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GUEST EDITORIAL

Nomenclature of sp^2 carbon nanoforms

Carbon's versatile bonding has resulted in the discovery of a bewildering variety of nanoforms which urgently need a systematic and standard nomenclature [1]. Besides fullerenes, nanotubes and graphene, research teams around the globe now produce a plethora of carbon-based nanoforms such as 'bamboo' tubes, 'herringbone' and 'bell' structures. Each discovery duly gains a new, sometimes whimsical, name, often with its discoverer unaware that the same nanoform has already been reported several times but with different names (for example the nanoform in Figure 1i is in different publications referred to as 'bamboo' [2], 'herringbone-bamboo' [3], 'stacked-cups' [4] and 'stacked-cones' [5]). In addition, a single name is often used to refer to completely different carbon nanoforms (for example, the 'bamboo' structure in [2] is notably different from 'bamboo' in Ref [6]). The result is a confusing overabundance of names which makes literature searches and an objective comparison of results extremely difficult, if not impossible.

There have been several attempts to bring order to the chaos of carbon nomenclature. An IUPAC subcommittee on carbon terminology and characterization that ran until 1991 produced a glossary of 114 terms for carbon materials. However the only carbon nanoforms included were fullerenes* [7] and graphene† [8] (which remain the only carbon nanoforms defined in the IUPAC "Gold Book" [9]), and this was in any case a list of defined terms rather than an attempt to classify carbon forms based on underlying shape. Following an international symposium on nanocarbons in Japan in 2002, Inagaki and Radovic proposed a nanocarbon nomenclature based on preparation methods [10], drawing the important distinction between nano-structured and nano-sized carbon nanomaterials. However no definitions were given for detailed morphological differences.

* Defined by IUPAC as "Compounds composed solely of an even number of carbon atoms, which form a cage-like fused-ring polycyclic system with twelve five-membered rings and the rest six-membered rings. The archetypal example is [60]fullerene, where the atoms and bonds delineate a truncated icosahedron. The term has been broadened to include any closed cage structure consisting entirely of three-coordinate carbon atoms." doi:10.1351/goldbook.F02547

† Defined by IUPAC as "A single carbon layer of the graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi infinite size. The term Graphene should be used only when the reactions, structural relations or other properties of individual layers are discussed." doi:10.1351/goldbook.G02683

There are various ways that carbon nanoforms could be classified. These include their synthesis conditions, physical properties such as density and internal surface area, or graphitic sheet texture [11]. In the current editorial we attempt to develop a coherent nomenclature for carbon nanoforms based on their morphological differences and the geometrical transformations that relate one form to another.

The structurally simplest carbon nanoform is graphene. Graphene is a near planar sheet of sp^2 -bonded carbon atoms in a hexagonal network. It can be considered as the final member of the series of fused polycyclic aromatic hydrocarbons, such as naphthalene, anthracene and coronene. Terms such as ‘single graphene layer’ and ‘graphene nanosheet’ are redundant since graphene is a layer/sheet, always single and necessarily in the nanoscale as it is one atom thick. The preferable term is simply ‘graphene’.

Graphene can serve as the initial building block for a series of thought experiments, generating other carbon nanoforms by the application of geometrical transformations. Morphological variation in sp^2 -based carbon nanoforms is a consequence of curvature, introduction of structural defects, and dangling bonds. The result of this variation is deviation from ideal infinite planar-sheet aromaticity, with corresponding localisation of states and variation in chemical reactivity.

We can classify an initial list of transformations as follows:

Stacked: one-dimensional ordered arrangement of multiple nanoforms of the same type (e.g. from graphene to graphite). When a stack length is significantly larger than the dimensions of the individual nanoform, the term ‘fibre’ can be applied.

Cut: breaking a line of C-C bonds, for example producing short segments from a longer nanotube via a cut perpendicular to the tube axis, or graphene nanoribbons from graphene.

Circularly Wrapped: wrapping an object around an axis at a fixed distance, resulting in matching edges (e.g. from graphene to a single-walled nanotube).

Scrolled: wrapping an object around an axis with continuously increasing distance, resulting in mismatched edges, i.e. spirally wrapped (e.g. from graphene to a graphene nanoscroll).

Coiled: object wrapped around an axis with an additional translation along that axis.

