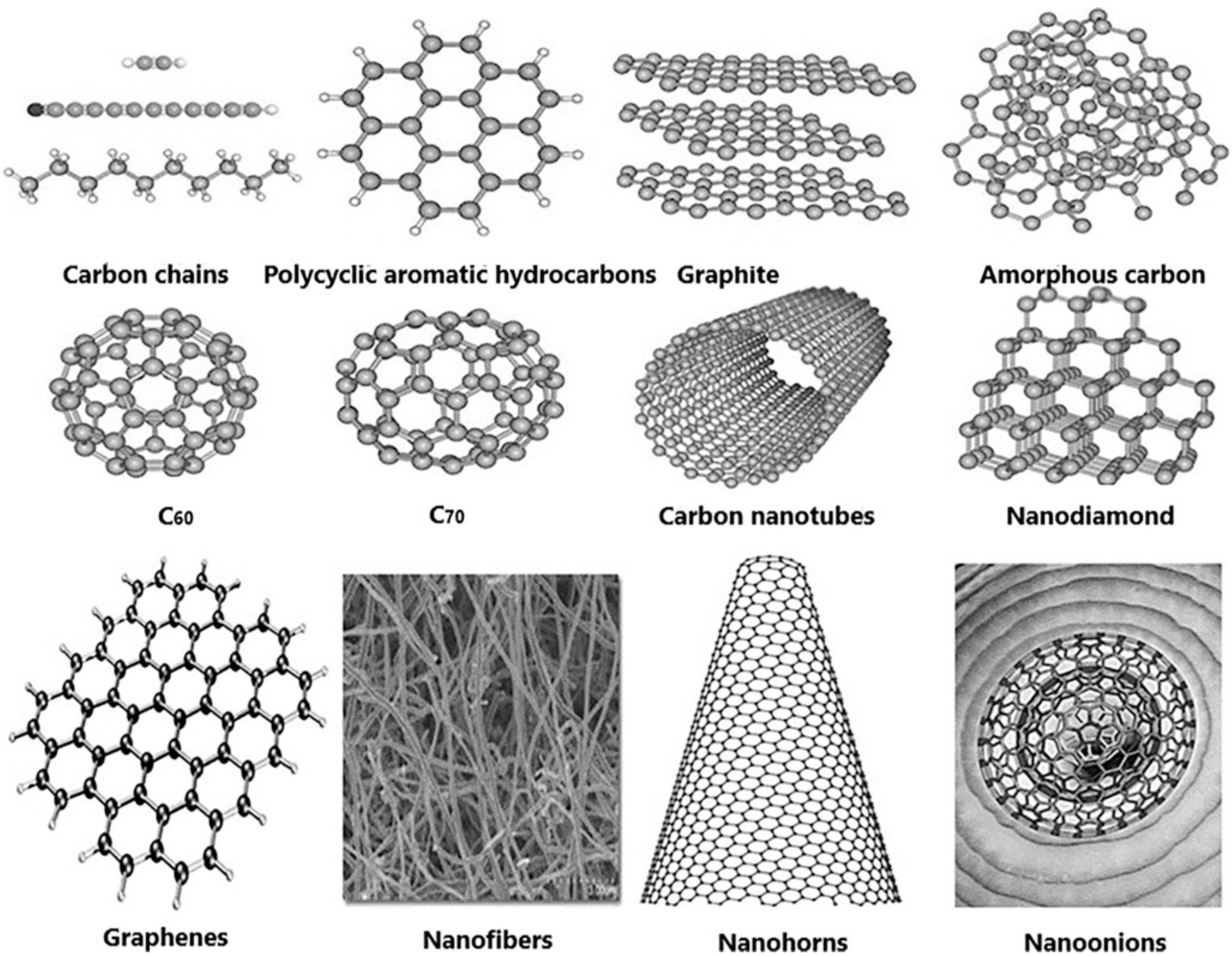
Chapter 1
General Data on Carbon Allotropes



Variety of carbon allotropes, hybridization, and dimensionality. (The image above is reproduced with permission of MDPI (*Materials*, 2015, *8*, 3068–3100).)

