

Materials Horizons: From Nature to Nanomaterials

N. Manjubaashini
T. Daniel Thangadurai
D. Nataraj
Sabu Thomas

Graphene Quantum Dots

The Emerging Luminescent Nanolights

 Springer

Materials Horizons: From Nature to Nanomaterials

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D. Nataraj · Sabu Thomas

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Preface

Outline

This cutting-edge transdisciplinary textbook comprises nineteen chapters, which cover the history and development of carbon nanostructures, synthesis and characterization techniques, and unique physicochemical properties of GQDs. It focuses on various applications such as agriculture, healthcare, environmental, anti-microbial and antibacterial, and other miscellaneous and multi-functional applications of GQDs. Furthermore, the density functional theory (DFT) is employed to calculate the tunable energy gap and dipole moment to explain the fluorescence phenomenon of GQDs. It also discusses the mathematical modeling and simulation in GQD and their nanocomposites concerning the biomedical and environmental domains. Since almost every analytical approach is covered in this book, it is an invaluable resource to graduates and postgraduates, engineers, research scholars, material scientists, engineers, and technologists from industry, who work in related fields (material science, chemistry, physics, nanoscience and nanotechnology, and biomedical and environmental) are expected to read and utilize it. Furthermore, this book helps readers solve basic and practical difficulties in graphene-based materials and devices for modern innovations.

The authors sincerely thank the contributions of leading graphene researchers from industry, academia, government, and private research institutes all over the world.

Usefulness of the Book to the Readers

A great opportunity lies in the future development of novel GQD-based nanomaterial products which are now being employed in a variety of fields, including electronics, biomedicine, environmental remediation, and agriculture. As the title indicates, the objective of this book is to provide a fairly comprehensive overview of the recent

achievements in the field of QDs. Materials with enticing properties at very low amounts of chemicals are required by modern technologies. We can expect beneficial qualities at extremely low amounts of QD-based nanomaterials due to the high aspect ratio. Furthermore, many experts have consented to share their extensive experience and knowledge in the field of QD-based nanomaterials and applications. This book is divided into different sections based on the findings of professionals in specific disciplines. This technical book's nature may make it a valuable reference or textbook for a wide range of scientists, industrial practitioners, graduate and undergraduate students, and other professionals working in the fields of nanoscience and engineering, materials science, surface science, bioengineering, and chemical engineering. We proposed a single volume with nineteen chapters to provide a clear understanding of QD's fundamentals and fascinating attributes to the readers.

Important Features of the Book

It is a handbook that explores the many unique characteristics of QDs, as well as their potential and advanced applications. This molecular-scale material is versatile, with outstanding electronic, mechanical, electrical, cytotoxicity, biocompatibility, and thermal properties with applications in a variety of disciplines. Interestingly, chemists, physicists, and engineers are all interested in developing QD functional materials. Though many excellent books have already been written on various aspects of QDs, however, to our knowledge, there is no single book that consolidates information across all aspects of QDs, engineering, and biomedical applications in a very detailed manner, spanning the entire gamut of up-to-date literature citations, current market, and patents. Therefore, we narrated all the considerable progress made in the experimental and theoretical research of several properties of QDs and their composites in recent years. In summary, this book aims to provide an in-depth investigation of the present state of the art in QDs, composites, hybrid structures, and other related topics.

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Chapter 1

History and Development of Carbon Materials



1.1 Overview

From primeval times, people have been aware of carbon, and one of the first forms of carbon that they used was charcoal. Charcoal was first used by ancient societies for drawing, but they also later learned that it could be used in metallurgy to remove metals from ores. C₆₀ is the name given to the molecule composed of 60 carbon atoms arranged in a sphere, or buckyball, by Richard Smalley, Robert Curl, and Harold Kroto. This finding created new opportunities for materials made of carbon with special qualities [1]. Graphite started to be used more frequently in the sixteenth century. Graphite, originally believed to be a type of lead, was used in writing instruments (pencils) because of its lubricating qualities. Since ancient times, people have valued diamonds as another type of carbon for their durability and brilliance. Over time, the understanding of the structure of diamonds and how they relate to carbon changed. An important turning point was reached in 1985 with the discovery of fullerenes [2].

