words, the orientation of the sample with respect to the direction of the incoming coherent beam should not play a role. It would be not right to designate a carbon **phase** as an **allotrope** based on a diffraction pattern which would not contain all the possible peaks merely because the carbon material would exhibit a non-isometrical **morphology** or an anisotropic **texture** (see Section 3) which makes it lying onto the sample-holder so that some atom planes cannot be under the Bragg angle. In that case, what discriminates such a carbon material from others is not **structure**-based but merely orientation-based, hence it is not an **allotrope**.

As a consequence, various carbon **phases** may be designated as distinct **allotropes** as soon as their diffractograms exhibit different diffraction peaks and/or bands at different  $2\theta$  locations. Fig. 1 already provided examples of two **allotropes** of  $sp^3$ C-based carbon materials. Apart from many hypothetical  $sp^3$ C **allotropes** predicted by calculation only (it is out of scope of this paper to make the list, but related references can be found in well-documented papers such as [16–18], only a few others do exist, yet more exotic, such as V-carbon, obtained from the high-pressure compression of  $C_{60}$  crystals [19]. Other  $sp^3$ C-based **allotropes** may be sometimes mentioned in the literature, such as adamantane [20] and its derivatives named diamondoids [21], or a 2D material named diamane synthesised recently [22] and so-called hydrographite [23]. However, none of them is pure carbon, as they are heavily hydrogenated, and their nanosize makes the hydrogen content quite significant (for instance, H/C at. = 0.5 in diamane). Same for other 2D  $sp^3$ C materials such as diamondol [24] and diamondene [25], which are presumably heavily functionalised with OH groups and other atoms, respectively. Anyway, none of them can be considered as a distinct **allotrope**, since their **structure** does not discriminate from that of genuine diamond or lonsdaleite.

Fig. 2 illustrates the best-known crystallised forms of  $sp^2$  carbon by their calculated X-ray diffractograms [26]. The top-two diffractograms in Fig. 2 are regular three-dimensional **structures** of carbonaceous materials (meaning that the carbon atoms are displayed periodically and coherently in the three dimensions of space). The rhombohedral **structure**, which was first described in 1942 [27], has to be calculated, because it is mostly found as stacking faults in the hexagonal **structure**. As a matter of fact, experimental X-ray diffractograms of the pure rhombohedral  $sp^2$  carbon **phase** cannot be found in the literature, because the latter is always mixed with that of **graphite** [28], or in so minor occurrence that only low-quantity-demanding methods (such as Raman spectroscopy [29]), can be used. The middle pattern in Fig. 2

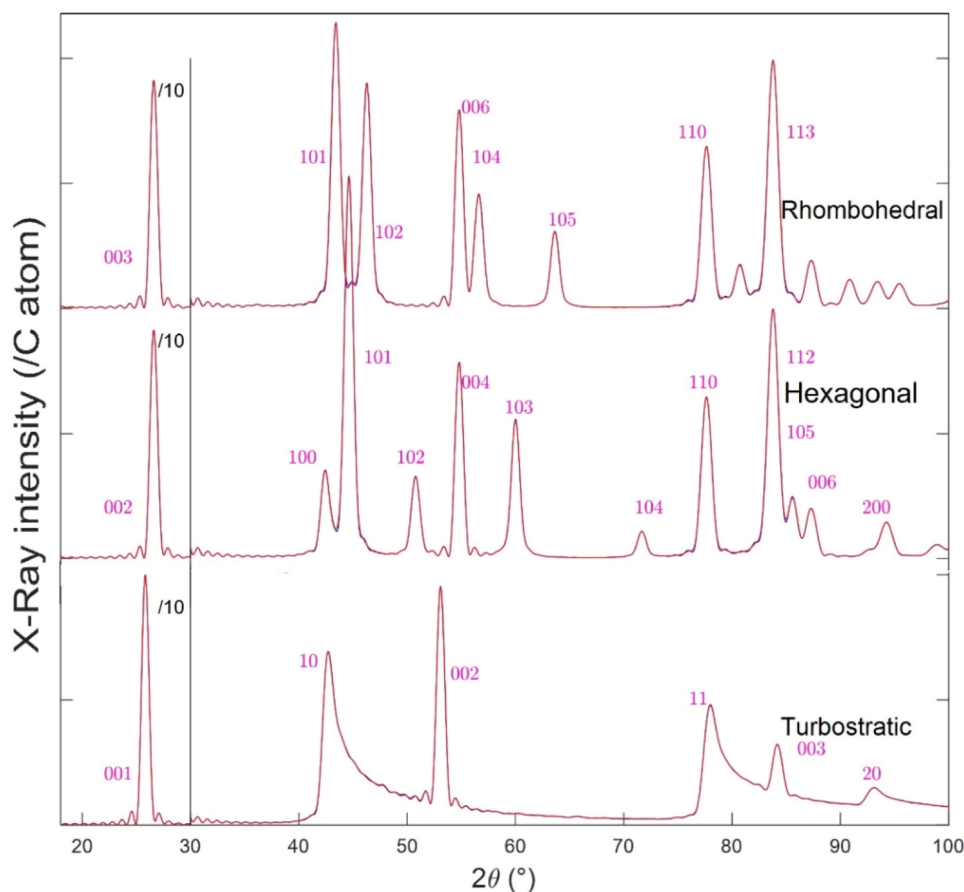


Fig. 2. Calculated X-ray diffractograms (Cu radiation) of the rhombohedral structure (top), the hexagonal structure (graphite), and the turbostratic structure (bottom) of graphenic crystals [26].

corresponds to the hexagonal structure of genuine graphite. It is worth noting that it is often referred to as the “Bernal” structure (as we did in Ref. [26] ...), from the name of the author who is assumed to have first determined the related structure in 1924 [30]. However, giving such a kind of nickname to a structure based on his discoverer’s name, or supposed to be, is dangerous because it happens that digging further into the literature may reveal some anteriority or other misunderstanding which makes the credit be definitively given to the wrong person. One example is the popular designation of “Stone-Wales defect”, which turned out to be wrong and should be replaced by “Dienes defect” instead [31]). The same thing happened here, since a paper by Hull described the hexagonal structure of graphite as early as 1917 [32]. Therefore, the “Bernal structure” designation should actually be replaced by “Hull structure” from now on (or “Hull-Bernal” for the least, in order to keep a link with the previous denomination so that the unaware carbon scientists are not confused) ...until a further anteriority is revealed one day. The problem is that, once a wrong term has become popular and widespread, it is almost impossible to have it changed for the right term. Habits are hard to get rid of, and the right knowledge spreads out more slowly than mistakes. The same happened with the use and meaning of “graphene” (see below).

As a matter of simplification, it is common for long to find in the literature the graphite structure to be identified only based on the 002 peak position, hence the  $d_{002}$  value [33], as in the graphitisation index  $g = (0.344 - d_{002}) / (0.344 - 0.3354)$  for instance [34]. It is right that, in principle, the lowest intergraphene distance of 0.335 nm can be reached only when the graphene layers involved are in 3D coherence, as in the Hull-Bernal or rhombohedral structures, and that, on the other hand, non-coherent stacking only allows a minimum of 0.344 nm, corresponding to the turbostratic structure commented further below [35].

However,  $d_{002}$  higher than 0.344 nm are commonly obtained in immature carbons and non-graphitisable carbons [36]. On the other hand, there might be reasons (e.g., internal stresses as developed by specific formation mechanisms and specific textures such as the concentric one when involving perfect graphenes [37]) for which the  $d_{002}$  value may not correspond to what is expected from the structure. Therefore, the unambiguous demonstration of the graphite structure requires the existence of the 112 peak in the diffractograms (in addition to the 00l and 100 and 110 peaks), keeping in mind that the 101 peak is not reliable for this because its occurrence can be affected by the presence of stacking faults [26,35]. This has suggested to consider the  $I_{112}/I_{110}$  intensity ratio as a more appropriate alternative to quantify the graphitisation rate [38]. It is also of a much easier use than the  $p$  parameter proposed by Franklin [35], based on the shape of the 112 peak. The absolute  $I_{112}/I_{110}$  reference value to consider in this case is 1.55, as obtained from the calculated XRD (Fig. 2, middle), a value which matches the experimental one obtained for a natural graphite such as Ceylon graphite [39], which is acknowledged as one of the best standards in this regard.