Carbon, the 6th element in the periodic table denoted by the letter "C" and true element of life, provides the chemical basis for life on Earth due to its ability to form stable bonds with other carbon atoms, oxygen, nitrogen, sulfur, and many other elements in *Mendeleev*'s Periodic Table. Carbon is found almost everywhere, and it is one of the most abundant materials on earth. It is the 4th most common element in the universe and 15th most common on earth's crust. All life on Earth contains various forms of carbonic structures, from proteins to the tallest trees [1]. Existence of a host of carbon inorganic forms is the also responsibility of stable single and multiple carbon-carbon covalent bonds. This process is called catenation, in which an

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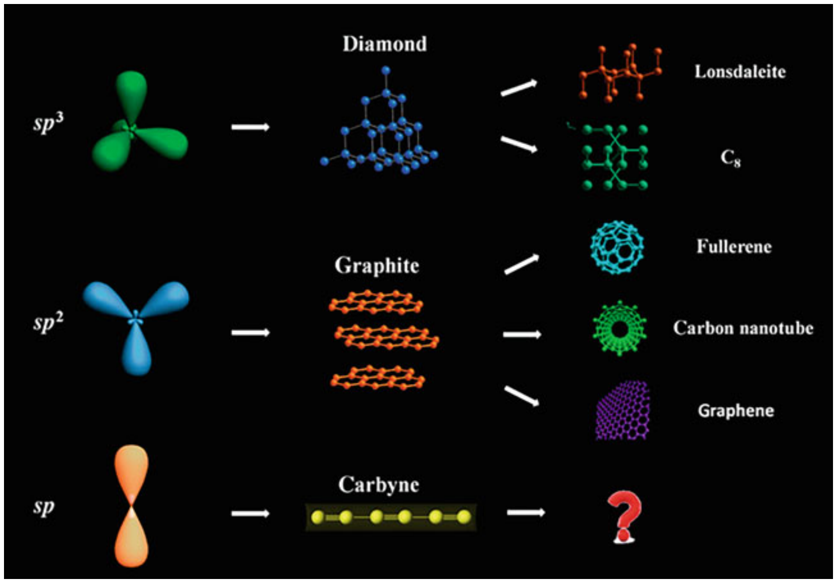

Fig. 1.1 Schematic illustration of the three kinds of hybridization of carbon. (Reproduced with permission of the *NCBI*)

element can bond with itself to form long chains. During much time, only two conventional carbon allotropes, graphite (black, soft, and conductive) and diamond (shiny, transparent, and extremely hard), have been known. Only in the last few decades have new synthetic carbon allotropes such as carbon nanotubes, fullerenes (buckminsterfullerene C_{60}, smaller and higher fullerenes), and graphene been discovered. Their outstanding properties, current and potential applications, testify their unique scientific and technological importance [2]. In addition, a host of other carbon structures, both obtained and still predicted, have been reported up to date.

Carbon exists in the form of many allotropes, which can be classified according to the character of chemical bond related with hybridization (*sp*, sp^2, sp^3): zero-dimensional sp^2 fullerenes,[1] the two-dimensional sp^2 honeycomb lattice of graphene (parent to graphite and carbon nanotubes), or three-dimensional sp^3crystals – diamond, lonsdaleite, and C_8 (Fig. 1.1) [3], as well as several mixed sp^2-sp^3 forms (e.g., Q-carbon or amorphous carbon), whose contributions sp^2-sp^3 can be measured [4]. Carbon can function either as a conductor, in *sp* chains, carbynes, and sp^2 planar structures, graphene and graphite, or as a wide-gap insulator in sp^3 tethrahedral coordination – e.g., diamond and alkanes. The origin of these properties can be traced directly to the type of hybridization: *sp*, sp^2, or sp^3. The first two have the potential to form bonds that are electrically conducting, while sp^3 has insulating properties [5].