Graphene is a revolutionary material with applications in electronics, energy storage, and other fields due to its exceptional mechanical strength, thermal properties, and electrical conductivity. During the second half of the twentieth century, carbon fiber composites became more and more popular in the aerospace industry. These materials are used in high-performance sports equipment, spacecraft, and aircraft because of their excellent strength-to-weight ratios, which come from carbon fibers embedded in a matrix [3]. The use of activated carbon in purification procedures is not new. It is useful for various industrial applications, air purification, and water treatment due to its large surface area and adsorption capacity. Energy storage technologies have advanced due to the widespread use of carbon materials, such as graphite and different types of carbon nanomaterials, in batteries and supercapacitors. Applications for carbon materials in medicine include drug delivery and imaging systems, as well as carbon nanoparticles [4].

In the late twentieth century, carbon allotropes became a popular research topic and eventually took center stage in nanoscience across nearly all domains. The carbon era and nanotechnology/nanoscience have benefited from the enrichment of carbon allotropes from well-known diamond and graphite to carbon nanomaterials in recent decades [5]. Carbon nanomaterials' light weight, excellent thermal and electrical conductivity, high strength, and high stability led to the development of nanoscience in the fields of electronics, optoelectronics, medicine, mechanical engineering, catalysts, and energy. The challenges posed by silicon-based electronic devices were overcome by the use of carbon nanomaterials in electronics to comply with Moore's Law [6]. Carbon nanomaterials are perfect for conducting skeletons for electrochemical materials because of their high conductivity and stability. Carbon nanotubes (CNTs) are cylindrical structures with extraordinary electrical, thermal, and mechanical properties that were discovered in 1991 by Sumio Iijima. Since then, CNTs have been used in a variety of industries, such as electronics, materials science, and nanotechnology [7]. A single layer of carbon atoms arranged in a hexagonal lattice, known as graphene, was isolated in 2004 by Andre Geim and Konstantin Novoselov.

1.2 Introduction

With an atomic number of six, carbon is found in Group IV of the periodic table. The three allotropic forms of carbon are graphite, diamond, and fullerene, in that order. Carbon-based materials have many uses because they can be chemically combined with other carbon-based materials and form strong covalent bonds with a wide range of elements [8]. As a result, they have extraordinary properties like high strength, high density, and high hardness. Because of their exceptional qualities, carbon materials are a great option for many applications involving advanced technology [9].

It is challenging to gain or lose electrons to form fully occupied or unoccupied orbitals in chemical reactions due to its peculiar electronic structure. Modifying carbon hybrids with different sp^3 , sp^2 , and sp^1 hybridizations or adding additional foreign atoms can change the desired characteristics [10]. The diverse orbital configurations of C hybridization, such as sp^1 , sp^2 , and sp^3 , may offer an ideal environment for the discovery and development of novel C materials. For instance, the sp^3 configuration, in which each C atom is tetrahedrally surrounded by four neighboring C atoms with a 109.5° directed bond, confers a strong σ bond to an adjacent atom [11, 12]. Regarding the three-fold coordinated sp^2 configuration, three of the four valence electrons form σ bonds in plane-style sp^2 orbitals that are directed trigonally [13]. The sp^2 atom's fourth electron is located in a $p\pi$ orbital, which is perpendicular to the σ bonding plane. With a π orbital on one or more neighboring atoms, this π orbital forms a weaker π bond [14].

1.3 Evolution of Carbon

Almost all organic materials are made of carbon networks; carbon is one of the elements that is most abundant on earth. We use carbon daily in many products, such as newspapers, pencils, refrigerators, and activated carbon. Among the non-metal elements that are most prevalent on Earth, carbon is essential to our day-to-day existence [15]. With 0D (fullerenes), 1D (carbon nanotubes), 2D (graphene), and 3D (graphite/diamond) structures, carbon is a very diverse family of materials [16] (Figs. 1.1 and 1.2). Carbon is derived from biomass, heavy oils and residues, thermosetting and thermoplastic polymers, coal tar, and polymer [17]. The historical evolution of carbon materials is listed below.

