Carbon nanostructures

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Allotropy – a property of a chemical element showing potentiality to exist in two or more distinct forms differing in the crystal structure and having thus significantly distinct physical properties (carbon).

In materials science, **polymorphism** is the ability of a solid material to exist in more than one form or crystal structure (iron(III) oxide). Polymorphism can potentially be found in any crystalline material including polymers, minerals, and metals. Polymorphs have different stabilities and may spontaneously convert from a metastable form (unstable form) to the stable form at a particular temperature.
Allotropes of carbon:
(a) graphite
(b) Diamond
(c) Lonsdaleite
(d) single-walled carbon nanotube
(e) multi-walled carbon nanotube
(f) fullerene – $C_{60}$
(g) fullerene $C_{76}$
(h) carbon nanohorns
(i) onion-like carbon
(j) Graphene
(k) carbon nanoribbons
With respect to their dimensionalities, carbon nanomaterials can be divided into four groups: (i) zero-dimensional (0D) such as fullerene, carbon quantum dots, and nanodiamonds, (ii) one-dimensional (1D) such as carbon nanotubes and carbon nanohorns, and (iii) two-dimensional (2D) such as graphene, carbon (graphene) nanoribbons, and few-layered graphenes. (Graphite and diamond are classified as 3D carbon allotropes.) Other classification criteria involve types of covalent bonds ($sp^2$ and $sp^3$) between carbon atoms in a respective carbon nanoallotrope or morphological features of carbon nanoallotropes (e.g., empty internal space vs. “flat” or curved structures). Besides these carbon nanomaterials, which have been extensively covered in the literature, other nanosized members of the carbon family have been reported, such as carbon nanofoam and aggregated diamond nanorods. In terms of orbital hybridization, carbon is found to display $sp^3$, $sp^2$, and $sp^1$ configurations, allowing a great variety of crystalline and disordered structures. According to the recent theoretical studies, other possible forms of carbon have been predicted, including body-centered tetragonal carbon (btc-carbon), T-carbon, M-carbon, nanorope, and prismane $C_8$. 
Carbon Atom Hybridization State Parameters

<table>
<thead>
<tr>
<th>Hybridization State</th>
<th># Of Hybrid Orbitals</th>
<th># Of 2p Orbitals Left Over</th>
<th># Of Groups Bonded To Carbon</th>
<th># Of ( \sigma ) Bonds</th>
<th># Of ( \pi ) Bonds</th>
<th>Geometry Around Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>( sp^3 )</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>4</td>
<td>0</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>( sp^2 )</td>
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<td>1</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>Trigonal Planar</td>
</tr>
<tr>
<td>( sp )</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>Linear</td>
</tr>
</tbody>
</table>
Diamond and Graphite. Diamond, the hardest known natural mineral, has tetrahedrally-coordinated $sp^3$ carbon atoms that form an extended three-dimensional network adopting features of the face-centered cubic Bravais lattice. In contrast, graphite has three-coordinated $sp^2$ carbon atoms arranged in a honeycomb lattice with layered planar structure, where the sheets of the carbon atoms are held together by weak van der Waals forces. The different layout of carbon atoms in the lattice of diamond and graphite endows them with completely different physical properties (e.g., graphite is opaque and metallic-to earthy-looking whereas diamond is transparent and brilliant).
Fullerenes. In 1985, a new carbon allotrope, known as fullerene, was discovered by Kroto et al.\textsuperscript{1} while studying the nature of carbon in interstellar space. 

