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Chapter

Introductory Chapter: Brief Scientific Description to Carbon Allotropes - Technological Perspective

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1. Introduction to carbon

In the second part of the eighteenth century, carbon was identified as an element for the first time. "A.L. Lavoisier" introduced the name carbon in 1789 and derived from the Latin word "carbo" which signified "charcoal (or ember)" to the Romans. After hydrogen, oxygen, and helium, Carbon is 4th frequent element in our solar system(sun, stars, comets, and planets' atmospheres), the 6th abundant prevalent element in universe and in earth's crust, it is 17th most extensive elemen. [1]. It is primarily found as hydrocarbons and other chemicals [2, 3]. Surprisingly after oxygen, carbon is found as 2nd abundant mineral in the human natural body [4], accounting for around 18% of a person's total weight. Although, carbon is in short supply on earth's surface, with hardly 0.2% makes of planet's whole mass [1, 3, 5]. In spite of that, its function is extremely vital because it has the ability to establish links with other atomic nuclei and with itself. As a result, carbon's ability of catenation cleared the path for the advancement of chemistry (basis of organic chemistry) [6], the rich diversity of structural forms of solid carbon [7], and biology, allowing for the emergence of life's marvels [4, 8]. Advanced carbon based material are considered backbone in coming generation technological scientific era especially in the divisions of materials based industry, and nanotechnology, respectively. During recent times, advanced carbon based materials are of significant highlight. Owing of efficient physical properties, from technological perspective, it has been employed in the environmnet, energy, electronic and thermal applications, respectively. Due to wide field of applications, twenty-first century is named as "Century of graphene". Graphene is considered as outstanding form of carbon owing to good electrical conductivity, suitable strength and efficient permeabile properties. In following chapter, we will review basics forms, properties and significant Structures of allotropes of carbon which will be beneficial from technological perspective.

2. Basic structure of carbon

Carbon is foremost exciting element in periodic table to chemists because of its electrical structure and atomic size [6].

2.1 Electronic and nuclei configuration of the carbon atom

Carbon's symbol is C, and its atomic number (Z) is 6, indicating that the neutral carbon atom (C-12 isotope) contains six protons and six neutrons in its nucleus and likewise, six electrons in its electronic shells. $1s^2 2s^2 2p^2$ is the electron configuration or the electronic arrangement in each orbital [2].

2.2 Atomic mass (atomic weight) of carbon

The basis for establishing the atomic mass unit is the element carbon. By definition, an atomic mass unit is 1/12th of the atomic mass of the (C-12) isotope. The "International Union of Pure and Applied Chemistry approved" this concept in 1961. The atomic mass unit is absolutely, incredibly small in comparison to the traditional definition of a mass: one gram requires 0.6022×10^{24} amu (also known as Avogadro's number or N_A). Natural carbon has 98.89 percent 12C and only 1.11 percent of 13C. Consequently, the average carbon atom's atomic mass is 12.01115 amu.

2.3 Carbon's radius

Carbon's atomic radius is half the gap between two carbon atoms in a planar graphite lattice. When compared to other elements (H, Li, He, B, Be, O, N, F), carbon has one of the shortest radii. Carbon has seven different isotopes out of which three isotopes have been identified (12C, 13C, 14C). The isotope 12C, which possesses six neutrons, is by far the most abundant. There are four to ten neutrons in the others (10C to 16C). C-12 and C-13 are the most stable isotopes of carbon, meaning they do not dissolve or change structure spontaneously. The other five-carbon nuclei are radioactive, which means they decay naturally by emitting particles, which are maybe an electron (β^-) or a positron (β^+) and are formed by neutron splitting [2]. In the study of organic reactions, the radioactive isotope 14C is used as a tracer. The magnetic moment (spin V2) of 13C makes it an appropriate probe for NMR research. For the atomic mass unit, 12C is utilized as the reference definition because of its enormous abundance and an emerging power. It is defined as having the Relative Atomic Mass of 12 precisely. This definition now governs all other nuclei and molecular masses [9].

3. Carbon allotropes

Allotropy is the property of an element that allows it to exist in multiple physical states. Carbon can be divided mainly into two types of allotropes which are as shown in the **Figure 1**:

- Crystalline Carbon Allotropes
- Amorphous Carbon Allotropes



Figure 1. *Flow chart of allotropes of carbon.*

Carbon is not the only element that has the ability to mix its atoms to produce allotropes. Silicon, germanium, and tin, all of which are found in the 4th column of the periodic table, share this property. Carbon, on the other hand, is distinctive in terms of its amount and allotrope's variety that it contains, due to its propensity to have variable oxidation states and coordination numbers [2].

