

Chapter 8

Graphene, Fullerenes, Carbon Nanotubes: Electronic Subsystem

8.1 Carbon: Allotropic Forms

The non-metallic tetravalent carbon element C belongs to the list of the most abundant elements due to the possibility to form organic compounds. Life on Earth is based on organic materials built up using various carbon molecular derivatives. Electronic configuration $1s^2 2s^2 2p^2$ determines the unique possibility of carbon atoms to create the interatomic bonds and also to create structural chains and cyclic compounds. Well-expressed chemical bonding in different ways pre-determines existence of various allotropes of carbon with different physical properties. Carbon is also important in various technological applications – from drugs to synthetic materials. This is due to the carbon's ability to create chemical bond with almost any item in various ways. The result is a variety of structural organic compounds with strong expressed physical and chemical properties as pointed by Hirsch [1].

Formation of the main allotropic forms is determined thermodynamically as presented in Fig. 8.1. Sublimation occurs at temperature about 3900 K. Triple point is present at pressure of $[10.8 \pm 0.2]$ MPa and temperature of $[4600 \pm 300]$ K [2].

Generally, carbon could form a great number of chemical compounds (molecular derivatives up to several millions). This fact could be explained by the existence of the unique electronic structure formed after sp hybridization (single–double–triple bonding, formation of π -conjugated system) which finally determines certain macromolecular physical properties – such as hardness, specific thermal conductivity, electrical conductivity, etc. [3]. Cambridge Structural Database [4] represents covalent radii of carbon for different hybridization, sp^3 , 76 pm; sp^2 , 73 pm; and sp , 69 pm, when van der Waals radius is equal to 170 pm.

Table 8.1 represents several typical carbon allotropes and molecular derivatives. The simplest plain molecular forms are known as benzene (one hexagonal ring), naphthalene (two rings), anthracene (three rings), etc. Carbon atoms can form

Fig. 8.1 Phase diagram of carbon near triple point at 10.8 MPa and 4600 K. Area 1 – phase of metastable graphite and diamond, and 2 – phase of graphite and metastable diamond

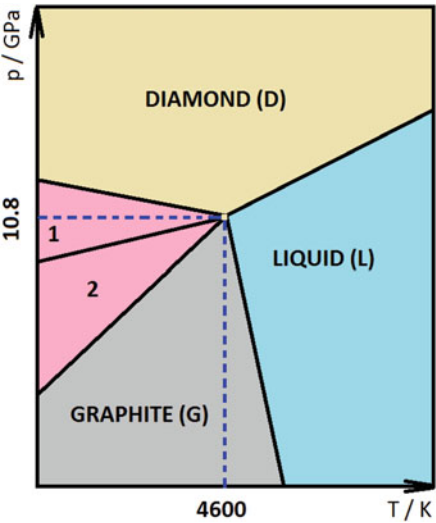


Table 8.1 Different structures of carbon

Allotropic forms	Molecular derivatives
Diamond	Benzene
Graphene	Naphthalene
Graphite	Anthracene
Fullerene	...
Nanotubes	Coronene

regular tetrahedral structures (diamonds, etc.), closed spatial loops (fullerene, etc.) or plane loops (graphite, etc.).

Two allotropic forms of carbon – diamond and graphite – are known as the classical crystallographic samples. The difference between the phases is 0.02 eV per atom. In order to make the phase transformation, due to the high activation barrier >0.4 eV per atom, a very high temperature and pressure are required.

Diamond represents one of the best known metastable allotropes of carbon. Figures 8.2 and 8.3 represent two projections of the diamond lattice, face-oriented and isometric, respectively. Structure parameters were obtained from Crystallography Open Database [5]; crystallographic parameters of diamond data were published by Straumanis et al. [6]. Cubic lattice parameters are the following: $a = 0.35667$ nm, $\alpha = 90^\circ$ and 8 atoms per cell: 1 atom at the corner, 3 atoms in the faces and 4 internal atoms on diagonals.

Three geometric figures are organized in a diamond lattice: cube, octahedron and tetrahedron. Eight external atoms (placed at the corners of lattice, denoted by C) create a cube. Six external atoms (placed in the faces of lattice, denoted by F) create an octahedron. Four internal atoms (placed at 1/4 of the distance along diagonal, denoted by I) create a tetrahedron. All bond lengths are equal to 0.154 nm, all bond angles – 109.5°. Diamond lattice *fcc* (face-centred cubic crystal structure) warrants

Fig. 8.2 Diamond lattice, face-oriented projection. *C* corner atom, *F* face-centred atom, *I* internal atom

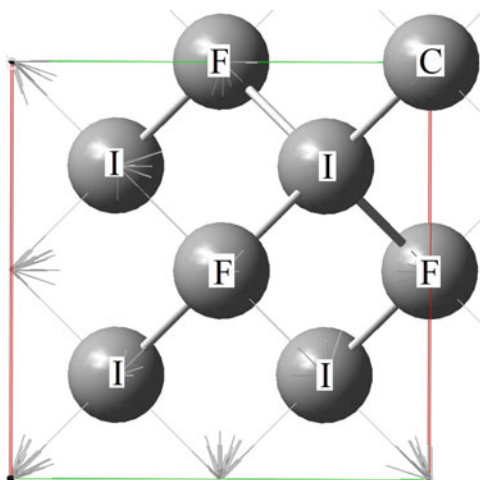
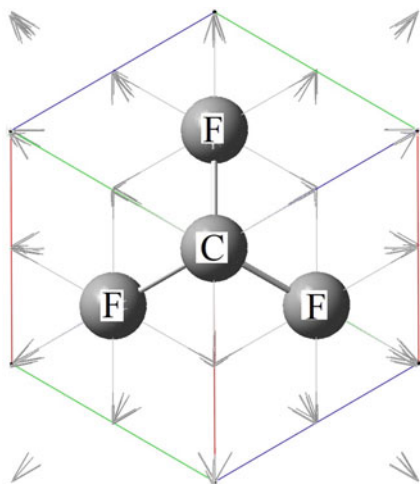


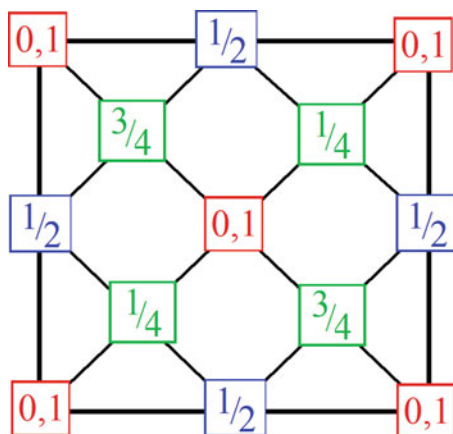
Fig. 8.3 Diamond lattice, isometric projection. Atom labels according to Fig. 8.2. Internal atoms are covered



superlative physical qualities due to strong covalent bonding between atoms – sp^3 hybridization. Every atom is surrounded by four neighbouring atoms situated at the corners of tetrahedron (regular).

Figure 8.4 represents formal diamond cubic structure as a combination of two interpenetrating sub-lattices of face-centred cubic type. Both sub-lattices are displaced along the body diagonal of the cubic cell by $1/4$ length of that diagonal. Origins of two face-centred cubic sub-lattices are placed at points $(0, 0, 0)$ and $(1/4, 1/4, 1/4)$. The points at 0 and $1/2$ are on the face-centred cubic lattice; those at $1/4$ and $3/4$ are on a similar *fcc* lattice displaced along the body diagonal by $1/4$ of its length.

Fig. 8.4 Formal diamond cubic structure



Graphene represents two-dimensional planar structure (so-called layer) where carbon atoms are bonded covalently making honeycomb hexagonal lattice (six atoms per one ring, sp^2 hybridization) (Fig. 8.5a). Graphene is also a basic element for another allotrope such as graphite, CNT and fullerenes. Looking from another point of view, graphene could be treated as infinite alternant polycyclic aromatic hydrocarbon [7]. In the hexagonal lattice, the interatomic distance is equal to 0.142 nm. Graphene belongs to the class of zero-gap semiconductors, and surprisingly, valence band and conduction band start at the same Dirac point. It means that the delocalized π -system realizes electron migration only in the plane but not between the planes. The practical usage of graphene includes light-emitting diodes (LED), solar cells, touch panels for displays and so on.

Graphite is known as the most stable allotrope of carbon under standard conditions. Several stacked graphene sheets (when the distance between planes is 0.335 nm) could form graphite. In the hexagonal lattice, interatomic distance is equal to 0.142 nm [8]. Graphite is more stable thermodynamically in comparison with diamond, and graphite is much more electronically reactive due to the properties of delocalized π -system.

Two types of graphite – amorphous and crystalline (including α (hexagonal) and β (rhombohedral) crystalline forms, also bilayer graphene) – represent semimetal derivatives of a layered planar structure, with the distance between planes of 0.335 nm (in case of graphene, two-dimensional planar structure represents one sheet only). In a layer, atoms are bonded covalently making a honeycomb hexagonal lattice (six atoms per one ring). The bonding between layers is realized through the van der Waals bonds.