The bottom diffractogram in Fig. 2 is that of the two-dimensional structure typical of the one that Biscoe and Warren [40] were first to designate as turbostratic (i.e. in which graphene layers are periodically piled-up while being randomly rotated). 100 % turbostratic carbon is a genuine allotrope indeed, since the related diffraction pattern does not exhibit all the diffraction peaks that the two others do (Fig. 2). In addition, some of the peaks (the  $hk$  peaks) exhibit an asymmetric band shape which witnesses the partly two-dimensional nature of the structure (“partly”, because the occurrence of the 00l peaks does reveal a periodicity in the  $z$  direction, but limited to the stacking distance). It is well-known that, depending on the chemical nature of their precursor

and their thermal history, **graphene**-based carbon materials may range within a continuum of materials in which the ultimate ones exhibit the 100 % turbostratic **structure** at one end, and the 100 % hexagonal **structure** (**graphite**) at the other end [41–43]. Only those two, in the continuum, are genuine **allotropes**. The other carbons, intermediate, are **partially graphitised** in a various extent, and then have to be considered as exhibiting defective **structures** derived from that of **graphite**, but do not make distinct **allotropes**. Similarly to  $sp^3$ C carbons, existing  $sp^2$ C **allotropes** other than those shown in Fig. 2 are seldom, and limited to exotic **phases** actually involving a contribution of  $sp^3$ C such as kinds of polymeric  $C_{60}$  (one being named graphullerene) [44,45] and U-carbon [46], although the **structure** of the latter is still uncertain. Again, thanks to scientists' imagination and nowadays powerful calculation facilities, some hypothetical ones are also proposed, either based on pure  $sp^2$ C [47], or  $sp^2$ C +  $sp^3$ C combinations [48].

In a countless number of papers, including review papers dedicated to carbon material diversity (see [49–58] for instance, to cite a few), fullerenes, **graphene**, carbon nanotubes, and even carbon onions, are designated as carbon **allotropes**. This is ignoring the progress made since Berzelius's time, and the input brought by diffraction methods since then. In an attempt to clarify the situation of carbon **allotropes**, Heimann et al. [49] claimed that (i) "the term **allotropy**" refers to an alteration of the equation of state of a substance" (but it is not clear where this statement came from, certainly not from Berzelius's work) and (ii) that "Addison's definition (referring to Ref. [10]) overlaps that of **polymorphism**" (but it does not because **polymorphism** is dedicated to multi-element **phases** whereas **allotropy** is dedicated to single-element **phases**). Heimann et al. then proposed to distinguish the various carbon **phases** in accordance to the type of hybridization of the valence orbitals. They ended up with a ternary **phase diagram** of carbon **allotropes** as shown in Fig. 3. Fullerenes and nanotubes, which were the focus of the carbon community at that time, are located on it, even **graphenes**, along with **amorphous** carbon, vitreous carbon, and several other **phases**.

Such a ternary diagram cannot be right: **graphene** (if a monolayer, which is the definition acknowledged by IUPAC [6]), fullerenes, and carbon nanotubes (if single-walled, see Section 3.3.4), are NOT carbon **allotropes**, they are carbon **molecular forms** (possibly macromolecular), as sometimes duly acknowledged yet too scarcely [53]. Unfortunately, this is a confusion that has become so viral that it has spread out

everywhere [49–52,54–58], including textbooks.

On the other hand, the periodic arrangement of **molecular forms** may generate genuine crystallographic forms. The most obvious one are **graphite** of course (hexagonal as well as rhombohedral **graphite**) and turbostratic carbon, built from **graphenes**. Fullerite, built from fullerenes [59] is another one, with three different possible **structures** (simple cubic, face-centred cubic, and hexagonal cubic [60,61]). Periodic assemblies of single-wall carbon nanotubes (SWCNTs) also exist [62], generating typical diffractograms (Fig. 4) hence corresponding to a genuine **allotrope** (once tentatively named nanotubulite [64]). All are genuine carbon **allotropes** because they generate X-ray diffractograms exhibiting specific periodicities.

Not all carbon **molecular forms** which are able to combine into periodic assemblies generate an **allotropic structure**, because they merely generate X-ray diffractograms (remember, in powder mode) which are not different from that of other **allotropes**. For instance, this is the case for so-called carbon shells or cages [65], or nano-onions [66] depending on whether they are hollow or solid. Same for multi-wall carbon nanotubes (see Section 3.3.4) and multilayer **graphenes**, the diffractograms of which do not discriminate from that of turbostratic carbon (or possibly from **graphite**, in some rare cases), hence they are merely nanofoms of carbon **phases**. Another reason for carbon **molecular forms** not to exist as genuine **allotropes** is when they cannot arrange periodically because they do not exhibit a specific and reproducible **molecular structure** (for instance, single-layer carbon nanocones [67,68], subsequently designated as carbon nanohorns [69]).

Because of the two-dimensional nature of (single-layer) **graphene**, its mechanical flexibility, and the tolerance of the  $sp^2$  C=C bond to strain which allows replacing hexagon cycles by others (pentagon, heptagon, octagon), most of carbon **molecular forms** which do exist are usually  $sp^2$ C-based. The most well-known are cited above (fullerenes, single-wall carbon nanotubes, **graphene**, nanohorns...) but there are so many of them that they could be dedicated an "Encyclopedia" [53]. In addition, there are a few exotic ones such as biphenylene [70], and graphynes and graphdynes which have been partly synthesised [71], although they are a mix of  $sp^2$ C and  $sp$ C. Pure  $sp$ C has some **molecular forms**, such as cyclo[18]carbon [72], in addition to the well-known linear carbyne chain, the instability of which, however, still makes its existence controversial, except if encapsulated [73]. And then, come the hypothetical ones [58]. All these **molecular forms** are not carbon **allotropes a priori**, unless they are able to assemble into periodic

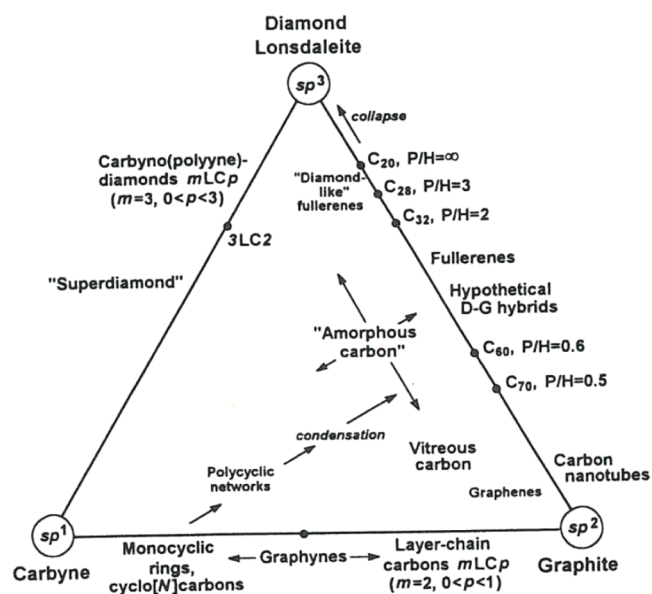


Fig. 3. Proposition for a distribution of the carbon **allotropes** in a ternary diagram based on hybridisation state, according to Heimann et al. [49]. Reprinted by permission of Elsevier.

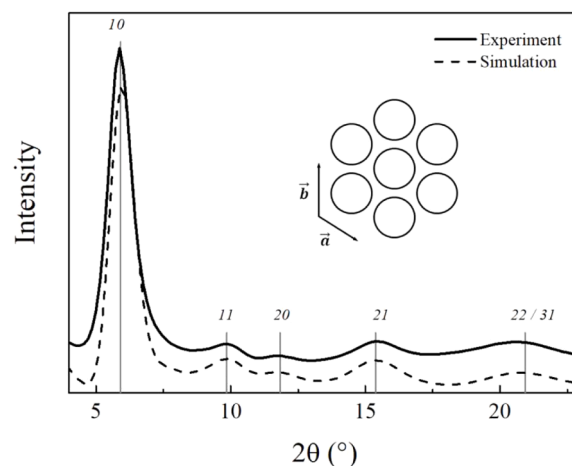


Fig. 4. X-ray diffractogram (Cu radiation) of an ensemble of SWCNT bundles in which all SWCNTs exhibit similar diameters (modified from Ref. [63] and obtained by courtesy of P. Launois). The diffractogram exhibits specific periodicities which make such a material a genuine **allotrope** named nanotubulite. To be compared to the diffractogram in Fig. 2-bottom, which corresponds – among other **graphenic** forms – to that of MWCNTs, whatever their **texture** (see below the definition used here for this term).

**structures.** Regarding  $sp^3C$  materials, there is no **molecular form** proposed, as far as I can tell, but possibly graphane [74] which, however, contains as many hydrogen atoms as carbon atoms, and the actual synthesis of which remains doubtful [75].