3.1 Crystalline carbon allotropes

Carbon has been thought to have life, in mainly two crystalline allotropic forms for a long period of time: graphite and diamond, which are consist of extensive networks of sp³ and sp² hybridized carbon atoms, respectively. As a result, we can say that diamond as well as graphite are the two most frequent allotropic forms of carbon. Both kinds have unique physical characteristics. In spite of that, the chemical composition of these two compounds differs significantly in terms of crystal shapes and characteristics [10–14]. Many other types of carbon allotropes may be produced chemically because of valence shell of the carbon atoms [15], which are chemically identical (same building block) but have dramatically different physical properties, such as buckminsterfullerene [16], also known as "Bucky-balls" [2, 17] carbon nanotubes [18], graphene [19–20], and so on [8]. The discovery of fullerenes by "Harold W. Kroto" in 1985 signaled the start of an era of artificial carbon allotropes that included, in 1991 the production of (CNTs) and in 2004 again the discovery of graphene [20]. Therefore nowadays, carbon is significantly more than charcoal, because it produces the strongest fibers, most excellent lubricants (graphite), the strongest crystal and hardest substance (diamond), optimal gas absorbers (charcoal-gray), and perfect helium gas barriers [2].

3.2 Amorphous carbon allotropes

Amorphous carbons and carbons with mixed phases exist alongside to crystalline carbon allotropes [17]. Carbon without crystalline structure is referred to as amorphous form of carbon. Like all other glassy materials, some (specific short-range patterns) may be seen but not any (specific long-range pattern) of the atomic positions are observed. The majority of amorphous carbon is made up of tiny lattices of either graphite or diamond like carbon. This Non-crystalline carbon refers to coal, soot, or carbon black colloquially [17].

4. Overview of graphite and diamond

At the mesoscopic scale, a material's properties are dictated not only by its chemical bonding but also by its dimensions and structure. This is especially true in the case of carbon-based substances. Carbon is abundant in nature, with most of it in the form of composite. Most of them are natural chemicals that are needed to make artificial carbon and carbon-based products. Natural graphite and diamond are the only two allotropes of carbon found as minerals on Earth [2]. Despite the fact that both materials are relatively inert at normal temperatures and pressures, they can transition into one another when subjected to certain conditions [19, 21]. In the lowest energy state, carbon possesses four electrons in its valence shell, two in the 2 s sub-shell and two in the 2p sub-shell. The development of three types of sp. composite orbitals (sp, sp², and sp³) depends on the amount of p orbitals (1 to 3) mingling with the s orbital. The bases of graphite and diamond are formed by carbon atoms with (sp² and sp)³ composite orbitals, which may make 3 and 4 bonds with nearby carbon atoms, sequentially [17].

4.1 Graphite overview

Graphite was proposed by "Werner and D.L.G. Harsten", who derived it from the specific Greek ' $\gamma\rho\alpha\phi\epsilon\nu$ ' (Graphein), which means "to write," and it was first used in pencils in 1594. "Abraham Gottlob Werner "was the first to name it in 1789 and is made up of large flat networks of carbon atoms layered on top of one another [17]. This carbon allotrope has a honeycomb layered structure and is made of flat two-dimensional layers of carbon atoms (sp2 hybridized). Each layer is specifically consist of the carbon atoms arranged in planar hexagonal rings with a carbon–carbon bond length of 141.5 pico-meters. A C–C covalent bond connects each C atom in each layer to three other C atoms [22].

5. Graphite is of two forms: α and β .

- In α form, the layers are organized in ABAB... order, with the third layer directly above the first. Each layer, on average, divides two levels that are identically orientated. Within a layer, all carbon–carbon bonds are identical (a finding that is explained in terms of total pi-bonding).
- The ß form, on the other hand in nature, a less prevalent form of graphite is organized in ABCABCA... stacking, in which every 4th layer is identical. Microcrystalline graphite forms the basis for non-crystalline carbon variations.
- Three of the four carbon atoms create sigma bonds, while the fourth form a pibond. Graphite is extremely flexible but non-elastic because of the delocalization

of the π –electrons [22]. It is also a conductor [19] in the basal plane and an insulator normal to the basal plane, with strong thermal and chemical inert characteristics [23].

- On the contrary, van der Waals forces slackly link the layers side by side. The layers are proficient to skate past each other because of inter-layer frailty generated by the attractive force of van der Waals interactions. This is the explanation, for graphite's soft and skiddy physical qualities, which make it excellent lubricant in generator and electric motors [8].
- The mineral (graphite) has a lustrous black color that is shiny and impenetrable (that is, it reflects light evenly without glitter or sparkle) [22].
- Carbon in the form of graphite is the most stable. Although, Graphite is difficult to melt. The strong molecular bonds that hold the carbon atoms together require a lot of energy to break [22]. As a result, in thermochemistry, it is utilized to define the heat of production of carbon composites as the standard state [2, 17].