Fullerenes. Fullerenes represent a carbon derivative class of spherical or ellipsoidal form (Fig. 8.5b). The most stable and best-known form is Buckminster C_{60} fullerene [9] which is composed as a network containing 60 carbon atoms. Geometrically, this structure could be titled as a truncated icosahedron with 60 vertices and 32 faces. Carbon atoms are placed only at vertices. 12 pentagons and

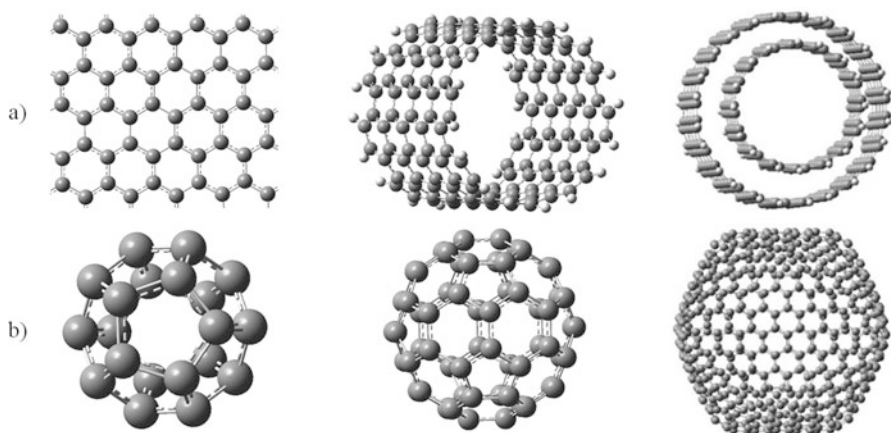


Fig. 8.5 Carbon allotropes: (a) graphene, single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT); (b) C₂₀, C₆₀, C₅₄₀

20 hexagons create a pseudosphere, the so-called ball. The van der Waals diameter is equal to 1.01 nm, and the radius of molecule is 0.357 nm [10]. The electronic structure is of sp^2 hybridization.

Figure 8.6 represents a nonplanar fragment of the fullerene C₆₀ – the so-called hat of a fullerene. The pentagon in the centre is surrounded by five hexagons. The bond length is different for the pentagon (0.143 nm) and hexagon (0.139 nm).

Fullerene C₆₀ is quite stable up to 1700 K in the surrounding argon and up to 500 K in the surrounding oxygen. The barrier of photoreaction is quite low: at room temperature – 0.55 eV (IR region).

Figure 8.7 represents a fragment of fullerene C₁₈₀ as half of the spherical structure. All fullerenes with the atom number <60 are unstable due to unrealized bonding properties on a plane surface. The smallest possible fullerene is dodecahedra C₂₀ with the biggest sphere curvature. Instability of fullerenes with the atom number >60 arises from topological aspects – the sphere radius increases, for series C₇₀, C₇₆, C₈₄, C₁₆₄, C₁₉₂, C₂₁₆, C₅₄₀, and the curvature decreases. For big structures, starting from C₁₈₀, the sphere reforms into several islands of pseudo plane surface – see, for example, C₅₄₀ in Fig. 8.5b.

This factor (the reformation of the sphere) increases the aromatic properties only on the local surface, but not on all derivatives.

Carbon Nanotubes (CNTs). Derivatives of the tubular structure, considered as single, rolled graphite sheets, are called carbon nanotubes (CNTs) (see Fig. 8.5a). CNTs can be formed by stranded filaments that intersect with atoms of the sp^2 hybridization atom, usually several nanometres in length, in a particular case up to several mm. Eatemadi et al. [11] described different forms of CNTs. The authors claimed that physical parameters such as size distribution, structure, surface area, surface charge, agglomeration state and purity of the samples have a considerable impact on the reactivity of CNTs.

Fig. 8.6 Fragment of fullerene C_{60} . Pentagon is environed by five hexagons

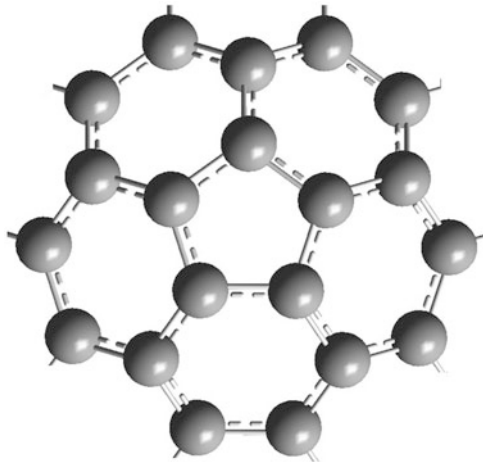
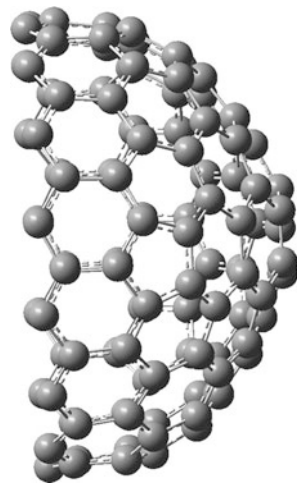


Fig. 8.7 Fragment of fullerene C_{180} . One half of spherical structure



The structure mathematically could be described by periodicity through the chiral vector C_h :

$$C_h = \left| \vec{O\vec{A}} \rightarrow \right| = n\mathbf{a}_1 + m\mathbf{a}_2 \rightarrow (n, m), \quad (8.1)$$

where (n, m) are integers, $0 \leq m \leq n$; the so-called pair of indices, $\mathbf{a}_1$ and $\mathbf{a}_2$, are the base cell vectors of graphene. Each hexagonal ring could be enumerated (n, m) as a numeric pair. Figure 8.8 represents a graphene sheet for manufacturing CNTs. The formation of CNTs can be achieved by bonding together various parts of the graphene sheet. To establish the chiral vector, two atoms in the graphene sheet must be selected: zero-point O and any point A. The main idea for this realization is to connect the points O and A by covalent junction. The vector $\vec{O\vec{A}} \rightarrow$ (between

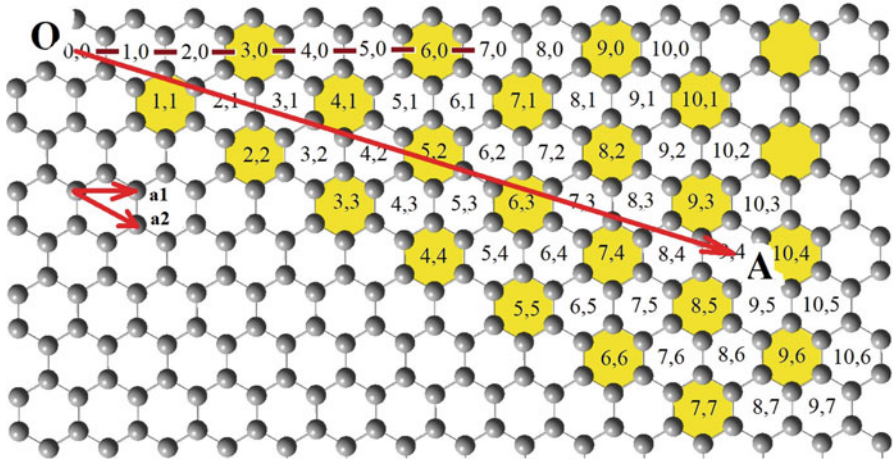


Fig. 8.8 Graphene sheet for manufacturing of CNT. Vector $\vec{OA} \rightarrow$ for CNT(9,4). Hexagons with indices if $(n-m)$ is divisible by 3 are yellow (for manufacturing of metallic CNT)

hexagonal rings (0,0) and (9,4)) and 0-*th* vector (between hexagonal rings (0,0) and (10,0)) describe the chiral angle θ . Graphene represents the plane surface constructed from identical hexagonal rings. Let us assume that a_0 is the shortest distance between two atoms in graphene plane surface, $a_0 = 0.142$ nm; a corresponds to the lattice constant (hexagon is constructed from six triangles):

$$a = a_0\sqrt{3} = 0.24595, \text{ nm}. \quad (8.2)$$

Length of chiral vector l and diameter d of CNT are determined by formulas:

$$l = a\sqrt{n^2 + nm + m^2} = 0.24595, \text{ nm} \quad (8.3)$$

$$d = \frac{L}{\pi} = \frac{a\sqrt{n^2 + nm + m^2}}{\pi} = 0.07828\sqrt{n^2 + nm + m^2}. \quad (8.4)$$

Chiral angle θ is very important from the structural aspects – allows relating the geometrical properties to the electronic ones:

$$\theta = \arccos \frac{2n + m}{2\sqrt{n^2 + nm + m^2}}. \quad (8.5)$$

Manipulating by indices (n, m) (according to condition $0 \leq m \leq n$) allows to generate a great number of different CNTs. Three different types of CNT are named ‘zigzag’ with indices $(n,0)$ (when $m = 0$ in any case), ‘armchair’ (n,n) (when $n = m$ in any case) and ‘chiral’ (any n and m). These structural variations result in differences in mechanical strength and electronic properties.

Figure 8.9 represents two bending directions of graphene sheet for manufacturing CNTs. The type of CNT depends on the rolling direction.

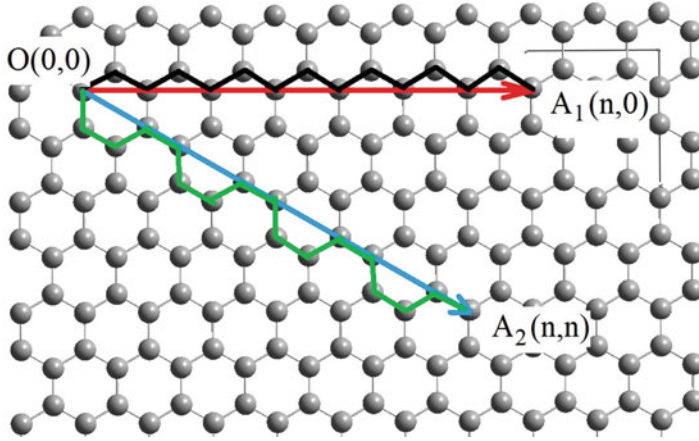


Fig. 8.9 CNT structure: zigzag type, vector $\mathbf{A}_1(n,0)$, and armchair type, vector $\mathbf{A}_2(n,n)$. Black and green figures represent zigzag and armchair, respectively

The zigzag type is determined by the vector $\mathbf{A}_1(n,0)$, also $(0,m)$, the chiral angle $\theta = 0^\circ$.