**Amorphous** carbons are not **allotropes** because (i) by definition, their X-ray diffractograms do not exhibit peaks corresponding to atom planes (unless they contain small periodic clusters, in such a case the materials are two-phase (the clusters + the amorphous surrounding) composites, which cannot be **allotropes**), except faint modulations revealing the periodicities of the contained molecules; (ii) they correspond to a continuum of composition which is having its own ternary diagram (the poles of which are the  $sp^2C$ ,  $sp^3C$ , and H % contents [76, 77]). For this reason, **amorphous**  $sp^3C$ -rich carbon materials such as “Q-carbon” [78] may be considered as **phases**, but not as **allotropes** of course. The case of “vitreous carbons” (also named glassy carbons), which can be found in Fig. 3, is the same. Glassy carbons are not **amorphous**, although it can be read otherwise in the literature [79]. Their name is only to refer to their macroscopic mechanical behaviour, which is brittle, similar to that of glass, and was initially a trade name, not a scientific name [6,80]. They are merely carbonaceous materials built-up with short **graphene layers** involved in tiny **crystallites** randomly oriented (actually oriented as walls of tiny - nanosized - pores). The **crystallite structure** is turbostratic. There is a whole range of glassy carbons indeed, mostly according to their precursor and their ultimate carbonisation temperature, hence they may exhibit various **crystallite** sizes, but they do not discriminate from each other and from other turbostratic carbons as far as the crystallographic **structure** is concerned.

To summarise, attempts such as that by Heimann et al. and related ones [49,56] may have some merit, but they cannot play the role of **phase** diagrams of carbon **allotropes** because (i) not all the **phases** shown are **allotropes** (**amorphous** carbon is a **phase** but not an **allotrope**); and (ii) genuine **allotropes** having similar  $sp^3/sp^2/sp$  composition are located on the same point (e.g. diamond and lonsdaleite are not discriminated, same for hexagonal and rhombohedral **graphite**). The description parameters used (the three hybridization states) cannot be enough to provide an identity map of the large variety of carbon forms either (**allotropes** or not). Reading statements (in one of the review papers previously cited) such as “*all the organic life on earth is made up of **allotropes** of carbon*” and “*Carbon has basically 8 **allotropes**, namely, (1) diamond, (2) **graphite**, (3) lonsdaleite, (4)  $C_{60}$  (buckminster fullerene or bucky ball), (5)  $C_{540}$ , (6)  $C_{70}$ , (7) **amorphous** carbon, and (8) carbon nanotubes (CNTs; buckytube)*” illustrates how far the nature of carbon **allotropes** can be poorly understood, and even the definition of **allotropy** itself. **Allotropy** is only a **structure**-based descriptor, and if **allotropy** could be enough to provide the identity card of crystallised forms of  $sp^3$ -hybridised carbons, it is not able to do the same for  $sp^2$ -hybridised carbons. As a specificity of **graphene**-related carbon materials, other descriptors are needed to describe them with all needed accuracy.

### 3. Comprehensively describing $sp^2C$ -based carbon materials

#### 3.1. Graphene, graphenic, graphitic, graphitisable, etc

There was a time when carbon scientists were mostly chemists, hence  $sp^2C$ -based solids were designated as polyaromatic carbons. Then came the era of carbon **molecular forms**, which started in 1985 with the disclosure of the fullerene molecule [81], then nanotubes, then **graphene**. Their **structural** simplicity (here the molecular structure) enabled to give coordinates to atom positions and inject them into computer models, making them objects of interest for physicists (not carbon scientists at first) to predict the properties, which appeared to be amazing. The term “**graphene**” then became generic, possibly after Novoselov et al. introduced the term “few-layer **graphene**” (FLG) in 2004, probably for the first time [82]. It was not the smartest choice

(unlike the rest of the paper), because it stated that a **graphene** could be made of more than one layer, in opposition to the 1995 IUPAC definition “*a single carbon layer of the **graphite** structure*” [6]. A much better option would have been to name the same material “few-**graphene layer**” (FGL). Same for nanotubes, by the way: geometrically speaking, a tube is a hollow cylinder with a wall, therefore, discriminating between “single-wall carbon nanotubes” and “multi-wall carbon nanotubes” (see Section 3.3.4) introduces the difficulty to name the nanotube wall (i.e. the cylinder wall) as a whole. Better terms, maybe, would have been “single-graphene carbon nanotube” and “multi-graphene carbon nanotube”, respectively, the nanotube wall then being either mono-layered or multi-layered. Anyway, as discussed in Ref. [31], what is important nowadays is that everyone understands “**graphene**” the same way, and the same for single-wall and multi-wall carbon nanotubes. When it becomes easier to change a definition than to change everyone’s understanding and habits, it means that it is about time to change the definition. This was done in 2013, when the editorial board of CARBON journal, which can be considered authoritative in such matters, proposed to admit that the term “**graphene**” may be both specific and generic. When specific, it designates “*an isolated single-atom-thick sheet of hexagonally arranged,  $sp^2$ -bonded carbon atoms*”, whereas “**graphene layer**” is for designating the same when being part of a stack contributing to build a carbon material; when generic, it designates carbon materials built from **graphene layers** providing it is combined with other terms as in “bilayer **graphene**”, “few-layer **graphene**”, “multi-layer **graphene**” [7]. Meanwhile, the adjective “**graphenic**” was introduced, along with “**graphenised**”, and “**graphenisation**”, which were unfortunately absent from the IUPAC nomenclature. “Unfortunately”, because “**graphenic**” is definitely better than “polyaromatic” to qualify the broad class of carbonaceous solids built from **graphene layers**. The reason is that “polyaromatic” is inherited from organic chemistry, hence suggesting a saturation of the edge carbons by hydrogen atoms, which is barely the case in **graphenic** solids, unless they are considered at the early steps of carbonisation. Even in old work discussing about **graphitisation** as in Ref. [83], the lack of the term “**graphenised**” as an alternative to the term “**graphitised**” generated confusion and inappropriate definitions. While acknowledging – already in 1986 – that “*the term “**graphitised** carbon” is widely misused and misunderstood*”, Knox et al. recommended to name “*two-dimensional **graphite***” carbon materials “*in which **graphitic** sheets are randomly oriented relative to one another*”, that is to say, turbostratic carbons. With such a broad coverage of the word “**graphitic**”, all **graphene**-based carbons should then be said **graphitised**. It cannot be right.

Despite these crossed definitions exist since 1995 [6], and were reminded and completed in 2013 – ten years ago already [7] – many authors still use the word “**graphitic**” to designate any kind of carbon built with **graphene layers**. Others try to be more accurate, and use “**graphitic**” only when they see stiff **graphene layers** in high resolution transmission electron microscopy (HRTEM) images, and to express this way that the material organisation is improving upon annealing. Both are wrong. “**Graphenic**” is generally righter than “**graphitic**” because **graphenic** carbons are carbon materials built from **graphene layers** regardless of their size and how many are stacked in **crystallites**, and whatever the type of **allotrope** the **crystallite structure** corresponds to (turbostratic, **graphitic**, rhombohedral). As stated in Ref. [6] “***graphitic** carbons are all varieties of substances consisting of the element carbon in the **allotropic** form of **graphite**, irrespective of the presence of **structural defects***”, otherwise confirmed in Ref. [7] which says “***graphitic** requires the existence of 3D order or layer registry, which is not directly observable by conventional TEM fringe imaging*”. Clear enough.

Of course, this also applies to related words such as “**graphitisable**” and “**graphitising**” which may be used only if it is known whether the carbonaceous material being discussed would actually be able to get the **structure** of **graphite** once heat-treated at the **graphitisation temperature** (ideally beyond 2800 °C). As already stated in the Introduction section, the language in science should be as accurate as equations, as far

as possible, so that everyone understands the same thing. Unfortunately, the literature is full of examples of wrong uses of the vocabulary, thereby contributing to promoting obscurity instead of clarity.

### 3.2. Proposal for four independent and complementary descriptors

When describing carbon materials, the literature uses words associated with quite vague meanings such as "structure", "nanostructure", "microstructure", "crystallite", "lamellae", "particle", "flake", sometimes in the same paper, without making any attempt to clarify what the relationships between all of them are. As a specificity of carbon materials, especially **graphenic**, a minimum of four descriptors are needed to describe them, which are listed and defined below. This does not apply to **molecular forms**, which have to be described as molecules are.