- Charcoal may have been the first carbon material to be used in a practical sense.
- Carbon was discovered in burned ashes dating back to the prehistoric era.
- During the Neolithic era, carbon was also used to adorn ceramic paintings.
- Graphite, the first carbon allotrope, was discovered and used for mold marking and casting in the sixteenth century [16].
- Diamond was originally found in India approximately 3,000 years ago. When the diamond was burned by Nobel laureate Antoine Lavoisier in 1772, it was discovered to be composed of carbon.
- The discovery of fullerenes was made in 1985 by Kroto et al., who were awarded the 1996 Nobel Prize in Chemistry [18].
- The scientific era of graphene is the twenty-first century.
- 2011 saw the synthesis of aluminum, steel, and iron from carbon.
- Carbon electrodes are used for silicon production.
- Lithium-ion batteries are made of graphite, carbon fibers, and carbon nanotubes.
- The highly oriented pyrolytic graphite (HOPG) was synthesized in 2004 by Geim and Novoselov, and graphene has garnered significant attention.

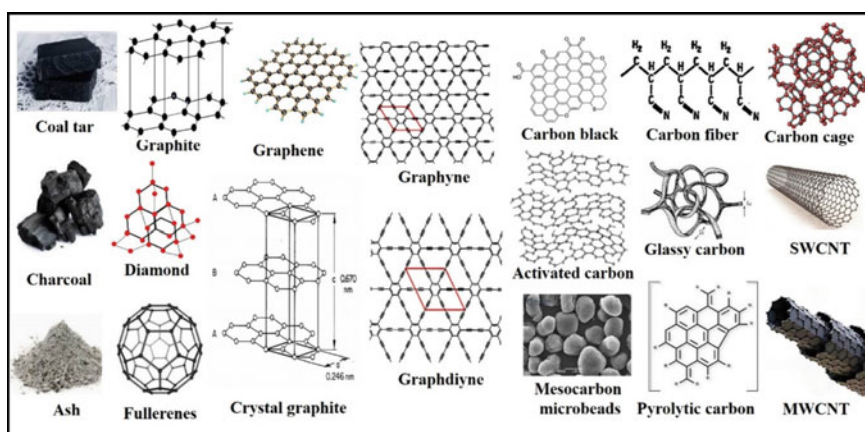


Fig. 1.1 Various structures of carbon allotropes

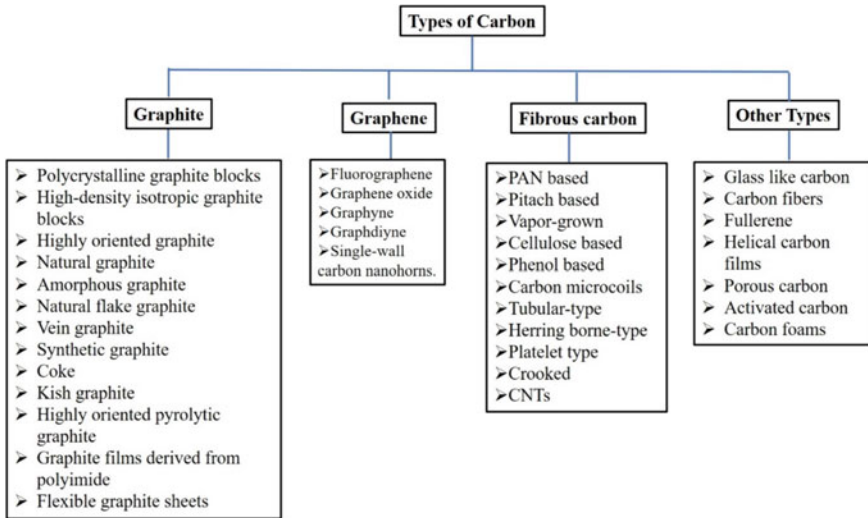


Fig. 1.2 Different forms of carbon

- In the 1970s and 1980s, carbon nanotubes were also produced through chemical vapor deposition (CVD) with structural characterization.
- At approximately 1800, the introduction of carbon materials as battery electrodes was performed [19].
- Large-sized carbon rods, known as graphite electrodes due to their crystalline graphite structure, were produced industrially by heat treatment at temperatures as high as 3000 °C and have been used as electrodes for iron refining since 1878.
- Before 1960, the basic science and technology of classic carbons, artificial graphite blocks, carbon blacks, and activated carbons were developed.
- In 1964, the formation of optically anisotropic spheres in pitches, mesophase spheres, and their coalescence sparked several fundamental studies on the structure of the spheres, their growth and coalescence mechanism, and the formation of bulk mesophase. These studies also produced new carbon products, such as needle-like cokes, which were crucial raw materials for high-power graphite electrodes, high-performing carbon fibers based on mesophase pitches, and mesocarbon microbeads for various applications.
- The invention of carbon fibers from poly(acrylonitrile), pyrolytic carbons by CVD process, and glass-like carbons from thermosetting resins, all of which were entirely different from the carbon materials used before 1960, can be considered the beginning of the era of new carbons.
- Before 1960, four distinct carbon materials were identified as having practical uses in a range of industries. These materials included natural diamonds, carbon blacks for ink and rubber reinforcement, artificial graphite blocks for steel refining, and activated carbons for water purification.