5.1 Diamond overview

Foremost well-known allotropes of carbon is diamond. Diamond is a Greek word that means "transparent" and "invincible." The layer organization sequence in diamond is ABCABCA... There are four spatial orientations of carbon atoms due to the direction and perception of the tetrahedral axis, resulting in two tetrahedral and two octahedral (eight-faced) forms of diamond [17]. Each carbon atom in diamond is sp3 hybridized, forming covalent connections (bond lengths equal to 1.54 Å) with four additional carbon atoms in the tetrahedral structure's corners. Diamond's strength comes from its steady network of covalent connections and hexagonal rings [2].

• Diamond is unable to conduct any electricity owing to the limited mobility of electrons in the lattice pattern [24], but it exhibits maximum thermal conductivity [25] of roughly 2200 W/(mK), which is way five times higher as of copper [26, 27]. Diamond is commonly utilized, in the semiconductor technology to avert silicon and all other related semiconductors from overheating [13, 28] due to its excellent thermal conductivity [29]. The average electric breakdown of the diamond is fifteen times that of typical semiconductors, while the average holes mobility is five times that of common semiconductors [2].

However, it has a dielectric constant half that of silicon, and when tested, it is likely to exhibit 'negative electron affinity'. According to many studies, it is a 5.5 eV [30] broad bandgap semiconductor when doped to (n or p types).

• A diamond is a massive carbon atom molecule. It has unusual optical qualities. Because it is tied genetically to carbon family [31], it is considered also as biocompatible inside a live organism. Diamonds are transparent and colorless (transmitting light from the far-infrared to the ultraviolet). They are classified as glossy because they shimmer and reflect light. These characteristics make them desirable in jewelry. It is particularly neutron radiation resistant and has an extraordinarily high refractive index. The scientific uses include an optical sensor component, diamond anvil cells, and so on. it has a natural lubricity in the air that is comparable to Teflon [8].

• Diamond is supposed the hardest natural mineral ever known to human and It is insoluble in water. It has a somewhat high melting point. As a result, it's ideal for cutting tools. This makes it a great abrasive with outstanding polish and luster retention. No known naturally occurring chemical has the ability to cut (or even scratch) [17]. Any electronics device built of the diamond should be able to operate in harsh situations [32] due to its physicochemical features (rugged and 'hard'). All of the features listed above are natural outcomes of the crystal structure.

6. Detailed overview of graphene

"Graphene" [20] is just a single thin layer of carbon atoms separated from the overall graphite structure. In the ideal scenario, graphene is an perfect (2D) material because it is an atomically thick and thermodynamically stable monatomic sheet of carbon atoms organized in a honeycomb structure [33]. "Hanns-Peter Boehm" was the first to create the name "graphene" in 1962. The idea of graphite layers had been investigated before to this date [32]. In 1947, Wallace exploring the graphite layers which proves as a beginning point for better understanding the physical properties of the three-dimensional graphite. Several papers were published during the next few decades in an attempt to isolate or grow graphene. In 2004, "Andre Geim and Kostya Novoselov" have been succeeded in isolating a single sheet of 2-D graphene from the raw graphite [19, 20, 34]. Single layers can be separated from graphite and produced using traditional CVD or micromechanical cleavage techniques [17, 19]. Recently, Single graphene layers have been successfully generated utilizing a basic mechanical exfoliation of graphite using Scotch tape [20].

In Graphene, only the layer extensions and characteristics of edges might be different, making it the most fundamentally uniform material [20]. In other words, graphene is a fundamental basis [35] for all fullerene allotropic dimensionalities, and it tends to evolve into different sorts of structures with greater structural stability. It can be rolled into (0-D)fullerenes [36], wrapped into (1-D) carbon nanotubes (CNTS), and layered into (3-D) graphite (with 3.37Ű separation distance) [37] and derivatives between layers [17, 34, 35]. Single-layer graphene (SLG) [38], Graphene Nano-platelets (GNPs) 100 nm to 100 μ m [37], Graphene oxide (GO) (single-layer material with a high oxygen concentration), Reduced graphene oxide (RGO) (monolayer form), and functionalized/chemically modified graphene are all examples of graphene. All of them are graphene-related compounds and can be classified as graphene family materials (GFMs) [39].

