

GREEN FUTURE OF NANOTECHNOLOGY: GRAPHENE

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I. INTRODUCTION

Nanotechnology had been attracted many scientists for its unique physical, chemical and biological characteristics that differ from those at macroscopic level for the same material. The alluring potential of nanotechnology is the modification of behavior of material at the nanometer scale and creation of novel materials exhibiting unique properties. Nanomaterials have abundance of applications in many fields such as medicine, drug delivery, diagnostics, electronics, fuel cells, solar cells, agriculture, water filtration, food safety, smart apparels, space exploration and much more [7] <https://pubs.acs.org/toc/ancac3/9/3?sortBy=DATE>]. Graphene which is considered as the “miracle material,” is composed of pure carbon and the thinnest material produced so far with unique crystal nanostructure and extraordinary physical and chemical properties [<https://nanografi.com/blog/60-uses-of-graphene/>]. The application of graphene is growing across all sectors, and its properties provide new horizon in the technological world. This chapter creates a brief understanding of graphene and family, its unique properties, with a discussion on potential applications in various fields.

How it began?

Long before the term "nanotechnology" was coined, on December 29, 1959, physicist Richard Feynman, the father of nanotechnology gave a lecture titled "There's Plenty of Room at the Bottom" at an American Physical Society meeting held at the California Institute of Technology (CalTech). In his address, Feynman described a procedure that would allow scientists to better understand and regulate individual atoms and molecules [5]. <https://www.nano.gov/nanotech-101/what/definition>]. The ability to see and control individual atoms and molecules has always been the fundamental to nanoscience and nanotechnology. Atoms make up everything, including the food we eat, the clothes we wear, the buildings and houses we live in, and even our own bodies. However, an atom on the other hand, is invisible to the naked eye. The age of nanotechnology was born once scientists had the right tools, such as the scanning tunnelling microscope and the atomic force microscope. <https://www.nano.gov/nanotech-101/what/definition>

What is Nanotechnology?

Nanotechnology surrounds the study, understanding, manipulation and engineering of materials on the atomic or molecular level typically at nanoscale between 1 to 100 nanometres, or billionths of a metre and can be utilized across all the other science fields, such as chemistry, biology, physics, materials science, and engineering <https://education.nationalgeographic.org/resource/nanotechnology>, <https://www.nano.gov/nanotech-101/what/definition>]. This technology offers scientific progress in a variety of fields, including medical, consumer goods, energy, materials, and manufacturing. Due to quantum mechanical processes, materials created at the nanoscale frequently display particular properties that influence physical, chemical, and biological aspects. The core of new technology is studying, creating, and utilizing these aspects. There are various disciplines where nanotechnology has proven applications. Three different kinds of carbon nanoparticles have drawn a lot of attention. The first nanoparticles to be identified in 1985 were buckyballs, also known as fullerenes or soluble carbon. Then, within a few years, single-walled or multiwalled carbon nanotubes, usually referred to as carbon filaments, were discovered in

1991[6]. Although graphene has long been suspected to exist, it wasn't until 2004 when two researchers at the University of Manchester, Geim and Novoselov, were able to produce and identify graphene sheets (GSs) from graphite for study. They received the Noble Prize in 2010 for their ground-breaking work [2, 5]. Since fullerenes and carbon nanotubes have drawn so much interest for their characteristics and uses, graphene is now doing the same. Graphene is a miraculous material [5, <https://nanografi.com/blog/60-uses-of-graphene/>]. Because of its distinctive qualities, it has attracted a great deal of interest from scientists ever since it was discovered. Graphene nanotechnology is evolving quickly, bringing new innovations, and has the potential to alter the course of coming technological era.

What is Graphene?