Each allotrope has notably different electronic and mechanical properties. For instance, graphene has the characteristic semimetal electronic structure with a linear band dispersion and an extraordinarily high electron mobility. In contrast, diamond is a wide-band-gap insulator and one of the hardest natural materials known. Carbon allotropes from sp^3-hybridized carbon (diamond) and sp^2-hybridized carbon (graphite, graphene, fullerenes, nanotubes) have well-established properties, many of which are technologically relevant. A carbon allotrope constructed from *sp*-hybridized carbon atoms (carbyne), on the other hand, remains rare and presents a challenging synthetic goal.[2] The properties of carbon allotropes are quite different; thus, as a simplest example, among carbon allotropes and forms, the carbon nanofoam (0.002–0.020 g/cm^3) and aerogel (0.020–1.00) possess minimal densities, being compared with others (nanodiamonds (2.97), graphitic cones (1.96), graphite (2.27), MWCNTs (1.98), carbon black (1.91), carbon xerogel (1.73), activated carbon (2.05), and ordered mesoporous carbon (1.63)) [6]. High surface area carbon materials mainly include activated carbon, porous carbon, carbide-derived carbon, carbon nanoonions, carbon aerogels, carbon nanotubes, carbon shell, graphene, and graphene quantum dots. New carbon forms are in a permanent search [7]; the discovery of novel carbon allotropes or *carbon nanostructures* [8], exhibiting unique structural and physical properties, has attracted intensive attention due to their fundamental and technological interests. A diagram of carbon nanostructures according to their hybridization state is shown in Fig. 1.2.

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[1] C_{60} fullerenes are now recognized by chemists as one of the three forms of true elemental carbon (along with graphite and diamond).

[2] Approximately two tens of various carbyne-like materials differing in structural parameters have been artificially synthesized and revealed in nature to date.

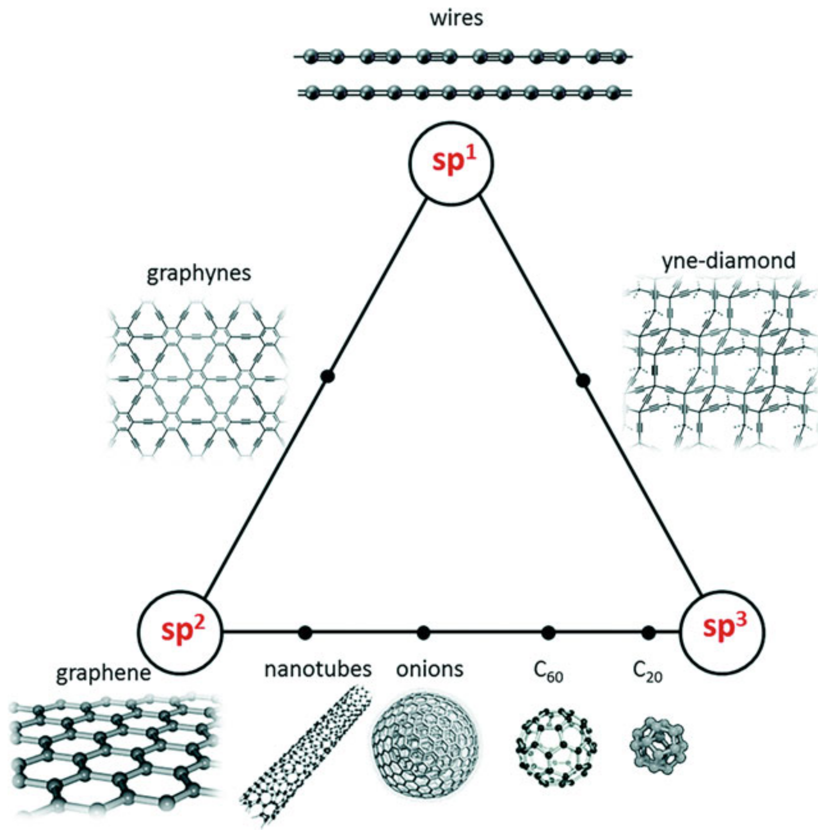


Fig. 1.2 Ternary diagram of carbon nanostructures according to their hybridization state [9]. (Reproduced with permission of the *Royal Society of Chemistry*)