- Three carbon materials were developed in 1960: glass-like carbons, pyrolytic carbons, and carbon fibers. These materials differed greatly from classic carbons in terms of both their properties and methods of production.
- The discovery of carbon materials' good biocompatibility circa 1970 paved the way for the creation of several prostheses, including tooth roots and heart valves.
- It was discovered that adding a small amount of carbon fibers to cement paste produced noticeable reinforcement in concrete around 1985.
- Another era for carbon materials began in 1985 with the discovery of buckminsterfullerene C₆₀, a carbon cage with 60 carbon atoms. This was followed by the discovery of other carbon cages, including C₇₀, C₈₆, and so on.
- The first report of a cage (cluster) made of 60 carbon atoms, or C₆₀ (buckminsterfullerene), was made in 1985. The soot was produced by laser irradiation on a graphite block, and the structure of the block was made up of 20 hexagons with 12 pentagons of carbon atoms.
- Carbon nanotubes were first reported in 1991, and, subsequently, single-wall carbon nanotubes were discovered.
- Following the discovery of single-wall carbon nanotubes in 1991, reports of multi-walled carbon nanotubes were made.
- In 2004, there was a report of a single hexagonal carbon layer. The discovery of these new carbons, or nanocarbons, spurred interest in nanoscale science and technology and advanced the field's scientific advancement.
- The preparation of a single, 2D sheet of carbon atoms, called graphene, was first reported in 2004.
- The discovery stage of carbon dots occurred between 2004 and 2006; the initial developing stage occurred between 2007 and 2011; the explosively developing stage occurred between 2011 and 2021; and the well-developed stage of carbon dots lasted until the present day [20].

1.4 Structure of Carbon Materials

A hexagonal carbon layer is the basic building block of the structure of carbon-based materials in the graphite family. Graphite crystal, hexagonal graphite with ABAB stacking regularity, and rhombohedral graphite with ABCABC stacking regularity are all produced by regular stacking of these layers [21]. Because it is simple to compare rhombohedral and hexagonal graphite, rhombohedral graphite is frequently expressed in a hexagonal system. As a result, two unit cells in each system are connected with equivalent points, thick lines denote rhombohedral unit cells, while double lines denote hexagonal unit cells (Fig. 1.3). The hexagonal structure of graphite shows P6₃/mmc space group with their interplanar spacing has 0 0 0, 2/3 1/3 0, 0 0 1/2 and 1/3 2/3 1/2 planes with the lattice parameters as $a_0 = 0.2462$ and $c_0 = 0.6708$ nm. Likewise, the rhombohedral graphite structure shows an R3m space group, with the lattice parameters of $a_0 = 0.3635$ nm, $\alpha = 39.49^\circ$ [22].

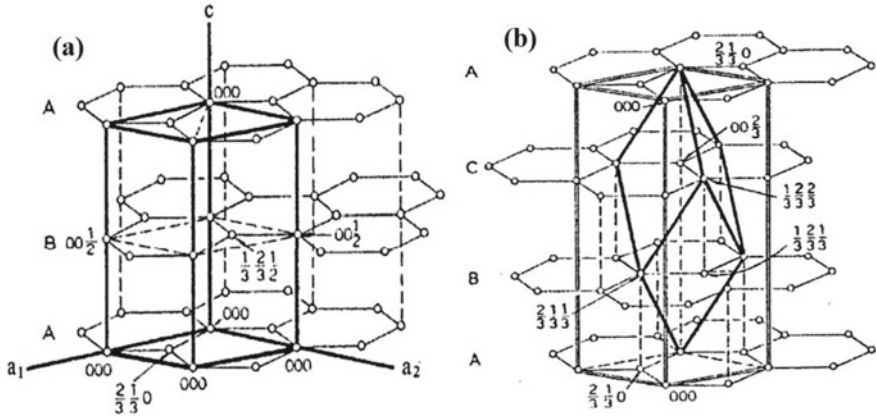


Fig. 1.3 Structures of graphite derivatives: **a** hexagonal structure and **b** rhombohedral structure. Reprinted with permission from © Handbook of Advanced Ceramics (2013)