Screwed: application of a screw dislocation along the periodic axis of a nanoobject or stack of nanoobjects. For 0D nanoobjects a screw dislocation dipole is required. This typically converts a stack of individual nanoobjects into continuous layers.

Coned: removal of an in-plane wedge of material, reconnecting any resultant dangling bonds, resulting in pentagons at the apex (application of a wedge disclination).

By applying the various transformations listed above to graphene we created a carbon nanoform “family tree” as shown in Figure 2. While the diagram is non-exhaustive (primarily for clarity), it helps to classify the nanoforms by morphology, and provides a first step towards a standardised nomenclature through use of these operations as adjectives to graphene. These transformations result in families of forms as follows (names are preferentially selected based on shape rather than analogy to everyday objects):

Nanotube: commensurately wrapped two-dimensional nanoform,

Nanoscroll: incommensurately wrapped two-dimensional nanoform,

Nanotoroid: commensurately wrapped one-dimensional nanoform,

Nanospiral: incommensurately wrapped one-dimensional nanoform,

Nanocone: nanoform constructed from one or more stacked conical layers,

Nanoribbon: layer subject to two parallel cuts resulting in a strip,

Platelet: layer cut in at least two directions giving a patch (e.g. polyaromatic hydrocarbon)

Fullerene: closed cage containing twelve pentagons*.

The description of the nanoforms given thus far can be further refined through the use of additional terms, not included in the “family tree” since they can be applied to most of the forms already there:

Single-/Double-/Multi-Walled: the wall of the nanoform consists of one, two, or multiple layers.

Hollow / Full-core: nanoform contains (/ does not contain) an interior cavity space equal to or larger than twice the graphite inter-layer spacing.

Double-/Multi-cored: two or more nanoforms encapsulated in another nanoform of the same type.

Partitioned: hollow-core nanoform with internal walls orthogonal to the object axis which divide the core into separate compartments.

Corrugated: the layer surface undulates without changing the overall shape of the nanoform. The term applies when the scale of the undulations is less than the dimensions of the nanoform itself.

Wavy: the nanoform itself undulates. Thus the undulations in a wavy nanoform are on a larger scale than in a corrugated nanoform.

Curved: a curved nanoform is considered as a wavy nanoform where the period of the undulations is larger than the dimension of the nanoform

Polygonised: layers are faceted, without continuous curvature.

Collapsed: the distance between two otherwise separated points on a surface is reduced to approximately that of the inter-layer spacing of graphite (typically due to Van der Waals interaction).

Vertical / Horizontal: orientation of the principal axis of the object with respect to a horizontal substrate.

Bundled: an ordered group of multiple approximately parallel one-dimensional nanostructures (e.g. single-walled nanotube bundles).

Crystallised: aggregate of nanoforms of the same type possessing long-range order (e.g. fullerite).

Clustered: aggregates of nanoforms with no long- or short-range order besides that of the objects themselves.

Closed / Open: object forms / does not form a continuous surface.

Open / Closed tip/edge: Object has / does not have functionalised or dangling bonds at its tip/edge.

For example closed-edge stacked platelets have carbon sheets which fold back on themselves, and an open-tipped nanotube has terminating functionalised bonds at its ends.

Certain terms used previously in the literature are replaced here. In this system for example the term ‘few layer graphene’ is incorrect and would be replaced by ‘few stacked graphenes’. For consistency with nanotubes, two and three stacked graphenes would be ‘double graphenes’ and ‘triple graphenes’ respectively. We propose the name ‘multi-walled fullerenes’ for multiply-encapsulated closed carbon layer structures (commonly referred to as “carbon onions” or “nested fullerenes”). While spherical structures such as those observed after extensive electron irradiation are ‘multi-walled fullerenes’, hollow faceted nanoparticles (e.g. produced during arc-discharge) would be ‘polygonised multi-walled fullerenes’. The terminology also distinguishes between closed nanocones in a ‘dahlia’ type arrangement, which would be referred to as ‘clustered nanocones’, from isolated individual multi-walled nanocones.

Scrolled structures, often misnamed ‘multi-walled nanoscrolls’, would be now ‘graphene nanoscrolls’. This allows, for example, nanoscrolls from two stacked graphenes to be named ‘double graphene nanoscrolls’.