There are many other classifications of carbon allotropes. On the basis of their dimensionality [10, 11], low-dimensional carbon nanomaterials can be divided into categories of ranging from zero-dimensional (0-D) to one-dimensional (1-D) and two-dimensional (2-D) depending on their nanoscale range (<100 nm) in different spatial directions. These carbon nanomaterials are focused on fullerene, onion-like carbon, carbon-encapsulated metal nanoparticles, nanodiamond (0-D), carbon nanofibers, carbon nanotubes (1-D), graphene, and carbon nanowall (2-D). Diamond, lonsdaleite, and C_8 are considered as 3D structures, sometimes together with graphite. According to one of other classifications, carbon has basically six allotropes, namely, (1) diamond; (2) graphite; (3) lonsdaleite (hexagonal diamond); (4) fullerenes C_{60} (buckminister fullerene or bucky ball), C_{70}, C_{82}, C_{540}, and others; (5) amorphous carbon; and (6) carbon nanotubes (CNTs; buckytube). At the same time, several other additional carbon forms have been recently discovered or predicted, as well as various hybrids between them [12], for instance, the 3D sp^2-hybridized graphene-CNT composite (Fig. 1.3) [13]. A generalization of most important carbon allotropes is given in a Table 1.1 and Fig. 1.4. For the nanosized carbon allotropes, the nomenclature "Carbon Nanotropes" was also assigned [14], but this term is currently practically unknown. Reports about new DFT-predicted carbon allotropes appear frequently, introducing such intriguing and exotic carbon structures as, for example, *protomene* (Fig. 1.5) [15], consisting of a hexagonal crystal structure, with a fully-relaxed primitive cell involving 48 atoms, or a proposed series of carbon allotropes called *novamene* [16]. In whole, around 500 hypothetical 3-periodic allotropes of

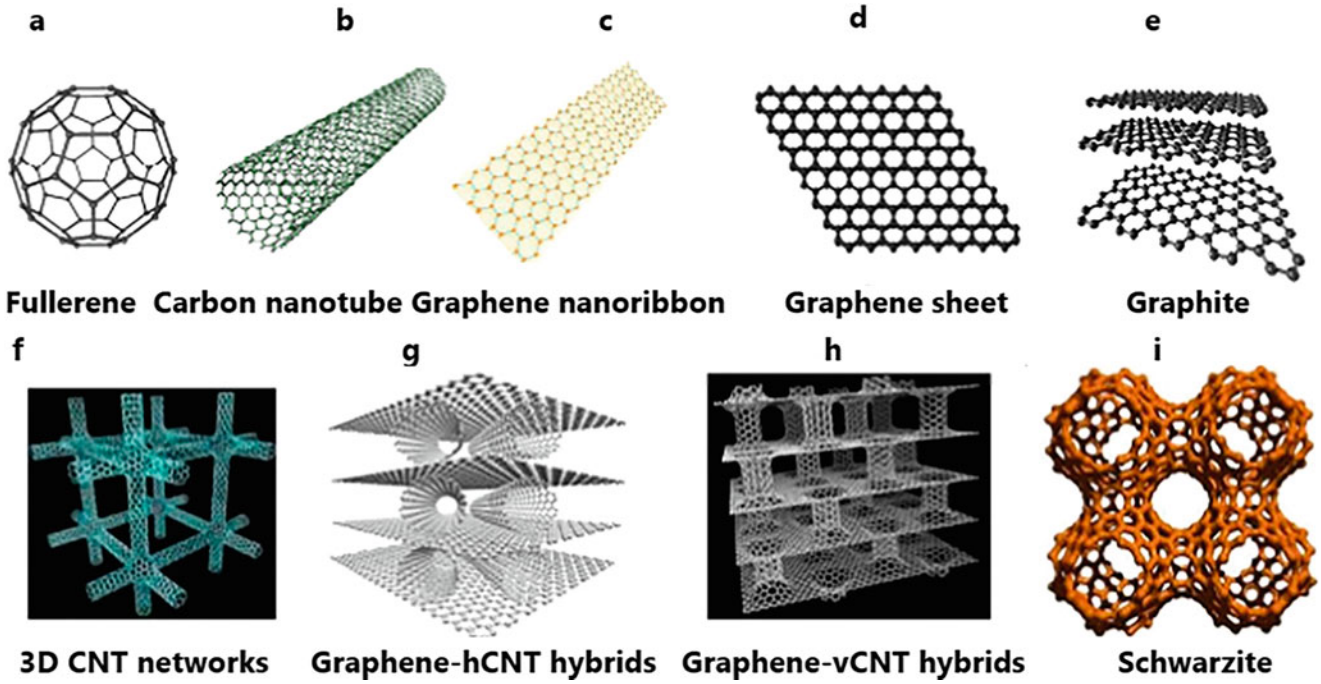
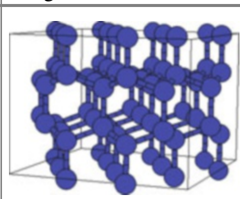
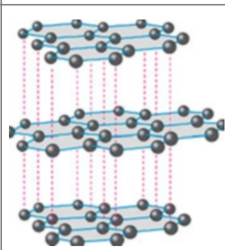
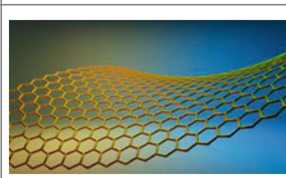