The armchair type is determined by the vector $\mathbf{A}_2(n,n)$, also $(2n,-n)$, the chiral angle $\theta = 30^\circ$.

Chiral type (intermediate) is determined by the vector $\mathbf{A}(n,m)$, where indices n and m are selected according to the condition $0 \leq m \leq n$ only. In that case, chiral angle θ is present in the range $[0; 30]^\circ$.

For CNTs, the difference of indices n and m could be related to the electronic properties. In the case if $(n-m)$ is exactly divisible by 3, the structure is called metallic (with band gap 0 eV). Figure 8.8 represents a set of hexagons coloured by yellow for metallic CNTs. In the case if $(n-m)$ is not divisible by 3, the structure is called as semiconducting (with band gap approximately 0.5 eV). The index I_{ms} – metallic/semiconductor – plays an important role of establishing electronic properties from the structure definition:

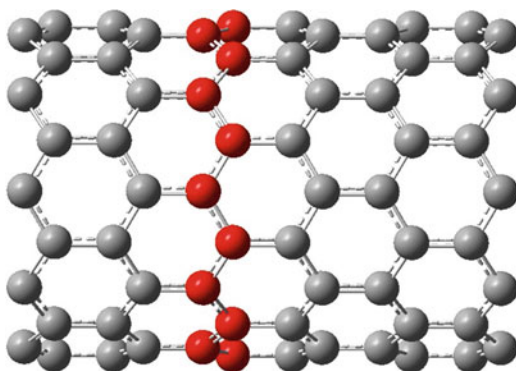
$$I_S = (n - m) \bmod 3 = 0, \quad (8.6)$$

$$I_S = (n - m) \bmod 3 = \pm 1. \quad (8.7)$$

The diameter of CNTs is not limited by any physical or chemical law, but with the increase of the diameter, the mechanical stability of CNTs decreases. Tersoff et al. [12] established the relation between CNT diameter and structural properties. CNTs with the diameter of 1 nm and less behave as rigid cylinders. For diameters over 2.5 nm, CNTs flatten against each other under the van der Waals attraction, forming a honeycomb structure. This structure exhibits an anomalous rigidity, which does not decrease with increasing the CNT diameter. With decreasing the CNT diameter, the surface tension increases rapidly. The equilibrium point between such two conditions could be achieved at diameter of 1.6 nm. According to

Table 8.2 Approximate values of diameter for CNT (n,0) of zigzag type

	Diameter, nm	<i>n</i>
Biggest, max	2.5	≈32
Optimal	1.6	≈20
Smallest, min	0.31	≈4

Fig. 8.10 CNT(10,0) structure of zigzag type

Eq. (8.4), it would be possible to estimate d and n relations for CNT of (n,0) type, when D is the biggest, optimal and smallest, respectively (see Table 8.2).

Figure 8.10 represents semiconductor CNT(10,0) of zigzag type; Figs. 8.11 and 8.12 represent metallic structures: CNT(12,3) of chiral type and CNT(10,10) of armchair type, respectively. Track atoms are coloured in red. Mentioned structures of CNT were generated using carbon nanotube generation applet, written by Veiga et al. [13].

CNT of single-wall type (SW-CNT) could be described as the long tube of diameter $1 \div 1.6$ nm, as presented in Figs. 8.10, 8.11 and 8.12. The ends of CNT are capped by hemispheres of corresponding fullerene – see Fig. 8.7. Due to the construction properties (CNT + hemisphere of fullerene), chemical activity of such structure will be much higher at the top (with hemisphere) in comparison to the body (regular CNT). This phenomenon could be explained as follows. CNT is constructed as the rolled sheet where all carbon atoms are placed in hexagons. Hemisphere of fullerene of corresponding diameter contains pentagons with vacant valences which significantly increase the chemical activity.

Figure 8.13 represents real structure, when the ends of CNT(15,0) are connected to two hemispheres of fullerene C_{180} .

Due to the extraordinary construction (multiple oriented bonding), mechanical properties of CNTs are extreme in comparison to another molecular compound. Ternones [14] compares physical properties of CNTs and several metals (see Table 8.3). The Young's modulus of SWNT is four times greater in comparison to steel, and thermal conductivity is five times greater in comparison to copper.

Fig. 8.11 CNT(10,10) structure of armchair type

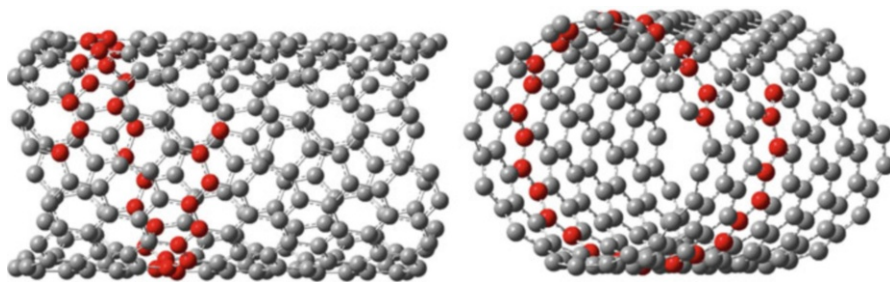
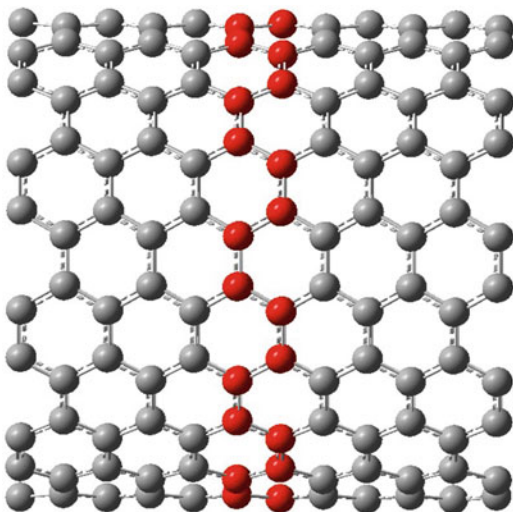
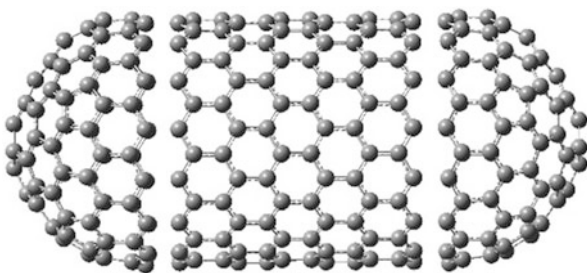


Fig. 8.12 CNT(12,3) structure of chiral type. Two projections

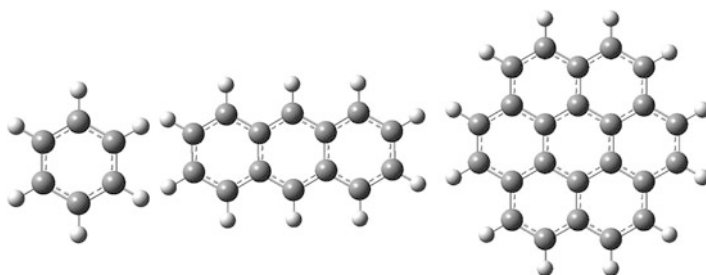
Fig. 8.13 Real structure: CNT(15,0) at centrum and hemispheres of fullerene C_{180} at the right and left side to cover open valences of CNT. Due to representational purposes, valence bonds between fragments are not shown



Multiwalled CNT (MWCNT) represents another type of CNT as the assemblies of SWCNT, which could be concentrically aligned. It means that several SWCNTs of different diameters could be aggregated in one derivative. Due to different dimensions, MWCNTs express different electronic properties.

Table 8.3 Physical properties of CNT and several metals

Property	SW-CNT	Steel	Copper
Young's modulus, GPa	1000	230	117
Density, kg/m ³	1300	7850	8940
Thermal conductivity, W/(m·K)	2000	50	380

**Fig. 8.14** Carbon: molecular derivatives – benzene, anthracene, coronene

8.2 Carbon Derivatives: Formation of Electronic System

The simplest carbon molecular derivative of hexagonal type is benzene (see Fig. 8.14). Planar molecule consists of six carbon atoms and six hydrogen atoms. All C–C bonds are of the same length $a_l = 0.140\text{nm}$. Due to similar electron delocalization between each of all C atoms, a_l is intermediate in comparison to the distance between atoms while creating single bond [$\text{H}_3\text{C}-\text{CH}_3$] and double bond [$\text{H}_2\text{C} = \text{CH}_2$].

Anthracene and coronene are the polycyclic aromatic hydrocarbons consisting of three and six fused benzene rings, respectively (see Fig. 8.14).

In the framework of molecular orbitals (MO), formation of three delocalized π -orbitals (in space of all six carbon atoms) warrants the stability of benzene molecule (condition of aromaticity).

Maps of electronic charge redistribution were depicted according to quantum chemistry simulations using *Gaussian09 package* [15]. Optimization of ground state energy was provided using DFT B3LYP method at 6-31G(d) basis including polarization functions. Excited electronic states were simulated by TD method (for singlets only).

Wang [16] presented large review of different simulation methods, which are applicable for predicting CNT properties: atomistic and molecular dynamics.