The term “herringbone” is often applied when the layers in a 1D nanoobject are at an angle to the tube axis (resembling the skeleton of a fish), but does not distinguish different core structures. In addition terms such as “herringbone nanotube” tend to link these nanoforms with conventional parallel-walled nanotubes, whose surface chemistry is very different. We suggest instead replacing the term “herringbone” with ‘stacked nanocones’, ‘hollow-core stacked nanocones’ and ‘partitioned stacked nanocones’ depending on the structure of the core. If the stacked cones form a continuous layer they would be ‘screwed stacked nanocones’[12] and if the stack is sufficiently long, it would be a ‘stacked nanocone fibre’. Another common term in the literature is “bamboo nanotubes”, which in this nomenclature is replaced by terms such as ‘partitioned nanotubes’ and ‘partitioned stacked nanocones’. By the same logic, “nanobells” are now ‘stacked open multi-walled fullerenes’. A full list of terminology from the literature and proposed standardised nomenclature is given in Table 1.

The internal structure of a nanoform is revealed by transmission electron microscopy (TEM) which produces a projected image of the nanostructure observed. For example high-resolution TEM of carbon nanotubes provides valuable information concerning the number and orientation of the graphenes. Based on high-resolution TEM images we classify various commonly observed one-dimensional carbon nanoforms as indicated in Figure 3. The option clearly remains to add further adjectives to refine description of the morphology, for example ‘incomplete’ if internal compartments are broken. Figure 3 depicts schematic images for the forms shown in Figure 1, and we note that these could also serve as standard symbols in chemical structure diagrams.

New nomenclature also needs to deal with hybrid carbon nanoforms consisting of two or more carbon nanoforms. There are near infinite possible combinations of these, but the majority observed experimentally to date can be classified either as one carbon nanoform filled with another, or one nanoform attached to the outer surface of another. The notation used by the fullerene community to describe endohedral fullerene structures is of the form ‘x@y’, where species ‘x’ is positioned inside species ‘y’. We suggest the wider adoption of this convention, thus for example “peapods” would instead be referred to as ‘fullerene-filled single-walled nanotubes’, written as $C_n@SWCNT$ [13], and one graphene nanoscroll encapsulated within another could be written as $CNS@CNS$. In addition, this convention can be extended through the use of ‘//’ where ‘x//y’ indicates nanoform ‘x’ is attached to the exterior surface of nanoform ‘y’, where ‘x’ is smaller than ‘y’. For example $C_{60}//SWCNTs$ would indicate C_{60} molecules grafted to the exterior of a single-walled carbon nanotube. We note that a similar scheme has been developed further to provide a shorthand for other nanomaterial treatments such as doping [14,15].

This nomenclature can be extended to describe the chemical composition of heterogenous carbon-based nanoforms. For example, a double-walled carbon nanotube containing substitutional nitrogen would be written $CN_x-DWCNT$, and CO_x -Graphene would be graphene oxide (graphene with a highly oxidized basal plane) following this convention. Similarly heterogenous

nanomaterials, for example a single-walled carbon nanotube with domains of boron nitride would be written as C(BN)_x-SWCNT.

We have deliberately focussed here on sp²-bonded nanoforms, since nanodiamonds and carbynes form separate categories of their own. This nomenclature could easily be extended further, for instance, it is possible to imagine all of the forms discussed here built using other theoretically proposed layered carbon structures such as haeckelites [16] and graphynes [17], as well as other layered nanomaterials such as TiO_x, MoS₂ and BN. We have not discussed atomistic orientation (nanotube chirality, graphitic stacking) since there are already well-defined terms for these.

The standardised nomenclature proposed here has been developed as a response to the mounting variety and confusion within the world of carbon nanoforms. We hope it serves to provide a coherent structure for carbon nanoform classification based on the underlying topology of the objects. In this way it provides a convention which unambiguously describes most carbon nanoforms, while remaining sufficiently flexible to adapt to new forms as they are discovered and added to the ever-expanding carbon nanoform family tree.