In the definitions below will be used the term "crystallite", which has already been used several times above. Let's remind, then, that a **crystallite** is the smallest coherent volume in a crystallised ensemble, and that coherence is achieved when atoms are displayed in a periodic manner in the three dimensions of space so that they scatter a coherent wave (electrons, neutrons, X-ray photons) in specific directions. These specific directions generate the diffraction peaks in a diffractogram. A genuine **amorphous** material is able to scatter such a wave, but is not able to do it in specific directions, as an illustration of the exact difference between scattering and diffraction. Applied to **graphenic** materials, a **crystallite** is a stack of perfect **graphene layers** piled up periodically. Fig. 5 illustrates what a **crystallite** is within a crystallised ensemble of **graphene layers**, a standard configuration in carbonaceous materials with turbostratic **structure**.

The first descriptor is the **morphology**, because it is what is seen first. It is accessible through the naked eye, or optical microscopy, or scanning electron microscopy (SEM), depending on the dimensions of the object. "Morphology" strictly designates the shape (outer or inner) of the material: bulk, filamentous, porous, aligned (when talking about nanofilaments for instance), coiled, tubular, hollow, bamboo-like, flake, lamella, film, crumpled, folded, particle, polyhedral, faceted, etc. are **morphological** terms. Clearly, those terms may apply whether the material is **amorphous** or crystallised, whatever the **crystallite** size or the pore size, if any. There might be a direct relationship between a given **morphology** and a crystallised state, but it corresponds to particular cases. For instance, it is likely that a faceted particle reveals a crystallised nature, although diffraction should confirm it, as it is not a rule (carbon blacks will provide an example where facets occur because of the improvement of the **nanotexture**, not because of a **structural** change). Such a direct relationship may also result from a previous study having used all the needed descriptors, afterwards allowing to make such a shortcut. For instance, when considering **graphene** flakes, a crumpled aspect of the flake was found to indicate a turbostratic **structure**, whereas a folded aspect indicates a coherent stacking (i.e. crystallised according to the **graphitic** - or possibly rhombohedral-**structure**) [85].

When describing carbons, the **morphology** does not consider the orientation or even the existence of **graphene layers**.

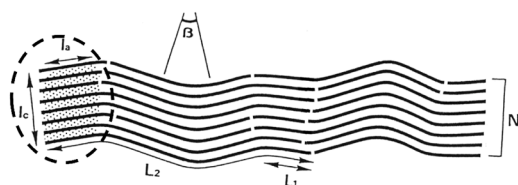


Fig. 5. Sketch of a crystallised ensemble of **graphene layers** in a turbostratic carbon. It is made of adjacent **crystallites**, one of them being shown as the shaded part in the circled area. **Graphene layers** are not perfect, but portions of them are, within the **crystallites**. Reprinted from Ref. [84] with permission of Springer.

The second descriptor is the **texture**, to account for the spatial relationship between **graphene stack** ensembles, whenever the **graphene layers** are distorted (as sketched in Fig. 5) or perfect. Therefore, the **texture** can only be obtained by using characterisation methods able to reveal the mutual orientation of **graphene layer** ensembles. To achieve this, HRTEM lattice fringe mode comes immediately to mind of course, but actually seeing the **graphene layers** is not necessary, and low-magnification TEM dark-field imaging mode [86], or local diffraction modes may also provide the appropriate information: isotropic, anisotropic, concentric, random, fibrous, radial, aligned, alternate (the last two when talking about **graphene layer** ensembles), herringbone or fishbone (when talking about nanotubes), platelet (when talking about nanofibres), etc. are **textural** terms. The term "fibrous" is a particular case, as it implies that the **textures** in the longitudinal direction (the fibre axis) and in cross-section should be described independently as they are usually quite different (see Section 3.3.3).

When describing **graphenic** carbons, the **texture** does not consider whether the **graphene layers** are perfect or defective.

The third descriptor is the **nanotexture**, to account for the **graphene** quality within a crystallised ensemble, as sketched in Fig. 5. Therefore, "nanotexture" relates to the dimensions of the **crystallites**, which standard designations are  $L_a$  and  $L_c$ . Ultimately, with increasing carbonisation temperature, distortions within the **graphene layer** ensemble shown on Fig. 5 will be healed and the whole will become a single **crystallite**. Defective, distorted, wavy, perfect: terms related to **nanotexture** are few because **nanotexture** is mostly and accurately defined and quantified by  $L_a$  and  $L_c$ . Fig. 5 shows other parameters, also all related to **nanotexture**, namely  $L_1$ ,  $L_2$ ,  $N$ , and  $\beta$ . They are all obtained from HRTEM lattice fringe imaging mode [87] and direct measurements on the fringes.  $L_1$  is supposed to be similar to  $L_c$ ;  $L_2$  is the average length of the continuous yet distorted **graphene layer** (in that case, the same **graphene layer** may contribute to several **crystallites**);  $N$  is the number of layers in a **crystallite;  $\beta$  is the average distortion angle within the **graphene layer** ensemble, as obtained from image analysis [88] or local diffraction [89].  $L_1$ ,  $L_2$ ,  $N$ , and  $\beta$  are then complementary to  $L_a$  and  $L_c$  and then are interesting parameters in principle, but the reliability is low, considering how far the values can be fooled by (i) **nanotexture** alteration brought by the TEM preparation method (if based on ion-thinning), (ii) **nanotexture** alteration induced by the sensitivity of **graphene layers** to high energy electrons (when using TEM with electron beam of energy above 80 keV); (iii) superimposition effects due to the more or less aligned **graphene layer** stacks within the whole specimen thickness (10–100 nm in the average, hence, the lower the **nanotexture** quality - meaning very small **crystallites** - the higher the chances of error). These error sources tend presumably to minimise  $L_1$  and  $L_2$  values, whereas the error on  $N$  and  $\beta$  can occur both ways. On the other hand, because probing the material by HRTEM is very local, the values of  $L_1$ ,  $L_2$ ,  $N$ , and  $\beta$  can be not representative of the bulk material in case any heterogeneity is missed by the operator.**

Therefore, more reliable values for  $L_a$  and  $L_c$  are obtained from XRD by applying the Scherrer law:

$$L_{hkl} = K \times \lambda / (FWHM_{hkl} \times \cos\theta)$$

$L_{hkl}$  is the **crystallite** dimension along the  $(hkl)$  planes,  $\lambda$  is the radiation wavelength,  $FWHM_{hkl}$  is the full width at half maximum of the  $hkl$  diffraction peak,  $\theta$  is the Bragg angle. The equation is applied to the  $11(0)$  band/peak (preferably to the  $10(0)$  band/peak, which is very sensitive to stacking faults [26]) to get  $L_a$ , and to the  $002$  peak (or  $001$ , in case of turbostratic stacking [26]) to get  $L_c$ . However, applying the Scherrer law to  $hk(0)$  bands/peaks requires to give an appropriate value to  $K$ , a correcting factor which relates to the shape of the peak.  $K$  is usually taken as 0.89 for  $00l$  peaks, the shape of which usually corresponds to a pseudo-Voigt function. For  $hk$  bands,  $K = 1.84$  is commonly taken in the literature (e.g., in Ref. [82]), but it remains an unsatisfactory approximation because the shape of the  $hk$  bands changes continuously

along their path to becoming  $hk0$  peaks and the full or partial development of the three-dimensional **structure** upon increasing annealing temperature. Correspondingly,  $K$  should change continuously as well (see the discussion about this in Ref. [43]). Therefore, bottom-up approaches which allow getting rid of the determination of  $K$ , as proposed in Refs. [26,43], should be preferred to obtain accurate  $L_a$  values.

The average value of  $N$  in a bulk carbon can be obtained from the  $002/001$  XRD peak from dividing  $L_c$  by the average intergraphene distance (obtained from the  $2\theta$  position of the  $002/001$  peak by using the Bragg equation:  $2 d_{hkl} \times \sin\theta = n \times \lambda$ ).

$L_a$  (and  $L_c$  as well, in some extent, *i.e.* when  $L_a$  is large and the number of **graphene layers** involved is a few only) can also be obtained by Raman spectroscopy [90,91], as a quite common method for characterising carbons. For this, specific features of the Raman spectra are related to  $L_a$  values by calibrating them on XRD results, ideally using a reference carbon series as close as possible to the carbon material to be studied. However, attention has to be paid that the values obtained from Raman and XRD are not necessarily equivalent because they do not see **graphene layers** the same way [92]:  $L_a$  from XRD is planarity-related, meaning that it relies on the ~~length~~ **diameter** of perfect **graphene layers** in the average **crystallite**. For XRD, it does not matter whether the **graphene layers** contain in-plane defects or not (such as rings other than hexagons, or vacancies) provided those defects do not alter the planarity of the layers, nor the long-range periodic display of the atoms. On the other hand,  $L_a$  from Raman is defect-related, meaning that it relies on the occurrence of **graphene** edges and in-plane defects, whether the **graphene layers** are wavy or not. In general, for very small  $L_a$  (say, few nanometres), the value differences between Raman and XRD are not distinguishable from the measurement uncertainty. For larger  $L_a$ , differences can be significant, especially in case an appropriate calibration is lacking. Therefore, when commenting about  $L_a$  values, a good habit would be to discriminate whether they are obtained from XRD or Raman by a specific notation, for instance  $L_{a(XRD)}$  and  $L_{a(R)}$ , respectively.