In fullerenes, the closed-cage structure is established by the presence of five-membered rings; the arrangement of carbon atoms is not planar but rather slightly pyramidalized as a result of a “pseudo” \(sp^3\) bonding component present in the essentially \(sp^2\) carbons. Among the known forms of fullerenes, \(C_{60}\) is regarded as the most symmetrical and stable fullerene molecule. It consists of 20 hexagonal and 12 disjoint pentagonal faces where a carbon atom is located at each corner of the individual polygons; the polygons are arranged into a highly symmetric truncated icosahedrons. The van der Waals diameter of \(C_{60}\) is \(~1.1\) nm and its nucleus-to-nucleus diameter is \(~0.71\) nm. The \(C_{60}\) molecule is often said to be not “superaromatic” because of its tendency to avoid formation of double bonds in the pentagonal rings.
As a result, poor electron delocalization is observed and thus the \( C_{60} \) molecule, behaving like an electrophiles with a large electron-acceptor capability (\( i.e. \), able to reversibly accept up to six electrons), reacts readily with electron-rich species. In mathematical terms, the structure of a fullerene is trivalent convex polyhedron with pentagonal and hexagonal faces. It follows from Euler's polyhedron formula, \( V - E + F = 2 \) (where \( V, E, F \) are the numbers of vertices, edges, and faces), that there are exactly 12 pentagons in a fullerene and \( V/2 - 10 \) hexagons. Besides \( C_{60} \), other fullerenes have been reported, \( e.g. \), \( C_{70}, C_{76}, C_{82}, \) and \( C_{84} \). \( C_{60} \) and other larger fullerenes are routinely produced by a low pressure method in which an electric discharge is passed across a gap between two carbon electrodes in a helium atmosphere. Alternatively, they can be formed using laser vaporization of carbon or arc vaporization of graphite in an inert atmosphere.
Fullerenes and their derivatives have generated significant interest due to their remarkable optical characteristics, heat resistance, superconductivity, and ferromagnetic behavior with Curie temperatures (up to \( \sim 33 \) K) much higher than those reported for any organic magnets. Most of the fullerene derivatives are described as soft organic ferromagnets when the low-temperature long-range magnetic ordering is, among other factors, governed mainly by orientational ordering of \( \text{C}_6\text{O}^- \) ions, short \( \text{C}_6\text{O}-\text{C}_6\text{O} \) distances along the fullerene \( c \) structural axis, and presence of ions of a charge-transfer compound. Fullerenes are frequently functionalized with a variety of organic and inorganic compounds to extent their range of potential applications. Functionalized fullerenes have found promising applications in the field of medicine (antioxidants and neuroprotective agents, enzyme inhibition, antimicrobial activity), electronics (organic solar cells, liquid crystals, photocurrent generation devices, etc.), and catalysis (sensors).
C-dots are quasi-spherical carbon nanoparticles with diameters of 2 to 10 nm that have high oxygen contents and consist of combinations of graphitic and turbostratic carbon in various volumetric ratios. C-dots contain mostly $sp^3$ hybridized carbon and are usually of amorphous nature. The most characteristic and significant property of C-dots is relatively strong photoluminescence, which depends on their size, the excitation wavelength, and the surface functionalization.

Graphene quantum dots (GQDs) are defined as the products obtained by cutting a graphene monolayer into small pieces (disks) with dimensions of a few nanometers (2-20 nm). GQDs are composed mainly of $sp^2$ hybridized carbon and they are crystalline. They owe their evolution to the observation that quantum confinement and edge effects in graphene nanosheets with sizes of less than 100 nm become more pronounced as the sheets get smaller, particularly once their dimensions fall below 10 nm. GQDs have non-zero band gaps due to quantum confinement and edge effects.
Photoluminescence properties of carbon quantum dots: (a) differently sized carbon quantum dots illuminated under white (left) and UV light (right; 365 nm); photoluminescence spectra of differently sized carbon quantum dots (red, black, green, and blue lines represent photoluminescence spectra of blue-, green-, yellow-, and red-emission carbon quantum dots, respectively); (c) dependence of photoluminescence properties of carbon quantum dots on their size; (d) relationship between HOMO-LUMO gap and the size of graphene fragments.

Besides many fascinating optical features such as photoluminescence tuned by dot size and surface functional groups, non-linear optical response, photoinduced electron transfer, and electrochemiluminescence, carbon quantum dots offer several advantages over heavy metal-containing semiconductor-based quantum dots, including chemical inertness, biocompatibility, and low toxicity.
Nanodiamonds are \( sp^3 \) carbon nanoparticles that consist of crystal domains with a diamondoid-like topology and diameters that are greater than 1–2 nm but less than 20 nm. They are not dispersible and are usually prepared by top-down methods such as jet milling or abrasion of microdiamonds. Nanostructures of this sort that have diameters above 20 nm behave like bulk diamonds. Conversely, \( sp^3 \) carbon nanostructures with diameters of less than 1 nm are usually called diamondoids and occur naturally in petroleum deposits. It has been suggested that nanodiamonds are stable if their surfaces are stabilized by termination with functional groups (various oxygen-containing groups in most cases) or induced to adopt \( sp^2 \) hybridization. Nanodiamonds are therefore sometimes said to have a core-shell architecture based on a diamond core (\( sp^3 \) carbon atoms), a middle layer (\( sp^{2+x} \) carbon atoms) and a graphitic outer shell (\( sp^2 \) carbon atoms) with dangling bonds terminated by functional groups. Nitrogen is the most common such impurity in both natural and synthetic nanodiamonds. Vacant sites adjacent to incorporated nitrogen atoms are termed nitrogen-vacancy color centers.
Like diamond, nanodiamond is a wideband semiconductor with the largest optical band gap (5.4–5.6 eV at room temperature) of all known materials. Nanodiamonds can exhibit strong absorption in the visible region and their band gap widths can differ substantially from those of bulk diamond. Both of these observations support the hypothesis that their surfaces contain some proportion of $sp^2$ hybridized carbon atoms. Nanodiamonds exhibit bright luminescence due to their content of non-carbon atoms (typically, nitrogen) with adjacent vacant sites. These centers are formed in two steps: a vacancy is generated by irradiation and then migrates through the crystal structure during annealing until it is trapped by a foreign atom. Nitrogen-vacancy centers can be either neutral or negatively charged; the two types generate different emission spectra.