An almost unlimited number of applications could eventually find a long-term solution in the pure carbon-based substance known as graphene. Graphene is a two-dimensional carbon allotrope consisting of a plane of sp²-bonded carbon atoms arranged in a sheet-like arrangement [1, 2, 4, 5, 6]. Thin flakes with several layers of carbon atoms, such as monolayer graphene, may be crucial from an engineering perspective due to their intriguing structural and physical properties and their potential for usage in a variety of technological areas. Graphene represents a conceptually novel class of two-dimensional materials, which are only one atom thick. In a hexagonal honeycomb lattice structure, the monolayer carbon atoms are perfectly distributed to form a graphene sheet (GS) [2, 4]. Each GS is seen as a single molecule, and modest dispersion forces hold the sheets together closely [2]. Theoretically, a GS would become a fullerene if it were coiled up into the smallest possible sphere rather than rolled into the shortest possible tube, which would produce a single-walled carbon nanotube [6]. Only the three fundamental

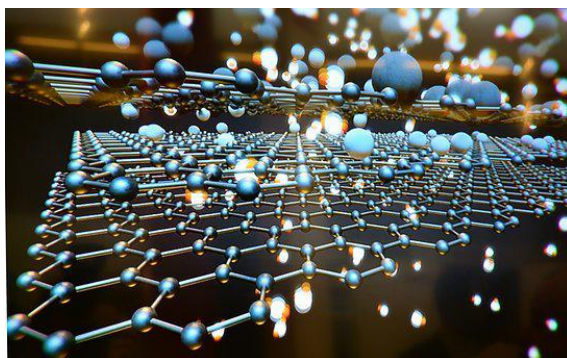


Figure: 1 Graphene

Allotropes of carbon—diamond, graphite, and amorphous carbon—were known in 1980 [1, 2]. The term "graphene" was first introduced in 1986 as a term for an isolated single two-dimensional sheet of carbon atoms. Later, fullerenes and carbon nanotubes were discovered. In 2004, graphene emerged on the scene [2, 5, https://www.nanowerk.com/what_is_graphene.php]

A 2D ultimate polycyclic aromatic hydrocarbon "graphene", which is etymologically derived from the prefix "graph" from graphite and the suffix "ene" for polycyclic aromatic hydrocarbons [5]. Since 2004, graphene has gained significant popularity in the development of numerous sectors, including smart wearables, electronics, sensors, medicine and

biotechnology, semiconductors, versatile coatings, membranes, and energy-related industries [1]. This huge popularity is due to the myriad of extraordinary properties found in graphene. Only in the single-layer or few-layer stage, the remarkable properties of graphene become apparent [1]. The extraordinary characteristics of graphene originate from the 2p orbitals, which form the π state bands that delocalize over the sheet of carbons that constitute graphene. Graphene can be produced in a number of different ways. The two most popular routes for the synthesis of graphene are mechanical exfoliation and chemical vapour deposition [4, 8].

- 1. Graphene Famil:** The graphene family includes members such as graphene sheets, graphene oxide (GO), reduced graphene oxide (rGO) and exfoliated graphene.
- 2. Graphene and Graphene Sheets (GS) :** The most pure form of carbon is known as graphene, which is an atom-thick layer of carbon atoms that are covalently bound together to form a hexagonal structure [1, 2, 5]. Graphene is considered to exist in its purest state as a single GS and when more GSs are stacked together, graphene starts to exhibit different properties [5]
- 3. Graphene Oxide (GO):** Unknowingly, British chemist Benjamin Brodie discovered graphene oxide in 1859 [https://www.nanowerk.com/what_is_graphene.php]. A single-atom carbon layer (monolayer) is created when graphene is chemically oxidised. Both of the layer's surfaces have functional groups that contain oxygen which results in the formation of GO. In multi-layer graphene oxide, the carbon layers are separated by functional groups bonded to each layer of carbon atoms. As the name suggests, GO is a graphene derivative that has undergone oxidation and is produced by using various strong oxidants on graphene molecules [3, 4, 5, 9]. The reliable and well established method for producing GO was reported by Hummers in 1958 [3, 4, 5, 9]. The unique properties of GO are a result of its unique chemical structure, which includes tiny sp^2 carbon domains surrounded by sp^3 domains and hydrophilic functional groups containing oxygen [9].