Attention has also to be paid that, although the **nanotexture** somehow describes the arrangements of **graphene layers** at nanoscale (that is why it is preferable to the term "**nanost**tructure"), the term is not for designating the same features as **texture** when the **texture** happens to be nanosized. "**Texture**" (see above) is an orientation-related descriptor, whereas "**nanotexture**" is a perfection-related descriptor. For instance, considering an elemental particle of carbon black (see Section 3.3.2), the common concentric display of the **graphene layers** is a **textural** feature, not **nanotextural**, despite it is nanosized. To get rid of any doubt, let's consider the effect of annealing: for most types of carbon materials built from multi-graphene layer crystallites (hence excluding those built from individual molecular forms such as fullerenes, SWCNTs, nanohorns...), the **texture** remains the same whatever the annealing temperature up to 3000 °C, while the **nanotexture** improves (provided the **graphene layers** to start with are distorted, as in Fig. 5) from a low grade **nanotexture** to a high grade **nanotexture**. Therefore, using "**microtexture**" to designate a **texture** with microscale dimensions should be prohibited as well, so that not to introduce any confusion in the meaning of "**nanotexture**". Likewise, "**microtexture**" should not replace the term "**nanotexture**" when it happens that  $L_a$  may be in the micrometre range.

When describing **graphenic** carbons, the **nanotexture** does not consider whether the **graphene layer** stacking is random (turbostratic) or coherent (**graphitic**, or rhombohedral, or a mix of both).

Finally, the fourth descriptor is the **structure**, which strictly designates the crystallographic state only, *i.e.* the crystallographic **structure** of the **crystallites** (if any), determined by powder-mode XRD. Therefore, it is fully independent from the **crystallite** size and orientation: **allotropic**, turbostratic, **graphitic**, **partially graphitic**, Bernal (now Hull-Bernal, see Section 2), rhombohedral, **amorphous**, are **structural** terms. Of course, electron diffraction, which is more local, possibly very local, may also provide the information, but attention has to be paid to the effects of preferred orientations of the specimen with respect to the

direction of the electron probe. For instance, in local diffraction, should an electron diffraction pattern show a  $112$  spot, then the **graphitic** or **partially graphitic structure** is ascertained, but the absence of it does not demonstrate a turbostratic **structure**. Indeed, a preferred orientation of the specimen which does not allow any of the three ( $112$ ) atomic plane families to be exposed to the electron beam according to the Bragg angle may always be suspected. Consistently with this definition, terms such as "**microstructure**" and "**nanost**tructure" do not make any sense as any prefix to the word "**structure**" is useless, and then should be prohibited within this four-descriptor scheme.

When describing **graphenic** carbons, the **structure** does not consider the size of the **crystallites**.

It has to be emphasised that the four descriptors above describe **different** and **independent** aspects, *i.e.* switching from a descriptor to another is not generated by a change of scale, although, for instance, considering the **nanotexture** necessarily requires to look at it at the nanoscale. Overall, this four-descriptor scheme may also apply to carbon materials other than **graphene**-based, *e.g.*  $sp^3C$ -based, however, considering descriptors 1 and 4 (**morphology** and **structure**) is usually enough in that case.

### 3.3. Application of the four-descriptor scheme to four examples of graphenic carbons

#### 3.3.1. Bulk carbons being carbonised, and graphitised

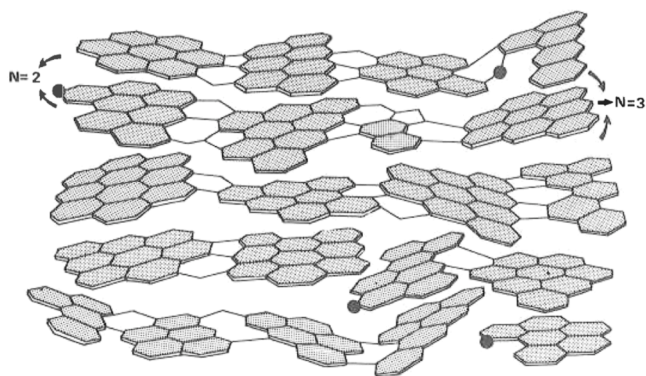
In order to address common mistakes, misuses, and confusions made in the literature when describing carbonaceous materials being increasingly heat-treated, possibly up to the **graphitisation temperature** (which does not mean that the **graphitic structure** has been successfully reached [6]), the descriptors defined in Section 3.2 are here used to describe the events taking place during the carbonisation/**graphitisation** processes and their effects on the materials.

At first, let us summarise the basics of the standard carbonisation and **graphitisation** mechanisms, according to Oberlin's model and subsequent developments [41,42,93–98]:

When subjected to an increasing heat-treatment, any non-gaseous organic precursor, hence typically with a chemical composition within the C, H, O, N, S system (where O, or N, or S could be nil) starts by losing chemical elements other than carbon. This promotes polyaromatisation and then polycondensation reactions which create small **graphenic** entities about the size of a coronene molecule (0.7–1 nm), possibly single, otherwise stacked by 2 or 3. These small **graphenic** stacks are called Basic Structural Units (BSUs), because they occur in all kinds of solid organic precursors. They mark the early step of **graphenisation**. At some temperature (variable with the precursor), the breaking of the bonds in the material tends to make it more or less soft (in some cases very soft), allowing the BSUs to be aligned by the flow of effluents leaving the material. However, the higher the content in O (and N, and S), the higher the possibility of cross-linking functions which oppose this alignment process. At some point (400–550 °C), the material recovers a solid state irreversibly, marking the end of the so-called primary carbonisation. The regions in the material in which BSUs are about aligned are named regions of Local Molecular Orientation (LMOs), which actually make the wall of pores. The higher the O, N, S contents at about the softening temperature, the less developed the LMOs (and the smaller the pores). Therefore, LMOs are areas where the BSUs are only slightly misoriented whereas neighbouring LMOs are highly misoriented relative to each other. At this step, the BSUs are **crystallites** gathered as LMOs (Fig. 6).

Then, as temperature proceeds, the so-called secondary carbonisation takes place, which ends at ~1800–2000 °C, during which the remaining non-carbon atoms are removed, and the slight misorientations within the LMOs are progressively healed so that the alignment progresses from neighbouring BSUs to others. In other words, BSUs no longer exist, and **graphenisation** proceeds and improves (Fig. 5 may illustrate what a LMO looks like at some point of secondary





**Fig. 6.** Sketch of an ensemble of tiny **graphenic** entities roughly aligned, forming a LMO (or a portion of it) as it can be found at the end of primary carbonisation of an organic precursor. Some of the entities are parallel, thereby forming BSUs (two are indicated with their number  $N$  of constituting **graphenic** entities), others are still single. At this step, **crystallites** are limited to BSUs, and  $L_a(XRD)$  is the average of the BSU diameters. Black dots are to represent heteroatoms (modified and reprinted from Ref. [93], by permission of Technip).

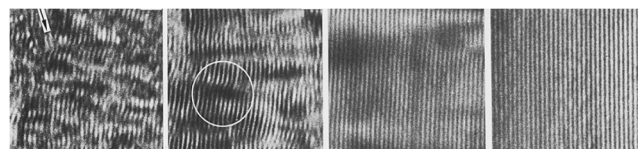
carbonisation: the BSU coalescence has started, but the healing of in-plane defects has not progressed much yet). Ultimately, each single LMO finally becomes a single **crystallite** in which all the **graphene layers** are parallel (resulting in the main increase of  $L_a(XRD)$ , the starting value of which being that of the average BSU diameter, and the ultimate value of which being that of the whole LMO). Meanwhile, the misorientations between the LMO areas, which are severe, cannot be healed. Meanwhile also, the remaining heteroatom-containing cross-linkers at LMO boundaries are replaced by all-carbon defects (e.g.,  $sp^3C$ , non-6 rings...).

Finally, during a subsequent thermal treatment up to **graphitisation temperature** ( $\sim 2900^\circ C$ ), further solid-state rearrangements occur so that the formally turbostratic **structure** within each **crystallite** tentatively turns into the **graphitic structure**. Precursors able to generate long-range LMOs during primary carbonisation (hence, ultimately resulting in extended **crystallites**) succeed in this process, whereas precursors able to generate short-range LMOs only (hence ultimately resulting in small **crystallites** at **graphitisation temperature**) do not. All intermediate cases occur, producing more or less **partially graphitised** carbons, also called “graphocite” [99], “poorly-ordered graphite” [100], or “semi-graphite” [101] by geologists.