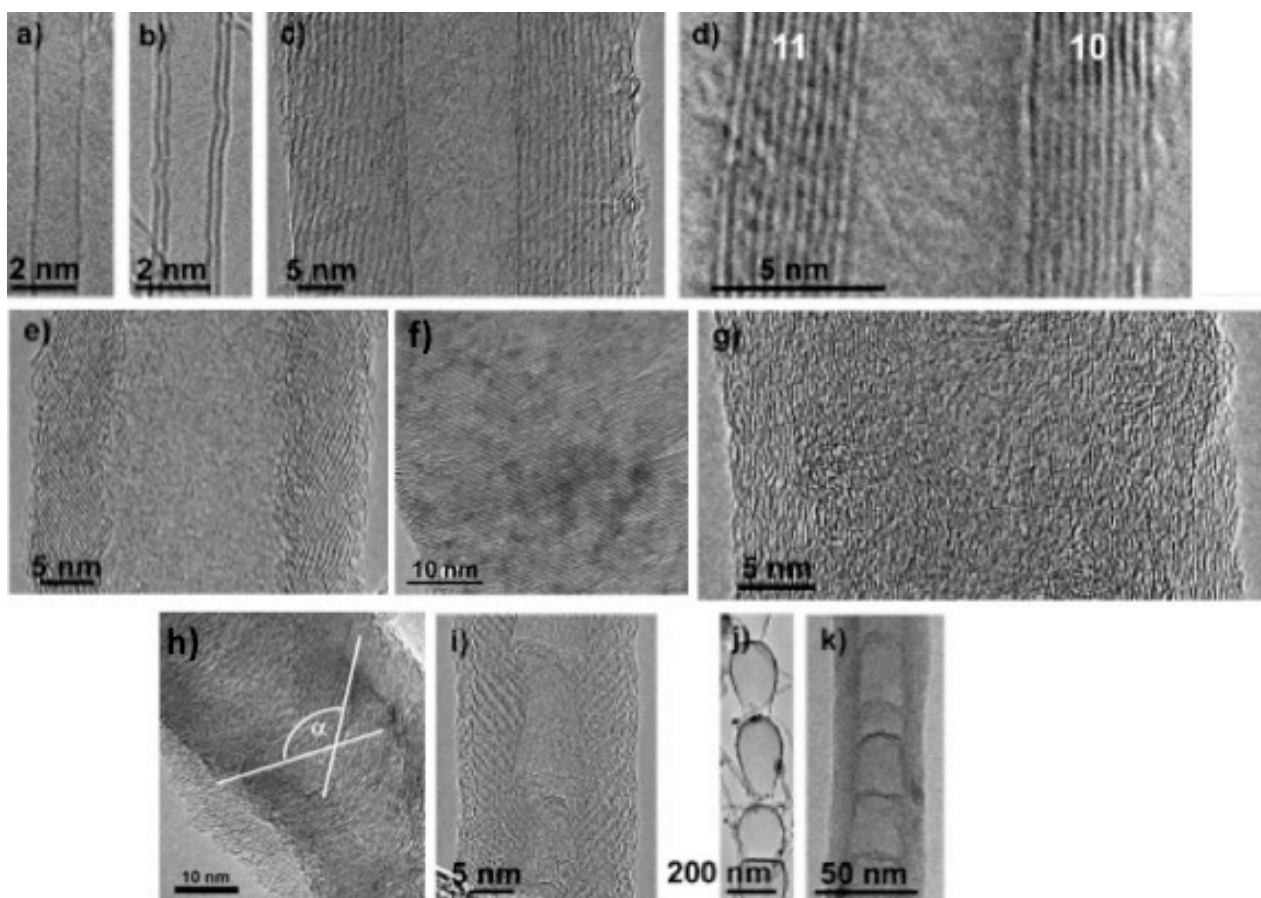
We are aware that the resultant nomenclature proposed here can sometimes be more complex than the common names currently in use. In the chemistry world it is quite easy to have alternative common names for molecules such as ferrocene instead of bis(η⁵-cyclopentadienyl)iron. Molecules are well-defined units but one should take care when adopting a similar route for carbon nanoform nomenclature, where forms can have the same shape at the macroscopic scale but atomically different variants. Thus if employing a common name it would be advisable to refer at least once to the 'complete' name, for example, as defined in this article.

While we would not presume to develop here the ideal solution to carbon nomenclature, it is our intention to raise awareness of the issue and stimulate debate. We hope that this editorial will serve as a platform for future development of an exhaustive, definitive, yet flexible nomenclature,

hopefully through the medium of an authoritative body within the carbon community such as IUPAC.