Figure 8.15 represents electronic charge redistribution of benzene molecule. Two one-particle transitions [$\text{HOMO}-1 \rightarrow \text{LUMO}$] and [$\text{HOMO} \rightarrow \text{LUMO} + 1$] of the same probability populate the first excited electronic state. The presented two MO are of great importance in the optical excitation; the last third MO (not depicted here) plays a significant role in high-energy photoelectron excitation only. Bonding orbitals [$\text{HOMO}-1$] and [HOMO] are constructed from three on the left and three on

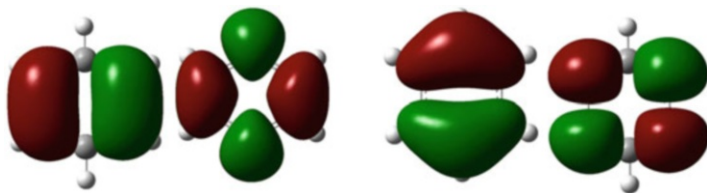


Fig. 8.15 Benzene. Maps of electronic charge redistribution related to the transition $S_0 \rightarrow S_1$

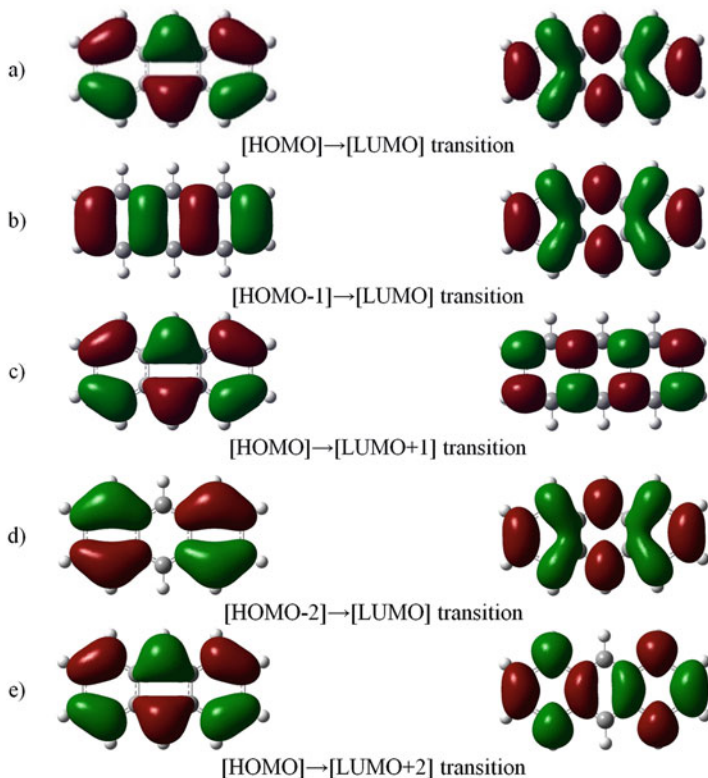


Fig. 8.16 Anthracene. Maps of electronic charge redistribution related to the transitions: (a) $S_0 \rightarrow S_1$; (b, c) $S_0 \rightarrow S_2$; (d, e) $S_0 \rightarrow S_3$

the right atomic orbitals (AO) when symmetry axis is vertical and horizontal, respectively (localized on three atoms). Antibonding orbitals [LUMO] and [LUMO + 1] keep the two-axis symmetry, but essential charge redistribution takes place. Atomic charge is delocalized along one of symmetry axis.

Figure 8.16 represents the electronic charge redistribution of the anthracene molecule. Two one-particle transitions are devoted to population of excited electronic states S_1 , S_2 and S_3 . Anthracene contains three benzene rings distributed

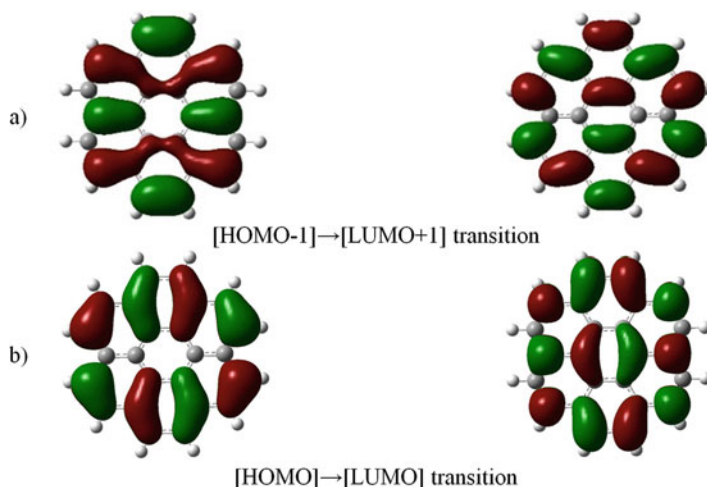


Fig. 8.17 Coronene. Maps of electronic charge redistribution related to the transition $S_0 \rightarrow S_1$

along the long axis. According to that, several bonding orbitals such as [HOMO-1] and [HOMO-2] are similar to benzene ones. [HOMO] bonding orbital contains three types of charge distributions: central parts and two axial symmetric outside parts. Antibonding orbital [LUMO] expresses specific type of charge redistribution (so-called ‘big X’ type – symmetric cross at the centrum). The antibonding orbital [LUMO + 1] expresses the charge redistribution on carbon atoms belonging to the neighbouring rings (and also on the outside atoms). It is necessary to point out that several MO contain substructure along the long axis for each ring (e.g. [HOMO-1]). Other molecular orbitals (e.g. [HOMO-2]) express axial symmetry properties.

Figure 8.17 represents electronic charge redistribution of the coronene molecule. Two one-particle transitions are devoted to population of excited electronic states S_1 . Due to molecular geometry (hexagonal rings are placed around, but not in the straight line as in the case of anthracene), new tendencies related to charge distribution occur.

Bonding orbitals [HOMO-1] and [HOMO] are constructed from a large number of atomic orbitals (AO), where the main part of electronic charge is depopulated outside the centrum of coronene. The antibonding orbitals [LUMO + 1] and [LUMO] express the charge concentration in the centre of the coronene. For antibonding orbitals [LUMO + 1] and [LUMO], the charge delocalization outside the coronene takes place.

8.3 Graphene Electronic Structure

Graphene represents infinite two-dimensional structure of sp^2 hybridization, where each carbon atom has four bonds, one σ -bond with each of its three neighbours and one π -bond that is oriented out of plane.

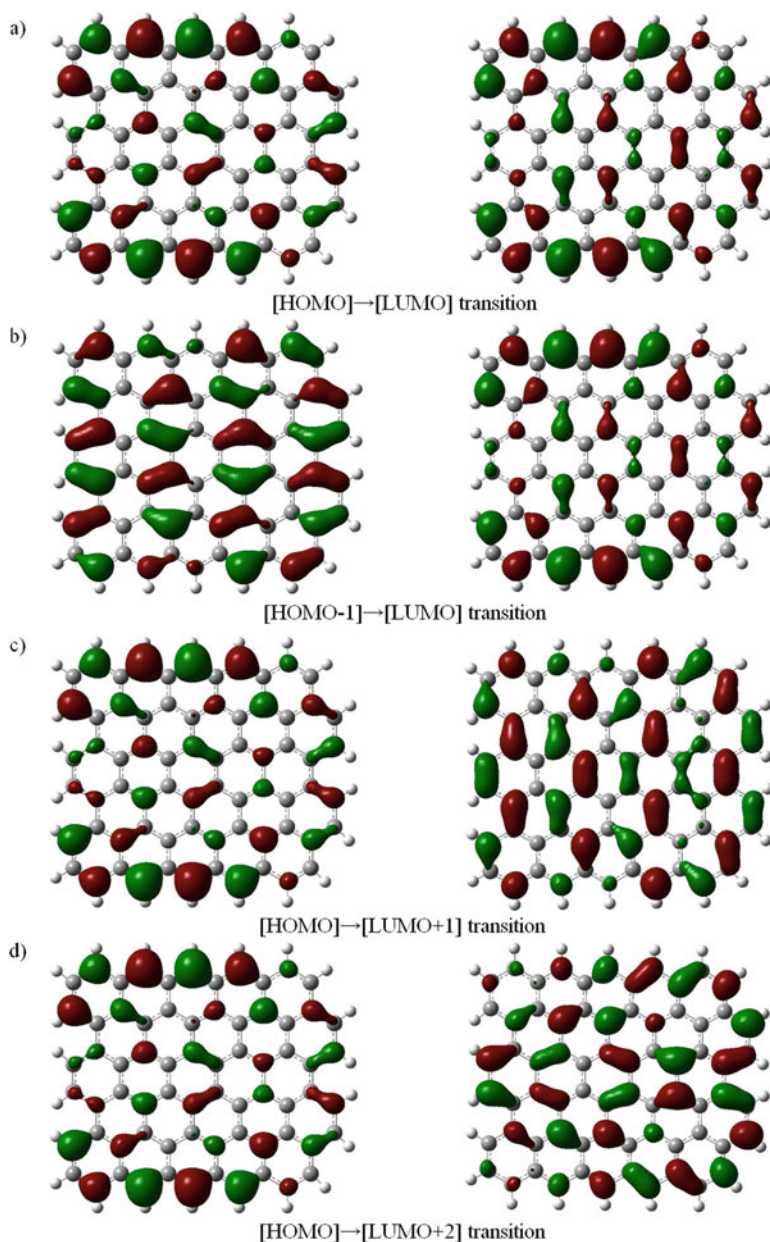


Fig. 8.18 Graphene. Maps of electronic charge redistribution related to the transitions: (a) $S_0 \rightarrow S_1$; (b) $S_0 \rightarrow S_2$; (c) $S_0 \rightarrow S_3$; (d) $S_0 \rightarrow S_4$

Figure 8.18 represents the maps of electronic charge redistribution of graphene-25 structure. Due to the technical troubles to simulate infinite structure, graphene has been presented here as a sheet with dimensions 5×5 with 25 hexagons (one array is created by five hexagons in the row; three arrays are bonded to each other

by covalent junction). To exclude the ionic states, free outside valences of carbons are filled by hydrogens (as in case of molecules).

Several one-particle transitions are devoted to population of excited electronic states S_1 , S_2 , S_3 and S_4 . As in the case of coronene, several equivalent maps or sub-maps could be observed.