These mechanisms are general and valid for all solid organic precursors (and even liquid precursors - e.g., anthracene oil - if high isostatic pressures in confined conditions are applied). Consequently, so-called glassy/vitreous carbons, previously mentioned, are not specific carbons, they are merely carbons originating from organic precursors with high O (+N, +S)/C with respect to H/C (e.g., furfurylic resin). Therefore, they are **non-graphitisable**. It is the same for natural organic precursors such as type-III kerogens (i.e., from humic origin, in other words terrestrial plants) [93]. Likewise, at the other end of the organic precursor range are industrial ones with high H/C ratios such as petroleum or coal tar pitches, or natural ones such as boghead-type coals (derived from algae) [93], which are **graphitisable**. All solid organic precursors roughly range in-between. When mentioning the ability of a precursor or an immature carbon to actually become **graphite** (or not) if heat-treated up to the **graphitisation temperature**, “**graphitisable**” and “**non-graphitisable**” are better terms than “**graphitising**” and “**non-graphitising**”, yet the latter are commonly used in the literature. The use of the present participle should only be limited to describing carbon materials actually being thermally treated, not to express their potential in becoming **graphite**.

Now considering the four descriptors applied to bulk carbons (bulk carbons are of paramount importance for industrial-scale applications, e.g., as constituents for anodes of any kind, or for chemicals adsorbers):

- **Morphology:** When considering organic precursors being carbonised, the resulting carbonaceous material has no specific **morphology** but porous, with an open porosity for large pores, and a tendency to close porosity for the carbonaceous materials with the smallest pores (as in glassy carbons). The related characterisation methods should have the magnification and resolution power to reveal the pore sizes, down to HRTEM for the smallest ones.
- **Texture:** Primary carbonisation ( $< 550^\circ C$ ) is the step where the **texture** is built. Starting by being isotropic until the softening point is reached, the material then remains globally isotropic as a bulk, but becomes locally anisotropic when the LMOs are formed. **Graphene layer** stacks within the LMOs make the pore walls and are parallel to the pore wall surface. Additional anisotropies may also locally develop (e.g., concentric, radial, so-called “Brooks & Taylor” type textures, etc.) depending on the precursors (e.g., in some pitches, or pitch components [96,97]). Then, consistently with the definition of the descriptor, the **texture** will not change all along, from the end of primary carbonisation to the final **graphitisation temperature**, meaning that the average LMO size barely increases all along. Dark-field TEM imaging at medium range magnification is the most appropriate method to reveal LMO sizes [86].
- **Nanotexture:** Secondary carbonisation ( $\sim 550\text{--}2000^\circ C$ ) is the step where the **nanotexture** improves the most significantly, marked by the increase of  $L_a$  (and  $L_c$ , meanwhile). **Graphene layers** then become larger, meaning that **graphenisation** improves. How the **nanotexture** progresses within increasing secondary carbonisation is illustrated by Fig. 7. Although Fig. 7 illustrates the **nanotexture** by means of HRTEM images, powder-mode XRD remains the most convenient method to obtain  $L_a$  and  $L_c$ , unless local information is deliberately sought (e.g., to reveal any surface anisotropy which develops at the contact to a surface, as in moulded glassy carbons).
- **Structure:** **Graphitisation treatment step** ( $> \sim 2000^\circ C$ ) is where the **structure** is subjected to the largest changes, specifically for **graphitisable** carbons. This corresponds to the temperature above which the diffusion of carbon atoms in **graphene crystallites** becomes significant [102]. With the appropriate precursor (High H/C and low O(+N+S)/C atomic ratios, which generate large LMOs), the crystallographic **structure** switches from turbostratic to **graphitic** or **partially graphitic**, otherwise it remains turbostratic. More in the detail, taking the example of a **graphitisable** coke series, the evolution of the **crystallite structure** includes (i) above  $1550^\circ C$ : the occurrence of **graphene layers** superimposed by pairs in AB positions (referring to the ABAetc. **graphene layer** positions in **graphite**) [43]; (ii) above  $2000^\circ C$ : the occurrence of **graphitic** sequences (ABAetc. within the crystallites, yet still containing turbostratic sequences) [43]; (iii) above  $2300^\circ C$ : the occurrence of stacking faults as single **graphene layers** in C position (in reference to the ABCAetc. **graphene layer** positions in the rhombohedral **structure**) dispersed in **graphitic** sequences [26]. This means that it can be said that **structuration** improves only if the material **structure** evolves from turbostratic to **partially graphitised** (which means a contribution of AB pairs, for the least, or more, i.e. the occurrence of small **graphitic** sequences within the **crystallites**) or fully **graphitised** (all the **crystallites** are made of **graphene layers** stacked according to the



**Fig. 7.** From left to right: Typical evolution of the **nanotexture** within a LMO with increasing temperature (HRTEM lattice fringe mode imaging). The inter-fringe distances are  $\sim 0.34$  nm. The white circle shows up a dark contrast so-called “Bragg fringe”, the occurrence of which is an indicator of local perfect **graphene** stacking and orientation with respect to the Bragg angle.

ABAetc. hexagonal sequence, possibly disturbed by stacking faults) [26,43]. In case the material remains turbostratic whatever the treatment temperature (which may happen with appropriate precursor compositions), only the **nanotexture** improves more or less upon heat-treatment.

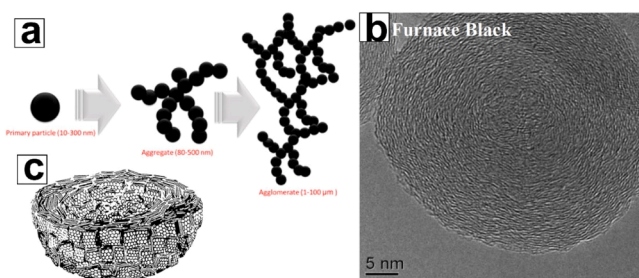
Therefore, the carbonisation/**graphitisation** of organic precursors is another example of possible shortcut (referring to the aforementioned case where the **structure** of **graphene** flakes could be deduced from their **morphology**), since the **texture** of the carbonaceous materials at an immature state (primary carbonisation step), quantified by the LMO size, governs the ultimate **structure** at **graphitisation temperature**.

Attention has to be paid that what is said in this section is to describe the big picture. Carbon materials are so complex, with an infinite number of possible organic precursors, that some exceptions may always be found.

### 3.3.2. Carbon blacks

Alike bulk carbons at macroscale, carbon blacks are overall isotropic materials even at nanoscale (see the "Texture" paragraph below). Carbon blacks are materials based on elemental nanosized particles obtained from various thermal processes, either partially oxidative or not, starting from a variety of organic feedstock (e.g., methane, oils...). They have a considerable impact on industrial-scale applications such as tyres, pigments, conductive fillers, and more. Information about their synthesis, properties, and applications can be found in textbooks such as Ref. [103].

- **Morphology:** the basic constituents of carbon blacks are elemental particles which, from the **morphological** point of view, usually exhibit the shape of more or less round nanoparticles (< ~100 nm) (Fig. 8), possibly with a hollow core. If subjected to high temperature annealing after the synthesis, the shape of elemental particles may become faceted, as a result from the improvement of the **nanotexture** (see below). Elemental particles can be individual (as in thermal blacks), but most often combine with each other in various ways and extent according to multi-scale arrangements so that a whole range of **morphologies** is obtained. They are bonded as aggregates through strong cohesive forces, and then aggregates gathered as agglomerates through weak cohesive forces (Fig. 8a). Aggregates can be more or less elongated, and more or less branched. Therefore, the term "carbon black" may designate either the elemental particles, or the aggregates, or the agglomerates.
- **Texture:** the term concerns the elemental particles only, and is almost systematically concentric (Fig. 8b and c). In spite of this, the overall **texture** can be said isotropic because, statistically speaking, all graphene orientations can be found when considering a single



**Fig. 8.** (a) Multiscale **morphology** of carbon blacks; reprinted from Ref. [104] with permission of Elsevier. (b) HRTEM image of an elemental nanoparticle of a furnace black; reprinted from Ref. [105]. (c) The well-known sketch of half an elemental particle proposed by Heidenreich et al. [106] showing both the hollow **morphology**, the concentric **texture**, and a common low-grade **nanotexture**, here with **crystallite** sizes 3–4 times larger than that of BSUs, but smaller sizes are quite common, as in (b); reprinted with permission of Wiley.

elemental particle, and, *a fortiori*, when considering an ensemble of them. Such a **texture** is likely to result from the carbonisation, in homogenous phase (*i.e.*, in the gas phase), of organic liquid nanodroplets containing tiny **graphenic** entities that surface tensions enforce to align parallel to the droplet surface. This mechanism was proposed long time ago [107], but recently received a strong support as the thermal cracking of methane and hydrogen was demonstrated to generate a transient, colloid-like organic liquid phase, even at temperatures far beyond 1000 °C, before it turns into solid carbon [108].