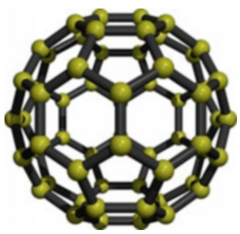
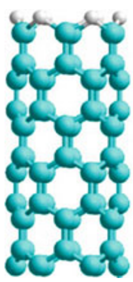
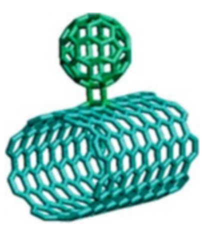
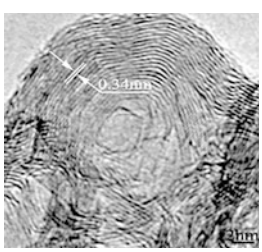
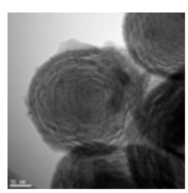
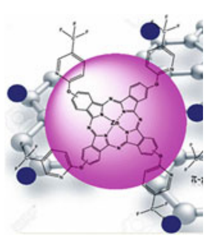
Fig. 1.3 Schematic presentation of dimensionality of sp^2-hybridized carbon nanostructures. (**a**) Fullerene (0D), (**b**) carbon nanotube (CNT) (1D), (**c**) graphene nanoribbon (1D), (**d**) graphene sheet (2D), (**e**) graphite (3D), (**f**) 3D CNT networks (3D), (**g**) hybrid of graphene with horizontal CNT (hCNT) (3D), (**h**) hybrid of graphene with vertical CNT (vCNT) (3D), and (**i**) graphene triple periodical minimal surfaces (or schwarzites 3D graphene). (Reproduced with permission of the *IOP Science*)

Table 1.1 Selected representative carbon allotropes

Carbon allotrope	Image	Structural properties
Lonsdaleite		The interlayer bonds are in an eclipsed conformation
Graphite		Planar structure of carbon atoms stacked in layers in a honeycomb lattice with a separation of 0.142 nm. Each layer is held together by a weakly unsaturated π-bond
Graphene		Flat monolayer of carbon atoms

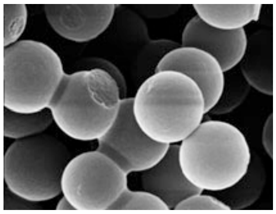
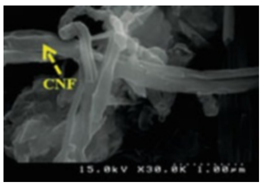
(continued)

Table 1.1 (continued)

Carbon allotrope	Image	Structural properties
Diamond		Carbon atoms arranged in a face-centered cubic crystal structure
Fullerenes		Buckminster fullerene C_{60} is an enclosed spherical structure with hexagonal and pentagonal rings made up of carbon in a *sp*^{2} hybridization. The other possible structures of fullerene are C_{20}, C_{26}, C_{28}, C_{32}, C_{50}, and C_{70}
Carbon nanotubes (main types)		Cylindrical structure: a SWCNT is a rolled up graphene sheet in the form of cylinder which is one atom thick. Two possibilities for MWCNTs: (1) more than one SWCNT is arranged coaxially where the outermost SWCNT's diameter is larger than that of the inner SWCNT; (2) a single graphene sheet rolls up on itself like a paper roll. DWCNTs have only two rolled up graphene layers arranged concentrically
Other CNTs		*Graphenated CNTs* (g-CNTs, a hybrid structure in which graphitic foliates are grown along the length of aligned MWCNTs); *extreme CNTs* (cycloparaphenylene); *nanotorus* (a doughnut-shaped CNT in which a SWCNT is organized to join head to tail to form a doughnut shape); *nanobud* (a combination of both fullerene and CNT through covalent bonding) [19]; *peapod* (a fullerene inside a CNT); *Cup-stacked CNTs* (straight long carbon nanofibers which have a hollow core are stacked one above the other); *carbon megatubes* (similar to CNTs but have a larger diameter exceeding a few microns)
Carbon onions		Spherically closed carbon shells which resemble fullerenes 
Carbon quantum dots		Electrons confined fluorescent nanoparticles