Bonding orbitals [HOMO] and [HOMO-1] are constructed from a very big number of atomic orbitals (AO), when the main part of electronic charge is depopulated outside the centrum of graphene-25. Wave functions for expressing charge distribution outside the substructure are not typical for graphene. Their occurrence could be estimated as outside effect (free outside valences of carbons are filled by hydrogens).

The bonding orbital [HOMO] contains the charge localization on two atoms as well as one atom. Otherwise, bonding orbital [HOMO-1] contains charge localization on three atoms as in the case of [HOMO] benzene or [HOMO-2] of anthracene.

The antibonding orbitals [LUMO] and [LUMO + 1] express the charge redistribution in the range of one hexagonal ring with changing the localization atoms.

Usage of 25 hexagons for simulation of graphene electronic properties is sufficient but not complete. Due to the outside effect, several MO could not be mapped in formally correct form. Otherwise, the main tendencies related to charge distribution could be perceived.

Graphene as the material could be characterized by two features: (1) zero-overlap semiconductor and (2) very high electronic mobility when holes as well as electrons are charge carriers.

The chemical bonding in graphene is organized using four outer shell electrons (in each carbon atom). Each carbon atom is connected to three neighbouring atoms due to the two-dimensional structure of the carbon net. One last electron, which is not included in the valence junction, could take part in electronic conduction (occurring of π -orbitals). Due to the overlapping of π -orbitals of bonding and antibonding types, the following formation of valence and conduction bands warrants the lability of the electronic system.

The electronic mobility of graphene μ is very high. Bolotin et al. [17] reported the maximum allowed value $\mu = 2 \cdot 10^5 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ with electron densities of $\rho = 2 \cdot 10^{11} \text{ cm}^{-2}$ which is limited by the scattering of acoustic photons of graphene.

The experiments show the lower value: $\mu = 1.5 \cdot 10^4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. High mobility could be explained by the assumption related to the planar distribution of the graphene sheet. Due to the ballistic transport phenomenon, graphene electrons could move long distances in hundreds nm without scattering. Due to their lack of mass, motions of graphene electrons and acoustic photons are similar.

Novoselov et al. [18] reported the quantum Hall effect in graphene at room temperature. The effect is due to the magnetic energy of the electrons in graphene, which is 1000 times greater than in other materials. Novoselov claimed that electronic quality of graphene could be estimated by mentioned phenomenon.

8.4 Π -Zones for Nanotubes (n,0), Nanotubes (n,n)

The geometrical form of CNTs is very important to estimate their electronic properties. All carbon atoms are distributed in space as points of hexagon apexes. Due to the curvature of CNTs, dihedral angles between hexagonal rings are not zero (different plane surfaces). It means that pure sp^2 hybridization (as in the case of graphene) is broken; with decreasing diameter of CNTs, the influence of sp^3 hybridization increases. This phenomenon is known as the factor of more active surface in comparison with plane graphene.

Saito et al. [19] studied electronic structure CNT and established the function of the diameter and helicity of the constituent CNT. Differences between metallic CNTs and semiconducting CNTs are discussed.

Primitive Cell. The task of establishing the electronic states of CNTs could be solved by several assumptions of solid-state physics. The Schrödinger equation allows estimating the system ground state energy due to several simple assumptions concerning the interaction conditions.

Let us assume the CNT is very long (in comparison to diameter) and the effects of open valences at the ends are negligible. Let us assume the existence of translational symmetry along the long axis.

As in the case of plane graphene, interactions are realized only through the π -orbital. For CNTs, let us assume the absence of interactions between π and σ orbitals due to different symmetry. These conditions are true only for graphene (plane surface structure). For CNTs, neglecting of the mentioned condition is allowed as the first assumption.

First of all it is necessary to define a primitive cell as a rectangle in order to define the first Brillouin zone. Figure 8.19 represents the primitive cells of CNT (n,0) and CNT(n,n).

Due to different rolling directions of the graphene sheet, primitive cells differ essentially. For the zigzag type CNT(n,0), two hexagons are connected through the side of polygon, and this side coincides with the symmetry axis (in the chart, oriented vertically). For the armchair type CNT(n,n), two hexagons are connected

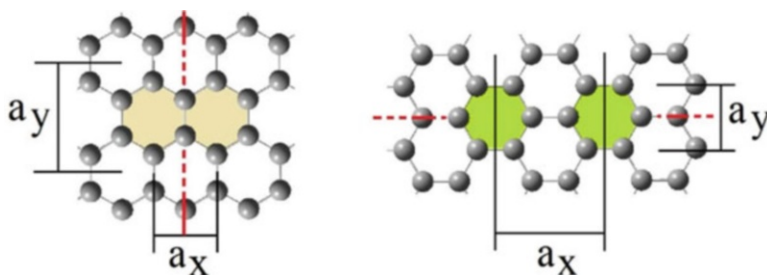


Fig. 8.19 Primitive cells of zigzag type CNT(n,0) (left) and armchair type CNT(n,n). Symmetric axes are depicted in red

Table 8.4 Parameters of primitive cells of CNT(n,0) and CNT(n,n)

Type	a_x	a_y
CNT(n,0)	a	$a\sqrt{3}$
CNT(n,n)	$a\sqrt{3}$	a

via [$>CC<$] bond, which coincides with the symmetry axis (in the chart, oriented horizontally). For CNTs (also graphene), a side of hexagon or [$\cdot C-C\cdot$] distance is equal to $a_0 = 0.142 \text{ nm}$. The distance between opposite edges of the hexagon is equal to $a = 0.2457 \text{ nm}$. Parameters of primitive cells are presented in Table 8.4.

Saito et al. [20] presented one-dimensional electronic band-structure model of CNTs. In both cases, a primitive cell contains $4n$ atoms and also $4n$ π -orbitals. Due to the translational symmetry of the system, the $4n$ basis Bloch functions will describe the system. The rotating symmetry (about long axis) allows decreasing the dimensionality of the secular equation.

CNT (n,0). Several features are significant due to CNT structure. According to the assignments of the primitive cell, $a_x = a$, $a_y = a\sqrt{3}$. Such two factors determine phase factor ka . The translational wave vector k could vary at k -space:

$$-\frac{\pi}{\sqrt{3}a} < k < \frac{\pi}{\sqrt{3}a}, \quad (8.8)$$

$$-\frac{\pi}{\sqrt{3}} < ka < \frac{\pi}{\sqrt{3}}. \quad (8.9)$$

After solving the Schrödinger Eq. (8.16), the dispersion of π bands energy on the phase factor ka is expressed by Eq. (8.3):

$$E_{n,m}^{\pm} = \alpha \pm \beta S_I, \quad (8.10)$$

where α and β are the Coulomb and exchange integrals, respectively, and S_I represents the so-called phase factor for CNT(n,0):

$$S_I = \sqrt{1 + 4 \cos \frac{\sqrt{3}ka}{2} \cos \frac{\pi m}{n} + 4 \cos^2 \frac{\pi m}{n}}. \quad (8.11)$$

The integer number m represents behaviour of rotational symmetry:

$$m = 1, \dots, n. \quad (8.12)$$

Let us divide Eq. (8.10) by value of the exchange integral β . Energy γ , normalized by value (α/β), will be used for estimations:

$$\frac{E_{n,m}^{\pm}}{\beta} = \frac{\alpha}{\beta} \pm S_I, \quad (8.13)$$

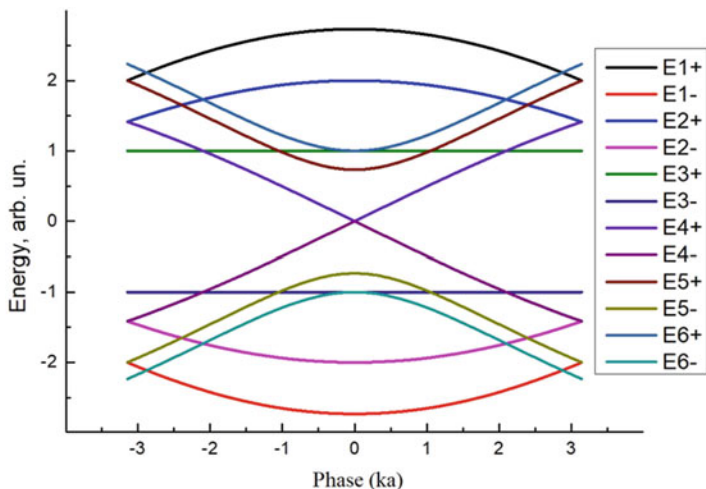


Fig. 8.20 Π -zones of metallic CNT(6,0). Fermi level is set at zero

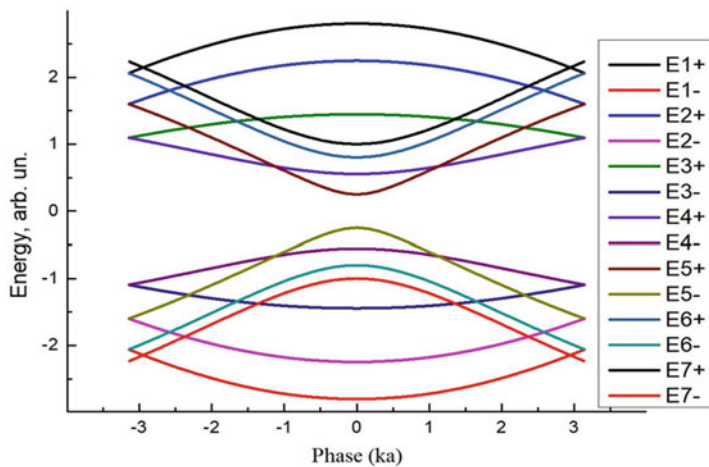


Fig. 8.21 Π -zones of semiconductor CNT(7,0). Fermi level is set at zero

$$\gamma = \frac{E_{n,m}^{\pm}}{\beta} = \pm S_I. \quad (8.14)$$

Figures 8.20 and 8.21 represent Π -zones of metallic CNT (6,0) and semiconductor CNT(7,0), respectively. The dispersion of π bands energy γ on the phase factor ka was calculated according to Eq. (8.14). Due to the energy normalization by value (α/β) , the energy dependency is shifted down when zero corresponds to the Fermi level.