As the least toxic carbon nanoallotropes, nanodiamonds have been studied extensively as fluorescence agents and biomarkers in various medical contexts.
In 1991, Iijima discovered a new structural form of carbon, known as multi-walled carbon nanotubes, in a carbon soot prepared by an arc-discharge method; two years later, he observed single-walled carbon nanotubes. A single-walled carbon nanotube is a graphene sheet that is rolled to form a cylinder with a typical diameter from ~0.4 to ~2 nm. In contrast, a multi-walled carbon nanotube comprises concentric cylinders with an interlayer spacing of 0.34 nm and a typical diameter ranging from ~2 to ~25 nm; the rolled graphene sheets are held together by van der Waals interactions. The length of single-walled and multi-walled carbon nanotubes can reach hundreds of microns or even centimeters. The aspect ratio (i.e., length-to-diameter ratio) frequently exceeds 10000 and thus, carbon nanotubes have been suggested to be the most anisotropic materials ever produced.

Depending on the chirality, the carbon atoms around the nanotube circumference can be arranged in several ways of which arm-chair, zigzag, and chiral patterns are the most common examples.

In carbon nanotubes, the carbon atoms are held together by $sp^2$ bonds, endowing them with a unique strength.

Structure of (12,0) zigzag, (6,6) armchair, and (6,4) chiral single-walled carbon nanotube
Carbon nanotubes are found among the strongest and stiffest materials yet discovered and existing in nature (Young’s modulus of ~1.2 TPa and tensile strength of ~100 GPa, about a hundred times higher than steel).

The electrical characteristics of carbon nanotubes are strongly governed by the diameter and chirality of the nanotubes. Armchair nanotubes (i.e., $n = m$) are expected to exhibit metallic behavior; they have a finite density of states at the Fermi level. However, they may become semiconducting if their diameter drops below a threshold value because the energy gaps in the semiconducting carbon nanotubes scale with $1/d$ ($d$ being the nanotube diameter). Chiral nanotubes, for which $m \neq n$ and $(m - n)$ is a multiple of three are semiconducting. The band structure of such nanotubes features a very small band gap with a zero density of states inside the gap due to the modest degree of $sp^2$-to-$sp^3$ hybridization induced by the non-flat nature of the hexagons on the nanotube walls.
Due to their remarkable electrical, transport, and optical properties together with their high surface areas, several other potential applications were quickly identified. In particular, they have been investigated as functional components of energy and gas storing devices, building blocks of nanoelectronic, spintronic, and nanophotonic devices (e.g., transistors and logic gates, memory, photoactuators, and sensory devices), and medical tools (e.g., drug-delivery carriers for cancer treatment, gene delivery systems, and in photo-thermal therapy). In addition to these practical applications, carbon nanotubes are often used as model systems for the study of various quantum phenomena that occur in quasi-1D solids, including single-electron charging, ballistic transport, weak localization, and quantum interference.
Graphene (sometimes referred to as “the thinnest material in our universe”), a flat 2D planar monolayer of $sp^2$-bonded carbon atoms arranged in a two-dimensional hexagonal honeycomb lattice and first isolated in 2004, constitutes other carbon allotrope that can be viewed as the building unit of 3D graphite (stacking of graphene sheets), 1D carbon nanotubes (rolling of a graphene sheet) or 0D fullerenes (wrapping of a graphene sheet). In graphene, two equivalent carbon sublattices can be identified. There are three extremely strong $\sigma$ bonds connecting each carbon to its three nearest neighbors, giving rise to the mechanical stability of the sheet; each carbon atom has a $\pi$ orbital contributing to a delocalized network of electrons, which is responsible for its electron conductivity.
In order to maintain stability, the graphene layer contains “intrinsic” ripples with an amplitude of ~1 nm. The ripples can be induced externally to tune the local electrical and optical features of graphene to meet the requirements of a given application. Proper graphene behaves as a semimetal or zero-gap semiconductor. Besides this, graphene shows unique physical properties, including large values for intrinsic mobility (~200000 cm²v⁻¹s⁻¹), Young’s modulus (~1 TPa), theoretical surface area (~2630 m²g⁻¹), thermal conductivity (~5000 Wm⁻¹K⁻¹), and optical transmittance (~97.7%).