Although GO and graphene are both 2D materials, they have quite distinct properties from one another. It exhibits substantially higher chemical activity, does not absorb visible light, and has a very low electric conductivity in comparison to graphene. GO has diverse applications, including in solar cells, photocatalysis, medical field, drug delivery, sensors, coatings, membranes, electronics, water purification and much more [2, 3, 9].

- 4. Reduced Graphene Oxide (rGO):** The following methods are used to generate rGO from GO: thermal, photothermal chemical, photochemical, microwave and various bacterial or microbial treatments. When oxygen content of GO is reduced by physical or chemical processes, partially deoxygenated sheets known as rGO are produced [5, 9]. When compared to GO, the electronic properties of rGO, such as conductivity and super capacitance, are enhanced [1, 5].
- 5. Exfoliated Graphene:** There are many ways to exfoliate graphite. Micromechanical forces that cause multilayer graphite to exfoliate and break under optimum conditions yield graphene in large quantities [5]. In 2008, N-methyl pyrrolidine was used as the medium in the first demonstration of exfoliation of graphite to generate graphene

immersed in a solvent [5]. Ultrasonication was used to aid in the process. Exfoliated graphene has fewer imperfections as compared to GO or rGO, which is very advantageous for electrical applications [4, 5].

- **Graphene Properties :** The development of nanotechnology has been greatly influenced by graphene's special physicochemical properties, which include high thermal stability, flexibility, a large surface area, excellent thermal conductivity, increased mechanical strength, high electron mobility of graphene-based materials, and impermeability to all gases and liquids [1, 2, 3, 5, 9,]
https://www.nanowerk.com/what_is_graphene.php
<https://matmatch.com/learn/material/graphene>
<https://www.graphenea.com/pages/graphene-properties#.Ywov831Bw2z>
<https://www.graphene-info.com/graphene-properties>
<https://www.visualcapitalist.com/sp/graphene-the-wonder-material-of-the-future/>

- **Mechanical Properties :** Graphene Has ~200 Times Better Mechanical strength than steel, extraordinarily lighter than aluminium, even harder than diamond [2, 5]

<https://www.visualcapitalist.com/sp/graphene-the-wonder-material-of-the-future/>
<https://www.graphene-info.com/graphene-properties>
<https://matmatch.com/learn/material/graphene>

Hence, Graphene is considered as an extremely lightest and the strongest material ever discovered. It is even more flexible than rubber because of the low density of each sheet [1, 2, 5, <https://www.visualcapitalist.com/sp/graphene-the-wonder-material-of-the-future/>] These impressive mechanical and physical properties of graphene originated from the high stability of the strong covalent sp² bonds that form the hexagonal lattice structure [1, 2, 5].

- **Electrical Properties:** Graphene's electronic properties are quite interesting and these properties are so appealing that scientists are working towards advancement of molecular electronics. Graphene is regarded as one of the most efficient electrical conductors having high electron mobility [2, https://www.nanowerk.com/what_is_graphene.php].

Its distinctive arrangement of carbon atoms and pi-electron system gives rise to the electronic-band structure [2]. In graphene, there is little overlap between valence and conduction band, as a result, it is categorized as both a zero-band gap semiconductor and a semimetal [2, <https://www.graphene-info.com/graphene-properties>]. Moreover, it was discovered that in comparison to other semiconductors, electrons in graphene conductor move far more speedily [2, <https://www.graphene-info.com/graphene-properties> <https://www.graphenea.com/pages/graphene-properties#.Ywov831Bw2z>]. The electrical conductivity of a single layer of graphene is 10,000 times greater than that of a few graphene layers [<https://matmatch.com/learn/material/graphene>]

- **Optical properties :** Monolayer thin graphene exhibits low incident light reflection and a wavelength-independent opacity of 2.3% in the visible spectrum [2, <https://matmatch.com/learn/material/graphene> <https://www.graphenea.com/pages/graphene-properties#.Ywov831Bw2z>]