The solution of the Schrödinger equation contains $(\pm)$ factor (see Eq. (8.10)). It is easy to check that the symmetry of the energy band distribution is defined by the mentioned factor.

Axis of symmetry is distributed at the position of the Fermi level. The valence bands (below Fermi level) correspond to HOMO, and lower states in molecular structures and conductive bands (before Fermi level) correspond to LUMO and higher states. The number of bands corresponds to the number $2n$ (due to $(\pm)$ factor, minus for valence, plus for conductive). At a certain position of the phase ka , some values of γ coincide.

For CNT (6,0), the gap between zones is absent – two state curves of the valence zone and conducting zone intersect only in the centre of the Brillouin zone (see Fig. 8.21), when $k = 0$.

Due to the absence of gaps, CNT (6,0) expresses the metallic properties. Another CNT such as CNT (9,0), CNT (15,0), etc. will be also of the metallic type.

For CNT (7,0), the gap between zones is present in the centre of the Brillouin zone, when $k = 0$. Due to any intersections between the curves of the valence zone and conducting zone (see Fig. 8.22), CNT(7,0) is called semiconducting with the optical gap. Graphene belongs to zero-gap semiconductors.

CNT (n,n). According to the assignments of the primitive cell, $a_x = a\sqrt{3}$ and $a_y = a$. Such two factors determine the phase factor ka . The translational wave vector k could vary at k -space:

$$-\frac{\pi}{a} < k < \frac{\pi}{a}, \quad (8.15)$$

$$-\pi < ka < \pi. \quad (8.16)$$

After solving the Schrödinger Eq. (8.16), the dispersion of π bands energy on the phase factor ka is expressed by Eq. (8.17):

$$E_{n,m}^{\pm} = \alpha \pm \beta S_2, \quad (8.17)$$

where S_2 represents the so-called phase factor for CNT(n,n):

$$S_2 = \sqrt{1 + 4 \cos \frac{ka}{2} \cos \frac{\pi m}{2} + 4 \cos^2 \frac{ka}{2}}. \quad (8.18)$$

Integer number m represents behaviour of rotational symmetry:

$$m = 1, \dots, n. \quad (8.19)$$

As in the previous case, energy normalization routine takes place:

$$\gamma = \frac{E_{n,m}^{\pm}}{\beta} = \pm S_2. \quad (8.20)$$

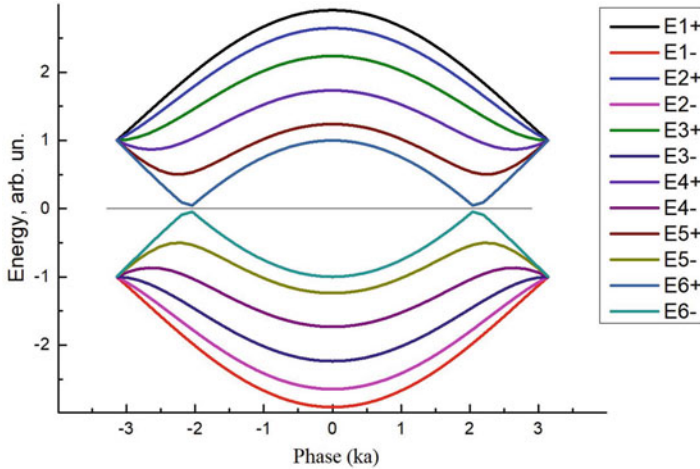


Fig. 8.22 Π -zones of metallic CNT (6,6). Fermi level is set at zero

Figure 8.22 represents Π -zones of CNT (6,6). The dispersion of π bands energy γ on the phase factor ka was calculated according to Eq. (8.13). All curves representing valence and conducting bands start from two points $\gamma = 1$ and $\gamma = -1$, respectively, when $ka = \pi$. Such two values could be obtained by the absence of the second and third factor in Eq. (8.11) due to $\cos(\pi/2) = 0$.

A gap between zones is absent – state curves of the valence zone and conducting zone intersect at the cross value phase:

$$(ka)_c = \frac{2\pi}{3}. \quad (8.21)$$

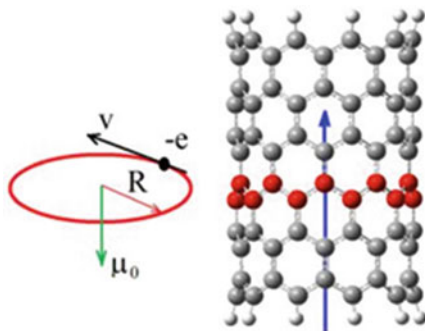
Due to the absence of the gap, CNT (6,6) expresses the metallic properties. Another CNT such as CNT (7,7), CNT (10,10), etc. will be also of the metallic type.

8.5 Nanotubes: Electronic Angular Momentum and Spin-Dependent Properties

A model of the hydrogen atom (a heavy proton in the centre and an electron in the orbital motion) is a classic example for explaining the orbital magnetic moment μ_{ORB} (see Fig. 8.23). A negative charged particle e performs a motion with a velocity v with a radius R , which acts as a current loop:

$$\mu_{\text{ORB}} = \frac{evR}{2}. \quad (8.22)$$

Fig. 8.23 Classical orbital magnetic moment for electron and CNT in magnetic field directed along the long axis (blue arrow)



Let us assume a CNT in the magnetic field, directed along the long axis (blue arrow). For a metallic CNT (diameter D), the transition of the conducting electron along the long axis as well as around the circumference of the CNT is allowed. The orbital magnetic moment μ_{ORB} could be created when electrons are moving around the tube (according to the mechanistic model similar to a hydrogen atom).

The potential energy E is proportional to the external magnetic field B , which is directed along the long axis:

$$\Delta E = -\mu_{\text{ORB}}B = \pm \frac{evDB}{4}. \quad (8.23)$$

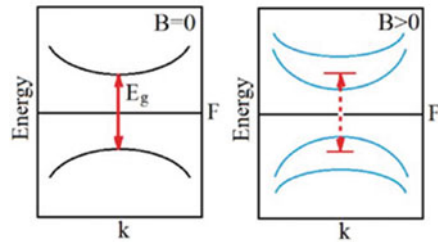
The influence of the magnetic field into the structure of the Π -zone is evident. Figure 8.24 represents a simplified chart of one CNT π -zone in the absence and presence of the magnetic field oriented along the long axis. Two serious phenomena occur. Firstly, the degenerated zone splits into two zones in the valence as well as conductance regions. Secondly, a significant decrease of the gap occurs in the presence of the oriented magnetic field. Minot et al. [21] announced the occurrence of μ_{ORB} for states near the energy gap. Minot found that the orbital magnetic moment (due to the motion around the circumference of CNT) is much larger than the Bohr magneton.

The orbital magnetic moment plays the main role in the magnetic susceptibility of CNTs [22]. It means that the electronic properties of CNTs can be modulated by a magnetic field. Oscillations of the energy band structure could realize the reversible switch of CNT properties between a metal and a semiconductor.

Several spin-dependent properties which are most promising in spintronics are presented as follows: chirality-dependent spin polarization, gate-dependent spin-orbit coupling and spin filtering.

Wang et al. [23] analysed chirality-dependent spin polarization through the spin density of a chiral CNT (9, m), which decreases gradually with the increase of m. Wang established that the spin of the ground state for the armchair CNT (9, m) mainly comes from the contributions of the frontier molecular orbitals and the energy gap decreases gradually with the spin density for chiral CNTs.

Fig. 8.24 Simplified chart of CNT π -zone in absence and presence of magnetic field along the long axis. Split of degenerated zone into two zones and following decreasing of gap



Analysing the interactions of orbital motions of electrons with the spin in the nanoscale systems, Jespersen et al. [24] reported systematic dependence of the spin–orbit coupling on the electron occupation of the CNT quantum dot. Jespersen confirmed that the spin–orbit coupling is a general property of CNT quantum dots.

Wang et al. [25] analysed transport of graphene nanoribbons through a longitudinal unzipped carbon nanotube in the longitudinal direction. Wang established the variation of the Fermi energy from (a) an insulator to a spin-down half metal and (b) an insulator to a spin-up half metal. He guessed that a spin-filter device can be realized using graphene nanoribbons.

8.6 Nanotubes of the Metal Type and of the Semiconductor Type

By estimating the electronic structure for different types of CNTs, it is necessary to analyse the inhomogeneous energy distribution on the one-dimensional density of states (DOS). Three-dimensional crystals have continuous DOS; otherwise, one-dimensional crystals are of another type. A characteristic evidence of the distribution is a gradual descend of energy followed by a fast increase (a sharp spike form). For one-dimensional crystals, sharp peaks in the energy distribution are called the van Hove singularities.

Figure 8.25 represents energy diagram of semiconducting and metallic SWCNT. The valence zone (green) and conducting zone (dark yellow) are separated by a gap (semiconducting CNT) or are joined at a contact level – the Fermi level (metallic CNT).

Transition from the valence zone to the conduction zone (absorption) for both semiconducting and metallic SWCNTs is dipole-allowed with the high oscillator strength: $V_1 \rightarrow C_1$, $V_2 \rightarrow C_2$, etc. The crossover transitions $C_2 \rightarrow V_1$, $C_1 \rightarrow V_2$ are dipole-forbidden with the low oscillator strength. Using the cross-polarized optical geometry, Miyauchi et al. [26] reported the presence of significant anisotropy from polarized photoluminescence measurements of the mentioned dipole-forbidden transitions.