1.4.1 Structures of One-Dimension (1D) Carbon

Based on sp^2 hybridization, carbon nanotubes are 1D allotropes of carbon with a cylindrical nanostructure. There are three common types of carbon nanotubes: single-wall (SWCNT), double-wall (DWCNT), and multi-wall (MWCNT) [23]. Two or more concentric SWCNTs make up the DWCNTs and MWCNTs. SWCNT, DWCNT, and MWCNT typically have diameters of 0.6–2.5, 1–3, and 2–100 nm, respectively. There are two types of carbon nanotubes: armchair and zigzag [24].

1.4.2 Structures of Two-Dimension (2D) Carbon

It was discovered that the fundamental component of many carbon-based materials, such as graphite, carbon nanotubes, and fullerene, is graphene, a common 2D carbon material. Graphene, with a lattice constant of approximately 2.46 Å and a space group of $P63/mmc$, is a hexagonal planar structure created by sp^2 hybridization [25]. The inner graphene also contained lattice defects with five or seven rings, which caused the graphene sheets to curl. A zero bandgap and tapered symmetry of the conducting and valent bands at six Dirac points (K point) point to a semimetal character [26]. Since the effective rest mass is zero around the Dirac points and the energy of electrons is linear with the wave vector, graphene's Fermi velocity is getting closer to that of light. Pure graphene's average electron-free path is submicrometric, comparable to trajectory transport, indicating a great deal of promise for fast devices [27].

1.4.3 Structure of Three-Dimension (3D) Carbon

Among the most prevalent 3D carbon allotropes are diamond and graphite. They have been studied for a very long time [28]. New 3D carbon structures have emerged recently, such as T-carbon, glassy carbon, cubic carbon, and amorphous diamond. By inserting a carbon tetrahedron into the locations of the diamond atoms, a cubic crystalline carbon with the space group of $Fd\bar{3}m$, or T-carbon, is produced [29]. Large specific surface area, a substantial pore structure, and a comparatively high adsorption capacity characterize active carbon (AC) [30]. AC contains oxygen, hydrogen, and other elements in addition to carbon. The cost of AC is less than that of expanded graphite, graphene aerogel tubes, and other 3D carbon materials. AC is frequently used in the separation of mixtures and purification of liquids [31].

1.4.4 Crystal Structure of Graphite

There are two crystalline forms of carbon: graphite and diamond. It was demonstrated that each carbon atom in a diamond is covalently bonded to four other carbon atoms arranged tetrahedrally in an early application of X-ray diffraction. The bond between carbon atoms is 1.54 Å. Because it would take the breaking of numerous strong bonds to rupture this isotropy structure, a diamond's extreme hardness is a direct result of its configuration. Because diamond turns into graphite so quickly at atmospheric pressure and temperatures above 1500 °C, it is useless. Naturally, diamond has a wide range of significant applications in mild to low temperatures [32].

A large variety of low-cost precursors can be used to prepare a wide range of materials at relatively low cost; porous carbons have indeed garnered a lot of attention. Because of their diverse porous structure, resistance to basic and acidic environments, low cost, easy accessibility, good recycling characteristics, low density, and most importantly the ability to introduce different functionalities through a wide range of activation, functionalization, and carbonization methods, porous high-surface-area carbons are typically good catalyst supports [33]. Materials made of porous carbon are categorized as microporous (with pore sizes less than 2 nm), mesoporous (with pore sizes from 2 to 50 nm), and macroporous (with pore sizes greater than 50 nm) based on their pore diameters [34].

1.5 Fullerenes

As the pentagons are introduced into the layer, as in the case of corannulene, the bonding nature of fullerenes differs slightly from that of graphite based on the sp^2 hybridization of carbon atoms [35]. From the smallest closed shell of C_{60} to giant fullerenes, the repetition of these curved layers can produce a variety of closed shells

with different sizes. By maintaining closed-shell morphology, the addition of extra hexagons among pentagons in C_{60} results in giant fullerenes [36]. Because all other carbon materials are not dissolved into any organic solvent, the majority of fullerenes behave like molecules and can be dissolved into an organic solvent, giving rise to a distinctive color. Thanks to developments in surface science, clusters have been studied, starting with chains of carbon atoms and moving on to rings of carbon atoms up to 15 atoms in size [37].