Acknowledgments

We are grateful to A. Schaper, P. Harris, M. Heggie, O. Chauvet, J. Hutchison, Y. Gogotsi and P. Thrower, and especially M. Monthieux for useful comments, critical reading and discussion. We are grateful to the Australian Research Council for the fellowship grant DP110104415 (ISM), the Royal Society (NG), the European Commission under the Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363 (NG), the ERC Starting Grant (ERC-2009-StG-240500) (NG), the EPSRC PIA Award (NG), and the French ANR project NANOSIM_GRAPHENE (CPE) for financial support.



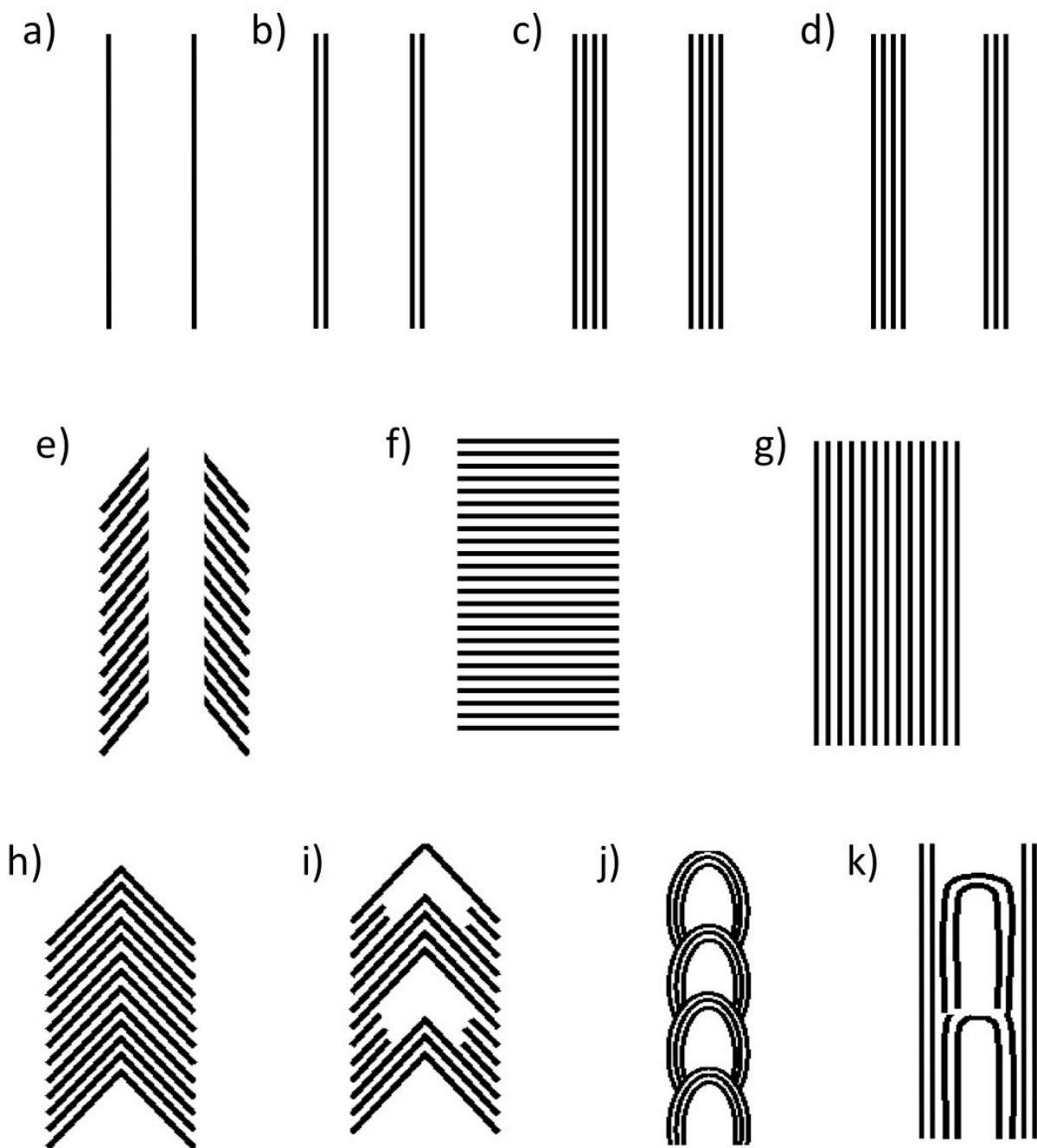


Figure 3. Schematic of several one-dimensional forms from Figure 1 a) single-walled nanotube, b) double-walled nanotube, c) multi-walled nanotube, d) scrolled graphene, e) hollow-core stacked nanocones, f) stacked curved platelet fibre, g) full-core nanotube, h) stacked nanocones, i) partitioned stacked nanocones, j) stacked open multi-walled fullerenes and k) partitioned nanotube.