The type of CNTs (metallic or semiconducting) could be recognized from the absorption spectrum in VIS and near-IR region.

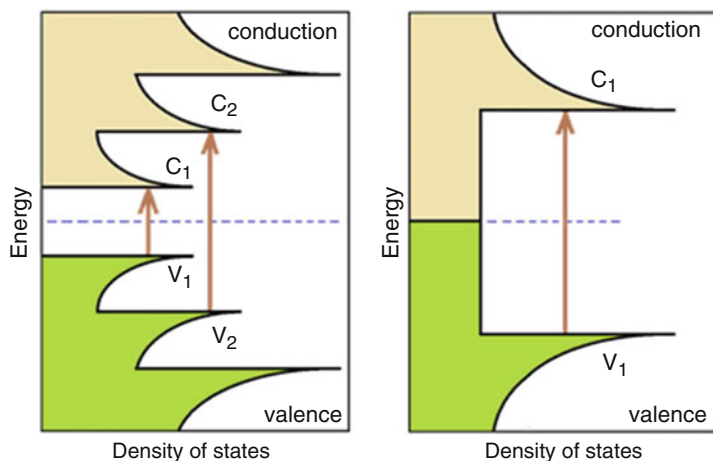


Fig. 8.25 Energy diagram of semiconducting (left) and metallic SW-CNT

A selective excitation of CNTs with indices (n, m) could be realized by exact absorption in the selected band restricted by the van Hove singularities. By varying the structure of CNTs, it is possible to tune optoelectronic properties of CNTs selected on demand. Iakoubovskii et al. [27] demonstrated that even weak UV light 1 mW cm^{-2} can irreversibly alter the SWCNT structure. These UV-induced changes are attributed to the creation of mid-gap PL centres.

Figures 8.26 and 8.27 represent the maps of electronic charge redistribution related to the transition $S_0 \rightarrow S_1$ for CNT (14,14) and CNT (24,24) of armchair type, respectively.

Both maps are devoted to the HOMO $\rightarrow$ LUMO transition. Electronic clouds distributed over the whole surface of the derivative are absent in both cases. The distribution of molecular orbitals is localized on the atom groups. For CNT (14,14), the HOMO state corresponds to a cloud localized on two atoms on the edge, and two neighbouring clouds create a pair of V-type. The LUMO state corresponds to clouds localized on two atoms and parallel aligned around the circumference. For CNT(24,24), the HOMO state corresponds to the cloud localized on two atoms parallel aligned around the circumference. For the LUMO state, localization decreases up to one atom.

As Wildoer et al. [28] and Odom et al. [29] stated, the electronic properties of CNTs depend sensitively on the tube diameter. Increasing the diameter of CNTs, the curvature of the tube becomes flatter, and the reorientation of the junctions changes the dihedral angles.

Molecules consisting of only one element (carbon) may have very different electronic behaviours – a shift from a metallic to a semiconducting state.

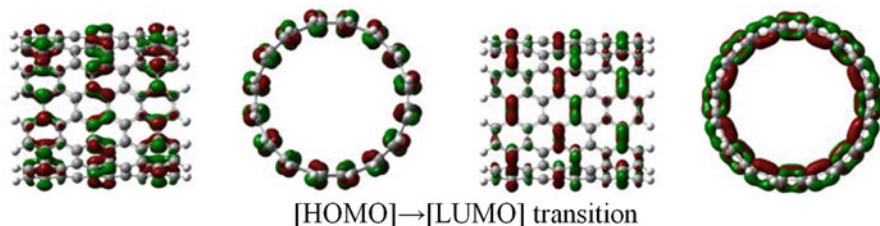


Fig. 8.26 CNT (14,14) of armchair type. Maps of electronic charge redistribution related to the transition $S_0 \rightarrow S_1$

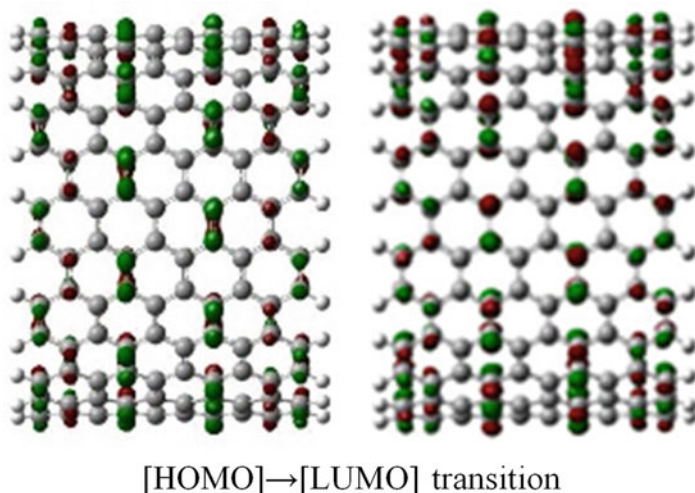


Fig. 8.27 CNT (24,24) of armchair type. Maps of electronic charge redistribution related to the transition $S_0 \rightarrow S_1$

8.7 Chemistry of Nanotubes: Catalysis and Toxicity

A CNT is a well-known active catalyst material due to several unique properties.

Firstly, CNT is a consistent material with an extra high thermal and mechanical stability. Without participating in any permanent chemical changes, CNT only increases the rate of chemical reaction and the subsequent yield of the product. Secondly, the choice of CNTs due to helicity and diameter (from 1 nm to 10s of nm) allows to control the surface impact. Due to that, CNTs sometimes are called a catalyst on demand. The use of large tubular surfaces allows the organization of efficient heterogeneous catalysts [14].

Thirdly, the geometrically fixed tubular surface of CNTs avoids high purity in the molecular environment with low dipole activity. This factor guarantees a high resistance to oxidation, called chemical inertness [19].

Fourth, the catalytic reaction can be carried out by controlling the electrical and thermal conductivity of CNTs. Depending on their helicity and diameter, metallic or semiconducting CNTs can obtain different parameters related to the charge transfer processes [11].

Fifthly, because of the high thermal conductivity of CNTs, preventing the agglomeration of the product and the subsequent separation of product phases can be organized as an additional stage in the reaction. The inhomogeneity of the annealing can be guaranteed with a very low gradient.

Luo et al. [30] observed the application of CNTs in fuel cells. The use of CNTs for such purposes can decrease the need for noble metals which are used as catalysts and improve the performance of fuel cells. In addition, the interaction between catalysts and carriers of CNTs and the conditions for the synthesis of a catalyst based on CNTs were discussed and evaluated.

Girishkumar et al. [31] reported the use of CNT-based electrodes that demonstrate an order of magnitude less reactivity of the charge transfer reaction for the hydrogen evolution reaction compared to commercial carbon black-based electrodes.

According to the constitution of CNTs, the electronic activity is very low. The electronic excitation of single CNTs is related to the charge redistribution localized in the framework of several atoms (or in the framework of primitive cell) (see Figs. 8.26 and 8.27). Otherwise, the environment effects can significantly change the behaviour of the charge redistribution and the following electronic activity.

As active material with well-expressed π - and n -electronic systems, indandione-related compounds were selected [32]. Figure 8.28 represents M66 merocyanine compound containing spiropyran and indan-1,3-dicyan-dione fragments, which are connected via the [$\text{..C} = \text{C..}$] bridge. The derivative of merocyanine expresses one of the biggest molecular nonlinear optical (NLO) coefficient β which is proportional to the oscillator energy and depends on the transition dipole moment. In addition, for the M66 merocyanine compound, high value of β could be limited by the molecular structure when the π -electronic system could be supplemented by the impact of the n -electron from fragments (cyano and carbonyl fragments). Due to the connection via [$\text{..C} = \text{C..}$] bridge, a big lability of the molecule delimits several forms of conformers.

Figure 8.29 represents a M66 merocyanine compound in the near surrounding of CNT (14,14). Due to well-expressed donor–acceptor properties for the pair [M66..CNT], the intermolecular charge redistribution takes place. It is interesting that intermolecular distances are too big in order to establish the valence function. For an excited state, the charge redistribution in CNTs could be titled as hemi tubular (divided into two parts). It is the influence of the M66 molecule, which could play a role of donor on n -electrons.

The toxicity of CNTs is related to the environment interactions. The presence of any material and subsequent deposition on the CNT surface dramatically changes the electronic properties of the molecule both in the ground and in the lowest excited states. In this case, it is necessary to emphasize a new field of use: CNT-mediated cytotoxicity (toxicity in the cell structure). Madani et al. [33]

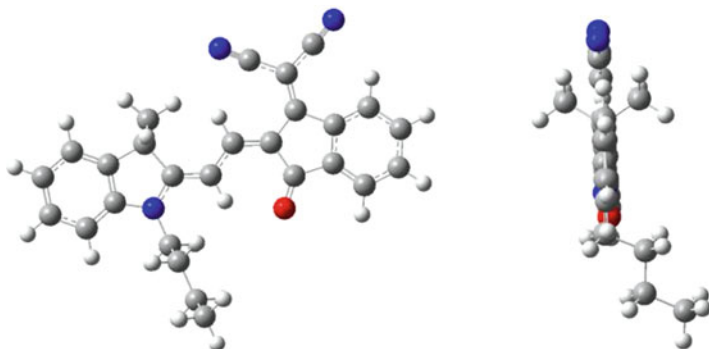


Fig. 8.28 M66: merocyanine compound containing spiropyran and indan-1,3-dicyan-dione fragments

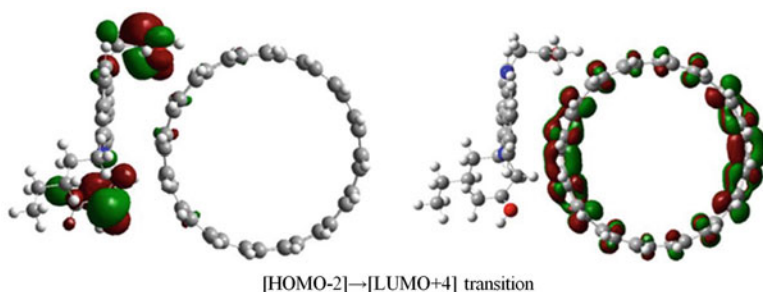


Fig. 8.29 M66 merocyanine compound in near surrounding of CNT (14,14). Maps of electronic charge redistribution related to the transition $S_0 \rightarrow S_6$

observed the potential use of CNTs as agents for cancer treatment and drug delivery. The ability of CNTs to absorb NIR light and generate heat can be considered as possible ways of intrusion into the cellular space. Madani et al. [33] described four factors, which are significant for CNT cytotoxicity: (1) the presence of impurities, (2) the shape, (3) functionalization and (4) the size.