- **Nanotexture:** That of carbon blacks is usually of low grade (Fig. 8b and c), but it actually depends on the synthesis process, and can be improved upon thermal annealing anyway, as illustrated by Fig. 7. The ultimate improvement of the nanotexture may induce a change in the particle morphology, through faceting [96,103].
- **Structure:** The starting **structure** of carbon blacks is always turbostratic. It usually remains as such because the **crystallites** develop within the nanosized elemental particles in a volume constrained by the concentric **texture**, hence they cannot reach large  $L_c$ . This prevents the **structure** to ever become that of genuine **graphite** whatever the annealing temperature.

### 3.3.3. Carbon fibres

Carbon fibres [109,110] are the key components for a variety of composites devoted to highly stressful conditions of use (where the stress can be thermal or mechanical). They are interesting to consider here because they are highly anisotropic materials [111], as opposed to overall isotropic carbons as described in Sections 3.3.1 and 3.3.2. They result from the same carbonisation-**graphitisation** mechanisms as bulk carbons. However, they are subjected to an additional step of partial oxidation applied after spinning and before the end of primary carbonisation so that the filamentous shape is maintained while the carbonisation temperature increases. On the other hand, carbon fibres exhibit the specificity to be highly anisotropic materials due to the stretching stresses applied during the spinning process. The latter event (stretching) may improve the natural **graphitisability** inherited from the precursor chemical composition due to the resulting enforced alignment of the **graphene layers**, but the former event (partial oxidation) does not alter the graphitisability significantly, because the alignment of the **graphenic** entities has taken place before the oxidation step.

- **Morphology:** Carbon fibres are individual filaments, with diameters in the range of several micrometres (smaller for polyacrylonitrile-based (PAN-based) fibres compared to pitch-based) although commercial carbon fibres are gathered into tows of several thousand filaments during spinning. More in the detail, the cross-section of carbon fibres is not always circular. It could be bean-shaped, flattened, oval, exhibiting an open wedge... (the latter being specific to pitch precursors). The surface state (smooth, rough, irregular, striated...) may also vary.
- **Texture:** because the organic precursor (polymer or pitch) is stretched during the spinning process, the polymer-chains are aligned with respect to the fibre-axis, then generating **graphene layers** more or less aligned with respect to the fibre axis upon subsequent carbonisation. This is called a fibrous **texture**. The alignment is low for polymers with short chains, and is high for polymers with long chains (such as the ladder-polymer of PAN) or precursors containing preformed **graphenic** entities, as in pitches. The extent of alignment of the **graphene layers** along the fibre axis is an important **textural** parameter governing the properties, and can be quantified by XRD applied to a single fibre tow subjected to a non-rotated X-ray beam (*i.e.* NOT in powder-mode) and measuring the opening angle of the resulting  $002/001$  arc. On the other hand, the cross-sectional **texture** is independent from the longitudinal **texture**, and may appear nanoporous and random (looking like that

of glassy carbons) as it is common for PAN-based fibres (Fig. 9c and d), or concentric (Fig. 9a), or “PANAM”-type (in reference to the logo of the former airline company), or radial (Fig. 9b) as it is common for carbon fibres based on so-called anisotropic pitches.

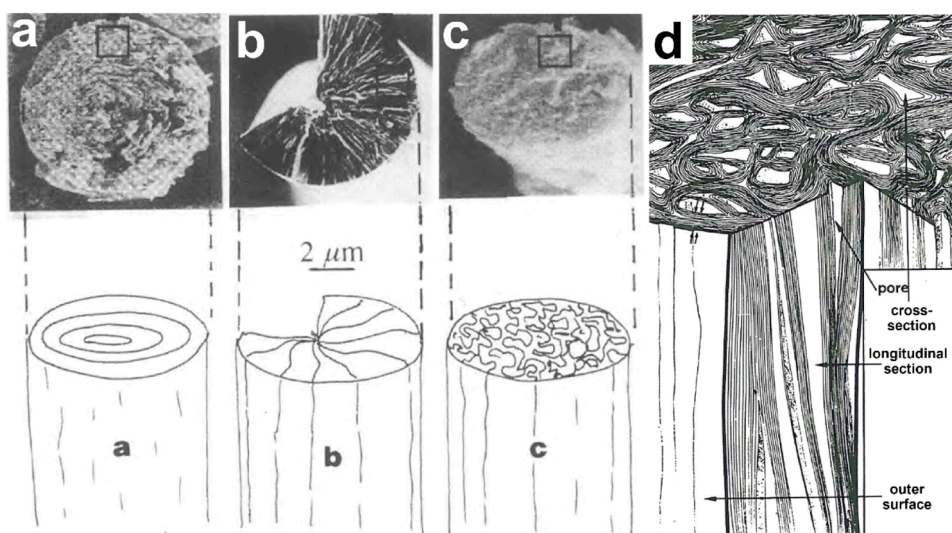
Other textures may exist, including mixed ones, for instance: PAN-based fibres may exhibit a ring in cross-section in which the **graphene layers** are anisotropically displayed within the overall cross-sectional isotropic texture [112]; carbon fibres obtained from mesophasic pitches may contain areas of isotropic texture visible in cross-sections as dispersed within the overall anisotropic texture. As opposed to the random texture (Fig. 9c and d), the radial texture (Fig. 9b) obtained for some pitch-based fibres favours the development of large **graphene layers** at long distance in both longitudinal and cross-sectional directions, allowing the material to maintain its natural **graphitizability**. Therefore, both textures, longitudinal and cross-sectional, are important for the properties and have to be described and quantified. In carbon fibres with fibrous texture, LMOs are ribbon-like.

- **Nanotexture:** Due to the overall fibrous texture, the dimensions of the **crystallites** are anisotropic as well. In particular, longitudinal and cross-sectional  $L_a$  are likely to be different, more specifically with polymer-based fibres. Longitudinal  $L_a$  can be obtained from the  $11(0)$  band/peak during the same XRD experiments carried out to measure the  $002/001$ -arc angular opening, but obtaining the same for cross-sectional  $L_a$  is experimentally tricky and/or time-consuming. Obtaining average  $L_a$  and  $L_c$  values by XRD on a powder of ground fibres is a quite convenient compromise for comparing the **nanotextures** of various fibres in first place, which could be sufficient in most of cases, specifically for carbon fibres with a similar fibrous texture.
- **Structure:** Because carbon fibres originate from organic precursors, their **graphitizability** exhibits a similar dependence on the chemical composition of the precursor as explained in Section 3.3.1. Therefore, it is no wonder that carbon fibres based on precursors such as cellulose/rayon or polyacrylonitrile (PAN) are **non-graphitizable**, whereas carbon fibres based on pitches can be **graphitizable**. This directly relates to the **textural** characteristics, *i.e.* that of the ribbon-like LMOs. The cross-sectional LMO dimension is in the nanometre range in PAN-based fibres, whereas it can be in the micrometre range

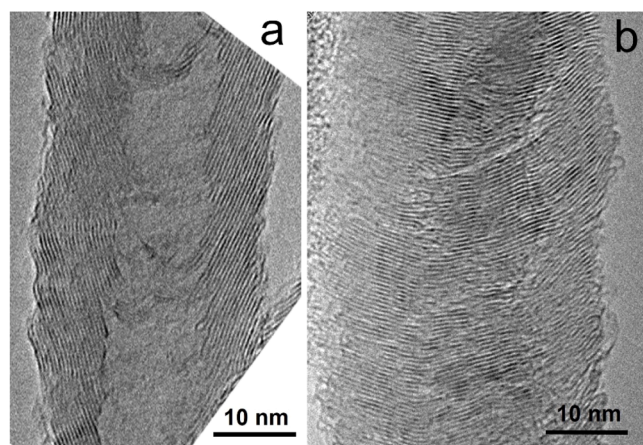
in pitch-based fibres (ultimately equal to the fibre radius - see Fig. 9b - assuming that the longitudinal LMO dimensions in both fibre types are alike). However, there are several examples of external stresses applied to **non-graphitizable** precursors which are able to enforce the **graphene layers** to align at long distance (hence generating larger LMOs than they naturally would), making them **graphitizable**: this is what may happen with natural terrestrial plant-derived organic precursors subjected to oriented lithostatic pressure during diagenesis and catagenesis [113], making them able to become natural graphite whereas their starting chemical composition would forbid it; it may also happen with polyimide polymers when deposited as thin films, within which the interaction with the substrate aligns the **graphenic** entities parallel to it when they form during primary carbonisation [114]. Therefore, the stretching stresses developed during the spinning of fibres may help **non-graphitizable** precursors to acquire a partial **graphitizable** character. However, since acquiring the **graphite structure** requires largely-developed **graphene layers** (large LMOs), there is no way that any carbon fibre exhibiting an isotropic cross-sectional texture (as in Fig. 9c and d) can be **graphitizable**.