Molecular Forms (0 dimensions)
Buckminsterfullerene [19] <i>Soccerene, footballerene, buckyball, carbon bucky-cages</i>
Fullerene
Multi-walled fullerene [20] <i>Onions, bucky onions, nested fullerenes</i>
Single-walled nanocone [21] <i>Nanohorn, nanocone</i>
Multi-walled nanocone [22] <i>Nanocone</i>
Single-walled nanotube bundle toroid [23] <i>Fullerene “crop-circle”, toroidal fullerene, nanohoop, carbon based toroid, doughnut shaped tube, nanotube ring, nanotorus</i>
Curved graphene platelet [24] <i>Dome-shaped carbon, nanoislands</i>
Open fullerene [25] <i>Bowl, bowl-shaped aromatic hydrocarbon, open-cage fullerene, bowlane</i>
Single-walled nanotube bundle nanospiral [26] <i>Nanotube ring</i>

Cylindrical nanoforms (1 dimensional)
Single-walled nanotube [27] <i>Single-layered nanotube, tubelenes, buckytubes, graphite microtubules</i>
Double-walled nanotube [15] <i>Double-layer nanotube</i>
Multi-walled nanotube [28] <i>“Russian doll” tubes, nested tubes, nested cylinder structures, coaxial cylinder structures</i>
Nanotube bundles [29] <i>Nanotube ropes</i>
Graphene nanoscroll [30] <i>Swiss roll tube, nanoscrolls, scroll nanotubes, scrolled graphene</i>
Collapsed nanotube [31] <i>Dog bone nanotube, dumb-bell nanotube</i>
Stacked platelets [3] <i>“Deck of Cards” fibre, nanofibre</i>
(hollow- or full-core) stacked nanocones [3] <i>Stacked-cups, stacked cones, herringbone nanotube, herringbone nanofiber</i>
Screwed stacked nanocones [32] <i>Stacked cones</i>
Partitioned nanotube [33] <i>Bamboo nanotube, surface modulated nanotube</i>
Partitioned stacked nanocones [3] <i>Bamboo, stacked-cups, stacked cones, herringbone, herringbone-bamboo, coalesced graphitic nanocones, conical layer nanotube, fishbone tube</i>
Stacked open multi-walled fullerenes [20] <i>Nanobells, carbon nano-necklaces, necklaces of pearls structure, necklace-like hollow carbon nanospheres, surface modulated spherical layered nanotube</i>
Coiled nanotube [34] <i>Helix-shaped nanotube, helical nanotube, corkscrew-like nanotube</i>

Graphene nanoribbons [35]

Layered nanoforms (2 dimensional)
Graphene [36] <i>Graphene nanosheet, single graphene layer</i>
Double graphene [23] <i>Bi-layer graphene</i>
Few stacked graphenes [23] <i>Few-layers graphene, multi-layer graphene</i>
Vertically aligned few stacked graphenes [37] <i>Nanowalls</i>
Disordered nanotube films [38] <i>Buckypaper</i>
Vertically aligned nanotube arrays [39] <i>Nanotube carpets, nanotube forests</i>

Table 1. Proposed nomenclature with other names found in the literature in italics. This table aims to help researchers in their literature searches, thus if employing a common name in an article it is suggested to refer at least once to the standardised name, for example, as defined here. Note that only forms reported experimentally in the literature are included in the table. References are to the first article which definitively characterises the given nanoform.

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Irene Suarez-Martinez

Institute des Matériaux Jean Rouxel, CNRS-, Université de Nantes, BP 32229, 44322 Nantes,

France and

Nanochemistry Research Institute, Curtin University, GPO BOX U1987, Perth, 6845, Australia

Nicole Grobert

Department of Materials, University of Oxford, Oxford, OX1 3PH, UK

Christopher P. Ewels

Institute des Matériaux Jean Rouxel, CNRS-, Université de Nantes, BP 32229, 44322 Nantes,

France