1.6 Diamond

Diamond is the metastable cubic form of carbon crystal. Three-dimensional extensions of purely covalent chemical bonds make up the sp^3 -hybridized carbons that make up diamonds. Because a diamond contains no p electrons, it is extremely hard and electrically insulating. A long-range periodic and regular repetition of the CeC bond is necessary to form a diamond crystal [38]. The purest form of crystalline carbon is diamond. Tetrahedral bonds hold a number of its carbons together. The carbon atoms that make up each tetrahedral unit are bonded to four other carbon atoms, which are subsequently joined to other carbons. As a result, the carbon atoms are arranged in three dimensions in an allotrope of carbon [39].

The glitter and shine of diamonds are a result of intense heat and pressure that occurs far below the surface of the Earth. The crystal structure of a diamond is known as an FCC lattice or face-centered cubic. Every carbon atom is connected to four other carbon atoms in a typical tetrahedron, or triangle prism [40]. Because of their cubic shape and extremely symmetrical atom arrangement, diamond crystals can take on a wide range of shapes that are known as crystal nature. The most common crystal form is the diamond form or eight-sided octahedron. Additionally, cubes, dodecahedra, and combinations of these shapes can be seen in diamond crystals [41]. Instead of having perfectly smooth faces, real diamond crystals have raised or indented triangular growths called “trigons” on them. Diamonds will split precisely along these lines rather than breaking in a jagged way because they have flawless cleavage in four directions. The diamond crystal has fewer chemical bonds in the plane of its octahedral face than in other orientations, which is why the cleavage lines are visible [42].

1.7 Structure of Activated Carbon

A raw form of graphite with a highly porous structure and different-sized pores is called activated carbon. Its surface area is significantly increased by the numerous molecular cracks and crevices that it possesses. The internal surface area of activated carbon can reach up to $1500 \text{ m}^2/\text{g}$. This makes it possible for activated carbon to perform the process of adsorption, which is the process by which molecules of a gas

or liquid are held in place by the interior or exterior surface of a solid [43]. Activated carbon's structure is essentially similar to that of pure graphite. Carbon-carbon bonds bind the hexagonal layers of the activated carbon molecules together.

- Activated charcoal has found application in medicine and adsorption—in 1773.
- Using the adsorption of gases on the surface of charcoal, it was possible to recognize the adsorptive power of charcoal—in 1773.
- Applying charcoal to different aqueous solutions for decolorization. This is the first time charcoal has been used in a liquid phase—in 1785.
- One can use charcoal made from animal tissue to remove color from an aqueous solution—in 1793.
- Sugar companies employed charcoal derived from wood to remove the color from sugar syrup—in 1794.
- Proven application of charcoal for decolorization of sugarbeet liquor—in 1805.
- First activated carbon was made by heating blood with potash and combining physical and chemical activation. Compared to bone char, it is 50 times more effective—in 1822.
- Made char by heating a mixture of flour, tar, and magnesium carbonate—in 1856.
- Made carbon ready to filter portable water—in 1862.
- Made activated carbon out of coconut shells and researched gas adsorption—in 1865.
- Activated carbon was prepared using phosphate heating and waste from paper mills—in 1868.
- Two processes were used to develop commercial activated carbon: (i) using metal chlorides before carbonization, and (ii) selectively oxidizing charcoal at a high temperature using carbon dioxide—in 1900.
- Using the Ostrejko method, activated carbon was first manufactured industrially and sold under the brand name—in 1911.
- A study found that heating Epoint with zinc chloride increased its decolorizing capacity—in 1913.
- Investigating the sorption phenomenon on activated carbon through the application of the capillary condensation method—in 1931 [44].

1.8 Applications of Carbon-Based Materials

Carbon-based materials have drawn interest due to their important contribution to the field of materials science (Fig. 1.4). These materials include carbon nanotubes (CNTs) with one or more walls, carbon nanofibres (CNF), fullerenes, carbon dots, and graphene and its derivatives (graphene oxide, reduced graphene oxide, and functionalized graphene nanosheets), in addition to the more recent generation of carbon materials such as graphene and its derivatives. High surface area, low cost, chemical stability, ultrahigh optical, thermal, and mechanical properties, remarkable electrical conductivity, and highly developed and tunable porosity are just a few of their many impressive qualities [45]. Water purification, catalysis, oxygen reduction reactions,