The band structure of graphene consists of two bands that intersect at two inequivalent points, K and K”, in the reciprocal lattice (K and K” are known as Dirac points, where the valence and conduction bands are degenerate). In other words, the conduction and valence bands touch each other at the six corner points of the first Brillouin zone. The band gap of graphene can be tuned from 0 to 0.25 eV by applying a voltage across its structure.
The charge carriers in graphene behave as massless relativistic particles with the properties of Dirac fermions. Therefore, electron transport in graphene is described by adopting Dirac’s relativistic equation.

In addition, graphene exhibits an ambipolar effect, a feature whereby its charge carriers can switch from electrons to holes under the influence of an applied electric field.
Graphene oxide

Fluorographene (C₁F₁)
Graphene nanoribbons are frequently described as a one-dimensional $sp^2$ hybridized carbon strip of finite dimension with defined edges at which carbon atoms are of non-three coordinated nature. Three types of graphene nanoribbons are currently recognized depending on the edge termination: (i) armchair, (ii) zigzag, (iii) and chiral nanoribbons. In particular, the width of the armchair graphene nanoribbon is expressed as a number of dimer C-C lines ($N_a$) across the nanoribbon while in the case of the graphene nanoribbon with zigzag edges, the width is given by the number of the zigzag chains ($N_z$) across the nanoribbon.

Owing to the finite size (i.e., width) of graphene nanoribbons, peculiar quantum phenomena are expected to evolve upon the confinement effect. Theory shows that the electronic properties of graphene nanoribbons significantly depend on their width and topology of their edges. Armchair graphene nanoribbons can be classified into three categories with respect to the band gap width, i.e., $N_a = 3p, 3p+1, 3p+2$, where $p$ is the integer (all having direct band gap at the Γ point); as the width increases, the band gap decreases reaching zero value as characteristic of 2D graphene. Armchair graphene nanoribbons are purely semiconducting.
The edges in zigzag graphene nanoribbons significantly alter the resulting band structure; the edge states introduce a flat band around the Fermi level which is extended along the nanoribbon edge. The edge states are spin-polarized due to their high degeneracy. Similarly as for armchair nanoribbons, the band gap for zigzag nanoribbons decreases with increasing their width.

(a) Variation of the band gap ($\Delta_a$) for armchair graphene nanoribbons as a function of the width ($w_a$). (b) The band structure of the zigzag graphene nanoribbons with $N_z = 12$. Up and down spin state are degenerated in all bands. $\Delta_z^0$ and $\Delta_z^1$ represent direct band gap and energy splitting at $kd_z = \pi$, respectively ($k$ is the wave number, $E_F$ is the Fermi level, and $d_z$ is the width of zigzag graphene nanoribbons with $N_z = 12$).
Magnetism in zig-zag graphene nanoribbons

(a) Graphene lattice with magnetic interactions:
- FM: Ferromagnetic
- AFM: Antiferromagnetic
- $+J_1$: Intra-zigzag interaction
- $-J_1$: Inter-zigzag interaction
- $J_0$: Intra-zigzag interaction

(b) Atomic structures at different widths:
- 5 nm
- 10 nm

Energy spectra ($E - \mu$) vs. $ka$ for different widths:
- $\pi / 2$ to $\pi$
Interconversions among carbon nanoallotropes
Carbon nanoallotrope superarchitectures

Graphene dot honeycomb
Nanotube/fullerene nanoreactors
Graphene/nanotube
Graphene/nanotube pillared structure
Nanobud