(continued)

Table 1.1 (continued)

Carbon allotrope	Image	Structural properties
Carbon spheres		Different structure compared to C_{60}
Carbon nanofibers		sp^2 hybridization-based linear filaments

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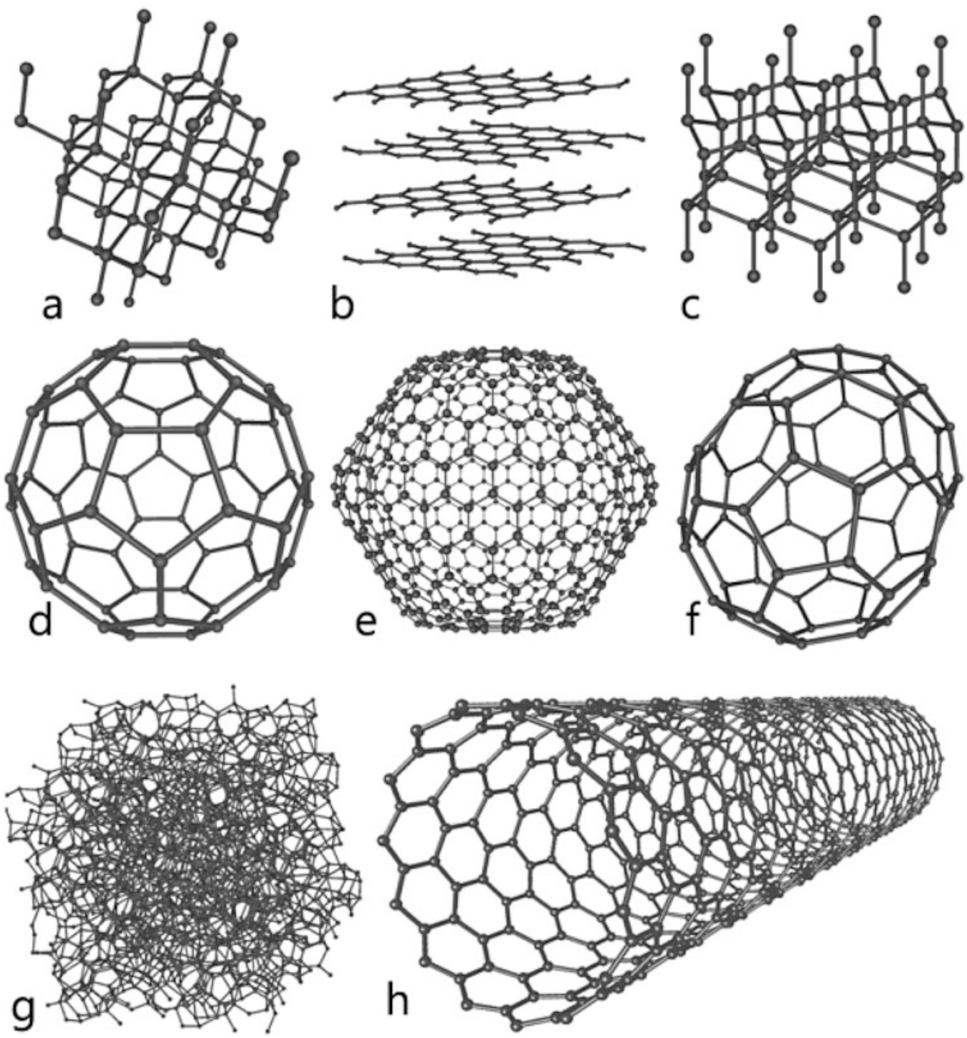