The impurities of transition metals, such as iron, cobalt and nickel after deposition on the surface of CNTs, disrupt the electronic system to create additional activated centres. The following deposition on the additional activated surface can be realized using the materials surrounding the cells. Transit through the cell membrane of a large CNT should be considered as a mechanical action. Because of the certain shape (rod or fibrous), CNTs can damage the cell membrane as bilayer of phospholipids [11].

The functionalization of CNTs can be increased or decreased by changing the environmental parameters by adding/extracting certain acids, polymer chains, cations/anions, etc. With increasing diameter, the mobility of CNT through cell membrane decreases.

Table 8.5 Typical fundamental properties of graphene [36–48]

Property	Value
Young’s modulus	1.0 TPa
Fracture strength	130 GPa
Tensile strength	100 GPa
Thermal conductivity	5000 w/mK
Shear modulus	280 GPa
Longitudinal sound velocity	20 km/s
Melting temperature	4900 K
Specific surface area	2630 m ² /g
Optical transmittance	97.70%
High electron mobility	250,000 cm ² /vs

8.8 The Influence of Defects on Electrical, Mechanical and Thermal Properties of Graphene

Defect types in graphene were considered in a number of papers. See, for example, Rajasekaran et al. [34] and Krasheninnikov et al. [35]. Table 8.5 demonstrates typical values of fundamental graphene characteristics, which usually are the subject of scientific and technological interest. However, in 2009 Taghioskoui [49] and Geim [50] paid attention to graphene nanofillers as some new trend of graphene technology development. This new research resulted in opening the defective states of graphene. Most of the research on nanofillers is usually concentrated on the pristine graphene. It was shown that the structural defects which are inevitable during the production process affect the mechanical properties as well as thermal and electrical conductivities of graphene and graphene-based nanocomposites [51, 52] (Table 8.6).

Stone-Thrower-Wales (STW) Defects. Robertson and Warner [55] analysed one of the unique properties of the graphene lattice. It is its ability to reconstruct by forming non-hexagonal rings. The STW defect is the 90° rotation of two carbon atoms connected by short-ranged covalent bond with respect to the midpoint of the bond. Transformation of four adjacent hexagonal unit cells into two pentagonal and two heptagonal unit cells, due to two pentagon and two heptagon transformation STW defects, is also known as 5-7-7-5 defects [55].

Vacancy Defects. Vacancies in graphene were considered in a set of papers (see, e.g., [65, 71, 74]). The absence of atoms from the lattice of graphene is usually termed as vacancy defects, which can be further subclassified as mono-vacancy, di-vacancy and multi-vacancy defects based on a number of atoms absent from the lattice of graphene. The absence of single carbon atom from the graphene lattice yields a mono-vacancy, which left the graphene lattice with three under coordinated edge carbon atoms; each of them possesses a single dangling bond. There are some typical graphene defects which arise from vacancies in a pristine graphene structure after relaxation of dangling bonds: stable 5-8-5 structure, 555-777 structure and 5555-6-7777 structure [34].

Table 8.6 Graphene defects research in the field of nanofillers

Graphene defect engineering	Research direction
Controlled distributions of topological defects [53, 54]	Mechanical properties, thermal and electrical conductivities of graphene
Atomic resolution imaging of graphene [55, 56]	Mechanical and fracture properties of graphene
Graphene sheets [57, 58]	Mechanical properties of graphene
Defect engineering of graphene for effective hydrogen storage [59]	Stone–Thrower–Wales (STW) and vacancy defects for improved hydrogen storage
Defect control engineering [60]	Defect control engineering-based tailoring of graphene’s electronic, chemical, mechanical and magnetic properties
Graphene doping [61]	Dopant and STW defects to improve gas-sensing properties of graphene
Intrinsic defects of bilayer graphene [62]	Mechanical properties and strength of pristine graphene in the frame of molecular dynamics (MD), finite element and experimental work

Dislocations and Grain Boundaries. Some particular investigations of Bitzek and Gumbsch ([63]) have shown a special class of defects such as dislocations and grain boundaries. It is known that the fracture toughness critically depends on the microstructures of the materials and, in particular, on how the dislocations are generated or multiplied at the tip of the crack [63]. This fundamental defect is of great interest to materials scientists. It is the form of defects where the excess half of the plane of the atoms can destroy the strength of graphene [64]. Due to the two-dimensional (2D) nature of graphene, only edge dislocations have been studied. Talking about the so-called grain boundaries, we define them as line defects (composed of dislocation), separating graphene grains (domains/crystallites) with different crystal lattice orientations. Namely, each grain boundary in a 2D graphene separates two grains whose crystal lattices are rotated/tilted relative to each other by a tilt misorientation angle θ , with the rotation axis being perpendicular to the sheet plane [65].

Following the general concept of atomic and electronic structure correlations, any local and distributed defects in graphene will generate new electronic states and change the conductivity and optical properties.

8.9 Defected Nanocarbon Systems

Carbon-based nanomaterials such as CNTs, graphene, mesoporous nanocarbon, carbon quantum dots and other nanocarbon formations due to their large *surface-to-volume ratio* possess good electrical and thermal conductivity and mechanical strength. These unique properties make them suitable for application in different

Table 8.7 Mesoporous carbon nanostructure applications

Carbon application	Technological comments
A glassy carbon electrode modified with mesoporous carbon [75]	Direct electrocatalytic and simultaneous determination of four DNA bases
Modified mesoporous carbon composite [76]	NADH sensor based on gold nanoparticle
Electrode modified with CeO ₂ -embedded ordered mesoporous carbon [77]	Strong electrocatalytic effect towards the oxidation of hydrazine
Mesoporous carbon with controllable defect density [66]	Electrochemical activity of synthesized materials, cyclic voltammetry and electrochemical impedance spectroscopy

fields, including energy storage [68]; chemical, biochemical and electrochemical sensing [69]; water purification [67]; catalysis [70]; and many more.

Structural defects have a crucial influence on the properties of carbon nanostructures and inevitably generate during production processes or intentionally induced by chemical treatments and ion irradiation [52]. The availability of defects in nanocarbon structures significantly affects the mechanical strength, electrical and thermal conductivity and optical properties [52, 71].

Various experimental techniques which are responsible for defect creation in nanocarbon structures (porous nanocarbons, nanofoams, defect graphene, heavy ion-based nanotrack structures, nanocarbon interfaces with dangling bonds, etc.) give many variants for design of nanosensors and nanotransducers.

Electrochemical Sensing. The essential impact of structural defect on the electrochemical activity has been proved by the study of heterogeneous electrochemical reactions, e.g. oxygen [72] and nitrate [74] and ferrocenemethanol [73] at the surface of nanocarbon-based electrodes. Some particular applications of electrochemical nanosensing application details are presented in Table 8.7.

Synthesis and Gas Sorption, Storage and Separation. Achievements and challenges in the syntheses of graphene-based materials with hierarchical pore structures, tuneable high surface area, chemical doping and surface functionalization for gas (NH₃, NO₂, H₂S, SO₂, H₂, CH₄, CO₂, N₂, etc.) sorption, storage and separation are based on graphene structure defect forms and states. This is a reason of intensive researches of various graphene modifications [78].

Hydrogen Storage: Expanded and Pillared Graphene Layers. The planar sheet of graphene with its inherent specific surface area of 2630 m²/g in the ideal case has further motivated theoretical calculations for gas adsorption from the well-established carbon nanotubes and graphitic structures. The adsorption of a monolayer of H₂ on a single side of graphene sheet can lead to about 3 wt% of H₂ [79].

Hydrogen Storage: Pillared Graphene Oxide Structures. The loosely stacked layers in GO similar to graphite, but with a much wider interlayer spacing (0.6–0.9) nm, would be more convenient to store H₂ [80].

Doped, Functionalised and Metal-Dispersed Graphenes. Simple graphene-based nanostructures show weak binding energy thus low H₂ adsorption capacity at ambient conditions [81].

Graphene-Based Materials. Grafane is nothing but graphene with alternately covalent bond hydrogen atoms on each carbon atom on both sides of the graphene sheet. Structurally graphene is crumpled, rather than planar, because each hydrogen atom bonded to carbon pulls it a small distance out of the plane [82].

Hydrogen Spillover. The H₂ adsorption by hydrogen spillover is a hydrogen dissociative atomic adsorption, and it has been found to be another alternative to enhance H₂ adsorption in the carbonaceous materials. The spillover is expected in some of the graphene-based materials with functionalized/doped structures [83].

CH₄ and CO₂: Sorption, Storage and Separation. Similar to H₂ adsorption, graphenes with ripples, defects, pores, functional groups, metal dispersion or doping and pillaring also show favourable CH₄ and CO₂ adsorptions [84].

Gas Separation Membranes Pristine and porous 2D graphene membranes with and without functionalization have been investigated for gas purification. The pristine graphene is impermeable to He and H₂ [85, 86].

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