<https://www.graphene-info.com/graphene-properties>]

Since the transmittance of light decreases linearly with the increase in number of layers, single layer graphene is nearly transparent to visible light [1]. The visible spectrum's transparency is mostly a result of thinness of graphene material. The luminescence behaviour of graphene can be obtained by slicing it into nanoribbons and quantum dots or by doping process which reduces the connectivity of the delocalized pi-electron framework [2]. Theoretically, graphene might be used to design effective solar cells due to its special optoelectronic properties [2, <https://www.graphene-info.com/graphene-properties>]

- **Graphene applications:** Graphene and graphene based materials with their unique nanostructures and remarkable properties have found unlimited applications for the enhancement of technological industries. From electronics to energy storage, medicine to pharmaceutical field, graphene and its derivatives have emerged as promising future materials with potential advantages because of their unique chemical structure, high surface area, electrical and thermal conductivities, and better biocompatibility [2, 3, 5, 9].
- **Graphene in medical field:** Biomedical applications for graphene are still emerging. It can be used in a wide range of medical fields due to its 2D allotropic structure [9]. Along with graphene, the applications of graphene's derivatives, such as GO and rGO, have increased significantly. Graphene derivatives especially GO and rGO show inhibition effect of bacterial growth on their surfaces [3, 8]. Studies show that rGO nanowalls with gram +ve and gram -ve bacteria have a greater antibacterial impact than GO. A few studies have reported the contradictory finding that on graphene surfaces, bacterial growth was promoted rather than hindered [3]. For bone and teeth implantation, graphene is employed as an antimicrobial agent [<https://nanografi.com/blog/applications-of-graphene-in-medicine/>]. Based on the study's findings, graphene is added to the list of materials used in dental implants to create composite materials and resins with graphene as a component [9, <https://nanografi.com/blog/60-uses-of-graphene/>]

The substrate used to interact with various cells and biomolecules, is graphene. Graphene's compatibility, selectivity, and solubility in a biological system are all improved by modification [9]. The biomedical applications of graphene include its use in gene and small molecular drug delivery. Gene delivery is a technique for bringing unfamiliar DNA into the cell. The surface of GO sheets is modified using polyethylenimine (PEI), and this PEI-functionalized GO is used as a carrier for efficient gene delivery [3, 9]. Graphene-based carriers have a superior ability to target cancerous cells while lowering the toxicity of the affected healthy cells, thus used in anticancer therapy [3, 9, <https://nanografi.com/blog/applications-of-graphene-in-medicine/>]

GO successfully prevents the development of tumour spheres in a variety of cell lines, including glioblastoma, ovarian, pancreatic, breast, and lung cancers. Drug delivery is affected to some extent by changes in temperature, pH, light, and salt concentration. Polymers are able to recognise changes in the environment and

deliver the drug. Since GO biopolymers are sensitive to pH, they can also be used as a transporter for intelligent drug delivery. Graphene's unaltered basal plane sites, which have unbound pi surface electrons, are hydrophobic and can generate interactions to load drugs. Water-soluble cancer related drugs are delivered using GO that has been modified as a carrier. GO is enhanced to serve as a medium for the delivery of cancer drugs that are water soluble [9]. As graphene is the smallest, lightest, and strongest carbon allotrope, it is a potential building material for stent and endograft scaffolding in the future [8].

The hazardous effect of graphene has lately been documented from several studies in addition to its broad application. The future strategy might attempt to eliminate the toxic effect while preserving the physical and chemical features [3, 5, 8, 9].



Figure 2: Graphene in medical field

- **Graphene in Energy conversion:** In lithium batteries, graphite is the most popularly used anode material. Studies have shown that GO and graphene have a higher energy storage and Li⁺ ion storage capacity as compared to graphite and other carbon-based materials when utilised as anodes for lithium batteries due to two dimensional honeycomb structure [6, <https://nanografi.com/blog/60-uses-of-graphene/> https://www.nanowerk.com/what_is_graphene.php

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