Fig. 1.4 Eight allotropes of carbon: (**a**) diamond, (**b**) graphite, (**c**) lonsdaleite, (**d**) C_{60} buckminsterfullerene, (**e**) C_{540}, fullerite, (**f**) C_{70}, (**g**) amorphous carbon, and (**h**) single-walled carbon nanotube. (Source: *Wikimedia Commons*)

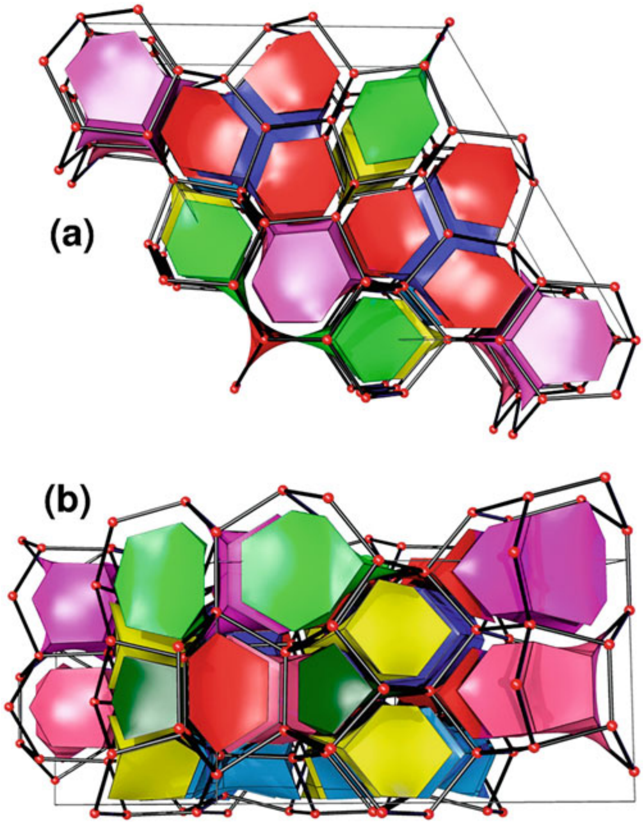

Fig. 1.5 Natural tiling for the protomene structure: (**a**) top view down from the }\hat{z}{ direction (**b**) side view in the $\hat{y}$ direction. (Reproduced with permission of the *Elsevier Science*)

carbon are known at present. In general descriptions of carbon allotropes in online encyclopedias [17], the following carbon forms are mainly present in distinct orders:

Diamond	Chaoite
Graphite	Metallic carbon
Graphene	*bcc*-Carbon (cubic carbon)
Graphenylene	*bct*-Carbon
Amorphous carbon	M-Carbon
Buckminsterfullerenes	Q-Carbon
Carbon nanotubes	T-Carbon
Carbon nanobuds	Prismane C_8
Glassy carbon (vitreous carbon)	Laves graph or K_4 crystal
Atomic and diatomic carbon	Penta-graphene [18]
Carbon nanofoam	Haeckelites
Carbide-derived carbon[3] (CDC)	Phagraphene
Lonsdaleite (hexagonal diamond)	Novamene
Linear acetylenic carbon (LAC) (or carbon-atom wires [9])	Protomene

Obviously, this set of carbon forms is incomplete. For example, if we would like to indicate production methods of carbon allotropes, we may add, to the CDC, the “MOF-derived carbon(s),” a relatively new research area, dedicated to the use of metal-organic frameworks for preparation of metallated nanocarbons from MOFs as precursors by pyrolysis. Indeed, because of a lot of synthesis techniques for carbon allotropes (e.g., CVD and spray pyrolysis, laser ablation, or hydrothermal methods),

[3]Distinct nanostructures, united according to the synthesis method

this classification would not be useful. At the same time, a host of less-common nanocarbons, described below, are currently out of serious attention of researchers, for instance, carbon nanoworms or nanobrushes, among many others, despite potential useful applications. Carbon allotropes can also be doped with nitrogen and decorated/immobilized with metals [20, 21]. Structure, bonding, and mineralogy of carbon at extreme conditions are also attractive research areas [22]. So, the main objective of this book is to show for readers all possible available carbon allotropes, forms, and nanostructures, both discovered and theoretically predicted. At the same time, the coordination and organometallic chemistry [23] of carbon allotropes and their composites/materials [24] requires a major attention due to many applications.

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