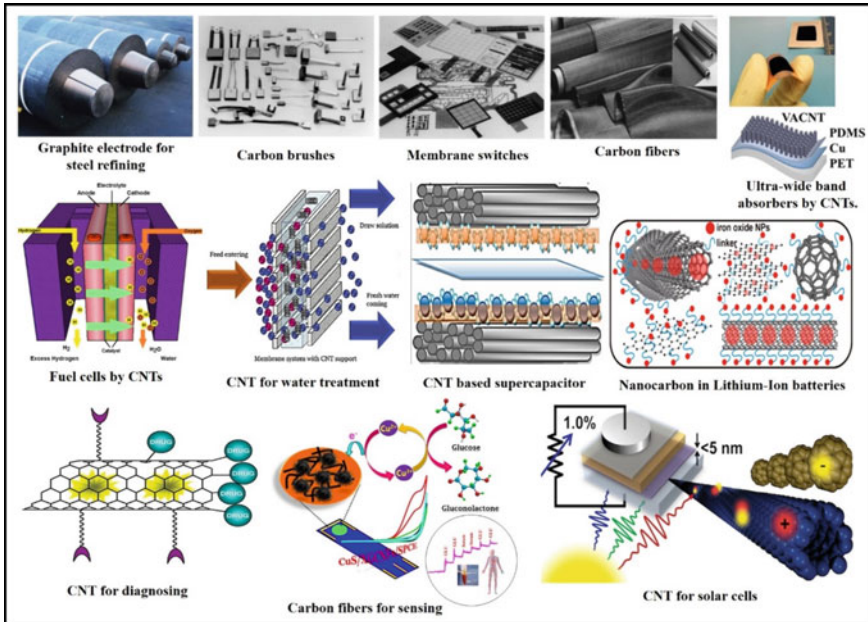


Fig. 1.4 Discrete applications of carbon-based materials

clean energy conversion and storage, polymer reinforcement, solar steam generation, biomedical engineering, advanced information encryption, and CO₂ capture are just a few of the processes that have found them appealing due to these qualities [46].

- Metal processing—artificial graphite blocks
- Electrical and electronic devices—polycrystalline graphite blocks
- Nuclear applications—Polycrystalline graphite [47]
- Molecular sieving carbons [48]
- Mesoporous carbons for car canisters [49]
- Porous carbons for electric double-layer capacitors and hybrid capacitors
- Carbon materials for energy storage—Rechargeable batteries [50]
- Electrochemical capacitors and pseudocapacitance [51]
- Storage of hydrogen and methane gas [52]
- Carbon materials for environment remediation [53]
- Carbon materials for sorption of viscous fluids [54]
- Sorption of biomedical fluids [55].

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Chapter 2

Roadmap: From Carbon to Graphene Quantum Dots



2.1 Achievements of Carbon-Based Materials

Two Nobel Prizes for fullerenes and graphene and two Kavli Prizes in Nanoscience to M Dresselhaus and S Iijima for work on carbon nanotubes have resulted from recent research on carbon materials [1]. The majority of materials that have piqued the interest of carbon science researchers thus far are constructed using the benzene ring, a hexagon that is sp^2 bonded, as the main building block [2]. Graphene is produced by combining an infinite number of benzene rings in a two-dimensional (2D) fashion [3].

2.2 Graphite

There are only three forms of carbon that occur naturally: diamond, amorphous carbon, and graphite. The structure and atom bonding within each of the three naturally occurring allotropes distinguish them from one another: graphite has a honeycomb lattice structure, amorphous carbon lacks a crystalline structure, and diamond has a diamond lattice crystalline structure. Although carbon can take on many different forms, graphite is the most stable form under normal circumstances and is of the highest grade [4]. As a result, it is frequently used in thermochemistry as the reference state to define the heat formation of carbon-based compounds. It occurs naturally in three different forms: lump or vein, amorphous, and crystalline flake graphite. Depending on the form, it can be used for a variety of purposes. As was mentioned earlier, the structure of graphite is planar and layered, with carbon atoms arranged in a hexagonal lattice to form each layer [5]. The carbon atoms in these bonds, or covalent bonds as they are more formally called, are only 0.142 nm apart, and they are incredibly strong. Strong sp^2 hybridized bonds hold the carbon atoms together in a single, 2D layer of atoms. In graphite, there is a 0.335 nm gap