6.1 Brief lattice structure of 2-D graphene

Graphene is consist of two interpenetrating Bravais sub-lattices, which allows us to define a primitive unit cell, which is the simplest building block from which the graphene lattice may be constructed. Due to the hexagonal shape, the primordial cell encompassed by the two lattice vectors below includes two atoms as shown in **Figure 2**, one of type A and the other of type B, which represent the two triangular lattices. The size of the graphite primitive unit cell is determined by how individual graphene layers stack together to form the graphite crystal [40]. The lattice positions (\vec{R}) are filled



Figure 2. Single layer graphene lattice with two lattice vectors.

with Type (A) atoms and the type (B) atoms are shifted with respect to the A atoms in each primitive cell by $\tau = (\vec{a}_1 + \vec{a}_2)/3$ [17].

$$\vec{a}_1 = \left(\frac{3}{2}a_o, -\frac{\sqrt{3}}{2}a_o\right), \ \vec{a}_2 = \left(\frac{3}{2}a_o, \frac{\sqrt{3}}{2}a_o\right), \ \vec{R} = m\vec{a}_1 + n\vec{a}_2.$$

Here, $a_{0} = 0.142nm$ is the bond length of carbon. Where *m* and *n* are integers.

6.2 Morphology of graphene

AFM, TEM, and FESEM can be used to study the morphology of graphene. AFM has measured the accurate thickness of single sheet of graphene to be (0.34–1.2 nm), and determining these thicknesses is crucial. Graphene has a higher thickness (2 nm) and the mean thickness of hydrazine-reduced GO, on the other hand, is only 0.8 nm, indicating the creation of single-layer graphene. The 'TEM and high-resolution TEM (HR-TEM)' are highly useful for detecting the number of layers in transparent graphene layers with crumples. The researchers looked into the microstructure variations between graphite and graphene and they found that Graphite layers are darker, thicker, and longer than graphene layers [41].

6.3 Physical properties of graphene

Graphene has attracted a lot of attention as a rising star in material science, solidstate physics, chemistry, and technology research because of its unique features, such as the quantum Hall effect, extraordinarily high (elasticity and tension), and optical transparency [17]. The 2p orbitals are responsible for graphene's amazing properties, as they cause the p bands to travel over the carbon sheets that make up the graphene. Graphene has a spectrum of remarkable features that other metals and semiconductors lack due to its unique lattice structure, shape, and surface morphology [17]. The material graphene is semimetal. Its zero bandgaps [37, 42], linear energy spectrum, excellent carrier mobility, frequency-independent absorption, and long spin diffusion length make it a popular material for electrical, photonic, and spintronic devices. Researchers discovered that graphene is highly rigid and extraordinarily good conductors of electricity and heat in the free-state, but are unstable at finite temperatures in the free-state [40], and is impermeable to gases especially [43]. Graphene is a semimetal with zero bandgap due to its Fermi level, which is located at the exact intersection of "conduction and valence bands" in pure substance and may be changed to make it (either N-Type or P-Type) by chemical modifications or more readily, by an electric field [44]. The inability to analyze the mechanical properties of single layer graphene is hampered by the fact that (SLG) is thermodynamically unstable and that an X-ray diffraction experiment on an (SLG) is not conceivable, owing to graphene's smallest size and outstanding surface-area-to-volume ratio. The tensile and compressive forces applied to the graphene lattice are tiny—around 1%. It's impossible to apply a substantially higher compressive strain without the sample slipping off the substrate (in the case of graphene). This can be accomplished by creating a monolayer graphene sample on a substrate having an aperture and pressing down on the graphene sample [40] with an (AFM) tip over the aperture. Graphene has been shown to endure a tensile strain of up to 20% using this method which will be beneficial from technological perspective.

7. Overview of carbon nanotubes (CNTS)

With its discovery in 1991, CNTS are carbon tubes (nanometer diameters range) also termed as "bucky-tubes", are significant contribution in technological nanosciences. CNTS are distinguished in "multi-walled CNTs (MW-CNT)" and "single-walled CNTS (SW-CNT), respectively. CNTS are synthesized using thermal decomposition, catalytic growth, and arc-ablation, respectively. Structure of graphite (crystalline) need to be well understood to visualize single walled carbon nanotubes. As graphite contains stacked-layers of hexagonally-arranged C-atoms with sp²-configuration. Owing to inter-molecular forces, stcking layer give us single layer which is graphene. Single nanotube consist of C-atoms (millions) but thickness of tube is ~1 atom which may prove benefucial from technological perspective. The structures of SW-CNTS and MW-CNTS are shown in the **Figure 3**.

8. Conclusion

In the second part of the 18th century, carbon was identified as an element for the first time. "A.L. Lavoisier" introduced the name carbon in 1789 and derived from the Latin word "carbo" which signified "charcoal (or ember)" to the Romans. After hydrogen, oxygen, and helium, Carbon is one of abundant element in earth's crust,



Figure 3. (*a*) SW-NT [8] and (*b*) MW-NTs [15].

solar system, and universe. The chapter sums up basics properties of various allotropes of carbon along with its advanced forms. Advanced carbon materials, which includes graphene and carbon nanotubes, are prospective additions in materials based technology due to their outstanding structures and physical properties. Advanced carbon materials will be future of next scientific revolution in electronics, bio medical, energy and electrical engineering from technological perspective.

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