### 3.3.4. Carbon nanofilaments

Carbon nanofilaments also are highly anisotropic materials but are interesting to consider in addition to carbon fibres because of their nanosize. Carbon nanofilaments are emblematic of the nano-world, because they are the nanomaterials from which the craze about nanoscience really started, thanks to the seminal paper by Iijima in 1991 [115]. Combining a carbon source, a nanosized catalyst, and medium-range-temperature conditions in inert atmosphere is the most common way to produce carbon nanofilaments [116]. Such a process may produce two kinds of carbon nanofilaments, namely nanotubes and nanofibres, depending on the dimensions, geometry, and chemical composition of the catalyst nanoparticles [117]. There is no standard definition to strictly discriminate between both, hence considering logics and simplicity helps in this regard: a nanotube is a rod with a hollow core, whereas a nanofibre is a rod with a solid core... that simple (Fig. 10). There is no reason why the orientation of the **graphene layers** making the nanofilaments should play a role to choose between these two terms, as they both relate to **morphology**. On the other hand, (i) CNTs can be single-walled, *i.e.* the tube wall is made of a single



**Fig. 9.** From (a) to (c): top: SEM images of fibre cross-sections with concentric, radial with a wedge, and isotropic textures, respectively; bottom: sketches of the same. (a) and (b) are pitch-based carbon fibres, (c) is a PAN-based fibre. The wedge in (b) does not exist for low carbonisation temperatures and increasingly opens as carbonisation proceeds. (d): sketch of a PAN-based carbon fibre showing the fibrous, dual texture, *i.e.* with **graphene layers** more or less aligned along the fibre axis (anisotropic texture), as well as the random display of the **graphene layers** in cross-section (isotropic texture) forming elongated nanopores. Modified from Ref. [42] by permission of Taylor & Francis.



**Fig. 10.** HRTEM images as examples of (a) a multiwall carbon nanotube with the herringbone-bamboo texture (*hb*-MWCNT); the core is mostly hollow, with only few layers crossing perpendicularly the inner cavity. (b) a carbon nanofibre with the herringbone texture (*h*-CNF); there is no hollow core. Photo credit: L. Noé, CEMES.

**graphene layer** (SWCNTs); (ii) CNTs and CNFs can be multi-walled (the former being abbreviated as MWCNTs), *i.e.* the nanotube wall or the nanofibre body is made of several superimposed **graphene layers** or of a single **graphene layer** wrapped on itself. Let's also note that high-temperature catalyst-free growth of nanofilaments is also possible when starting from a sublimed **graphite** source, generating MWCNTs only [115,116].

Therefore, unlike SWCNTs which, as said previously, have to be considered as **molecular forms**, CNFs and MWCNTs are not, although they grow as individual nano-objects, because XRD of a bunch of them randomly oriented provides a diffractogram similar to the bottom one in Fig. 2. This ascertains that they do not correspond to a different **allotrope**, they are merely nanoforms of the **turbostratic allotrope**. However, there are many types of them the discrimination of which requires all four descriptors to be used, as reported in Fig. 11. Alternatively, CNTs may also be built with a single **graphene layer** wrapped concentrically as a scroll (forming a *s*-MWCNT), or a single **graphene** ribbon wrapped helically (forming a *hw*-MWCNT). In that case, strictly speaking, they may be said “multi-walled” yet made with a single **graphene**, thereby also generating a stacking periodicity. It is the same for CNFs, except that the scroll-type was never observed. As seen by HRTEM, the scroll texture barely discriminates from the concentric texture, and likewise, the helical wrapping texture looks like the herringbone texture. Therefore, an accurate description of nanofilament types requires more than HRTEM images (*e.g.* local electron diffraction, and/or grinding experiments [117]). Examples of the various **morphologies** and **textures** of CNTs and CNFs can be found in Ref. [118]. On the other hand, the fact that several **graphene layers** are superimposed stabilises the material, which is quite stable despite the **graphene layers** can be far from perfect, generating large **nanotexture** variations from a material to another, governed by both the chemical composition of the catalyst and the growth temperature.

It is significant that, in contrast to carbon nanofilaments built-up with several **graphene layers**, only obtaining the (*n,m*) helicity coordinates (by nanoprobe electron diffraction [119] or through the radial breathing modes in Raman [120]) is sufficient to fully characterise a SWCNT [121]. This is consistent with their molecular nature, as opposed to MWCNTs, which are not **molecular forms** but nanomaterials. In this picture, the peculiar case of double-wall carbon nanotubes (DWCNTs) corresponds to an ambiguity. Indeed, as SWCNTs, they usually gather into bundles and do not exhibit **nanotexture** variations (meaning that the **graphene layers** always appear straight and perfect in HRTEM longitudinal view of DWCNTs). Although I could not find an example of

The description chart of graphenic carbon nanofilaments	
1a. Outer morphology (eye, OM, SEM)	Regular, coiled, branched, conical, ...
1b. Inner morphology (Low-resolution TEM)	NanoFibre (CNF)   NanoTube (MWCNT)
2. Texture (Dark-field TEM, bright-field HRTEM, local electron diffract.)	<div style="display: flex; flex-direction: column; align-items: center;"> <div style="display: flex; justify-content: space-between; width: 100%;"> <span>Scroll (s-)</span> <span>←</span> </div> <div style="display: flex; justify-content: space-between; width: 100%;"> <span>→</span> <span>Concentric (c-)</span> <span>←</span> </div> <div style="display: flex; justify-content: space-between; width: 100%;"> <span>→</span> <span>Herringbone (h-)</span> <span>←</span> </div> <div style="display: flex; justify-content: space-between; width: 100%;"> <span>→</span> <span>Helically wrapped (hw-)</span> <span>←</span> </div> <div style="display: flex; justify-content: space-between; width: 100%;"> <span>→</span> <span>Bamboo (b-)</span> <span>←</span> </div> <div style="display: flex; justify-content: space-between; width: 100%;"> <span>→</span> <span>Platelet (p-)</span> <span>←</span> </div> </div>
3. NanoTexture (XRD, Raman, HRTEM)	$L_{or}, L_c, N$ $L_1, L_2, \beta$
4. Structure (XRD, electron diffract.)	turbostratic → graphitic $d_{002}, hkl$ with $h$ and/or $k \neq 0$ , and $l \neq 0$
OM = optical microscopy, SEM = scanning electron microscopy, TEM = transmission electron microscopy, HR = high resolution, XRD = X-ray diffraction	

**Fig. 11.** Description chart for carbon nanofilaments (nanofibres or nanotubes: a nanotube is hollow, a nanofibre is not) resulting from the use of the four descriptors defined in Section 3.2, in relation with the analytical methods needed (corrected and completed from Ref. [118]).

in the literature, it is likely that bundles of DWCNTs of similar outer diameters would exhibit the same periodicity as the turbostratic **allotrope**, added with new periodicities typical of their assembly as bundles. These features would make them a specific **allotrope**, different from both nanotubulite and MWCNTs.

#### 4. Conclusions

A common language is needed when discussing carbon materials. At a minimum, authors should use words within the strict definitions provided in authoritative work such as Refs. [6,7]. Such definitions for words among those which are the most misused in the literature are reminded here. But this is not enough to clarify the field. Indeed, there was no methodology available to comprehensively describe carbon materials of any kind in a standardised manner so far, and this situation is responsible for confusions and misunderstandings regarding the published data. An easy protocol using four strictly independent descriptors (**morphology / texture / nanotexture / structure**) is proposed here in order to address this issue. It also simplifies the vocabulary to be used because words such as **microtexture**, **microstructure**, and **nanostucture**, the meaning of which is never clear, are no longer necessary. It is believed that the systematic use of this protocol from now on would significantly contribute to making much clearer the description and the understanding of what the carbon materials which the studies will be reported in the forthcoming literature actually are.

#### CRedit authorship contribution statement

**Marc Monthioux:** Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Methodology, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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