Chapter

Introductory Chapter: Graphene and Its Applications

Raphael Mmaduka Obodo, Ishaq Ahmad and Fabian Ifeanyichukwu Ezema

1. Introduction

Presently, graphene is widely researched worldwide because of its unique properties such as zero bandgap, remarkable electron mobility at room temperature, high thermal conductivity and stiffness, large surface area, impermeability to gases, etc. Graphene charge carrier exhibits core mobility, is massless, and moves a few micrometers distance maintaining its structure at room temperature. Recently, graphene-based materials have gained intense awareness on energy storage systems, electronics, chemical sensors, optoelectronics, nanocomposites, and health such as osteogenic. Graphene is among the allotropes of carbon; its carbon atoms are arranged in a single layer. These carbon atoms are organized in a honeycomb lattice with a two-dimensional arrangement. The carbon–carbon bond distance in a single graphene sheet approximates 0.142 nm [1]. One of the unique and major properties of graphene is that increased researcher's interest is its constituent's electrons that seem to be massless relativistic particles, hence, anomalous quantum Hall effect and the absence of localization [2, 3]. Graphene has been used in many applications, which include energy storage devices like supercapacitors and lithium-ion batteries [4], gas detection [5], and conducting electrodes [6]. Recently, the rate at which graphene awareness is rising is highly remarkable and suggests that it is a good route of the scientists' search for new materials for advancement in science, engineering, health, and composite industries. This brief introduction of graphene narrates its brief history, synthesis method, derivatives, and applications. Addition of graphene in a composite inhibits the fabrications of active material in a nanosize, enhances non-faradaic capacitive behavior, increases conductivity, and prevents disintegration. Graphene also induces a physical barrier in between the electrolyte and active material, hence increasing cycling stability, specific capacitance, and rate capability.

2. Synthesis of graphene

Graphene synthesis means any process of fabricating or extracting graphene from graphite. The method to be chosen is governed by the desired size, quantity, and purity. Synthesis technique contributes to the structure and properties of graphene produced. There are variations of graphene layers from different techniques such as a single layer, double layer, or multiple layers, and they have different applications in various fields of science and technology like energy storage devices, biotechnology, memory, electronics, sensors, etc. Researchers employ different techniques especially when a large quantity is required. Subsequently, we will discuss various synthesis techniques, applications, its status now, progress so far, and future prospects.

In the synthesis of graphene-based materials, ball milling and hydrothermal methods show to be cheaper, the electrospinning method exhibits the benefits in the nanowire composite assembly, and the microwave-assisted method is easier and superfast in fabrication. We also explained methods of graphene synthesis while its derivatives are discussed in the second chapter of this book. The third chapter explained the new technique such as liquid phase exfoliation method for the synthesis and concentration enhancement of graphene which is suitable for the fabrication of the highly efficient modern electronic devices (**Figure 1**).

2.1 Cleavage and exfoliation technique

This method is divided into two: (1) mechanical exfoliation and (2) chemical exfoliation. Mechanical exfoliation is the distortion of weak van der Waals force holding carbon–carbon atom together. The chemical method is the production of colloidal suspension which produces graphene from graphite compounds. Graphite is several densely packed layers of graphene sheets, hence, fixed together by weak van der Waals force. High-purity graphene sheets can be produced from graphite sheet by breaking the bonds that held them together. Therefore, exfoliation and cleavage are the use of mechanical or chemical energy to break down these weak bonds and separate distinctive graphene sheets. Viculis et al. [4] were the first to apply this principle by using potassium metal to separate pure graphite sheet and then exfoliate them using ethanol to form a dispersion of graphene sheets.

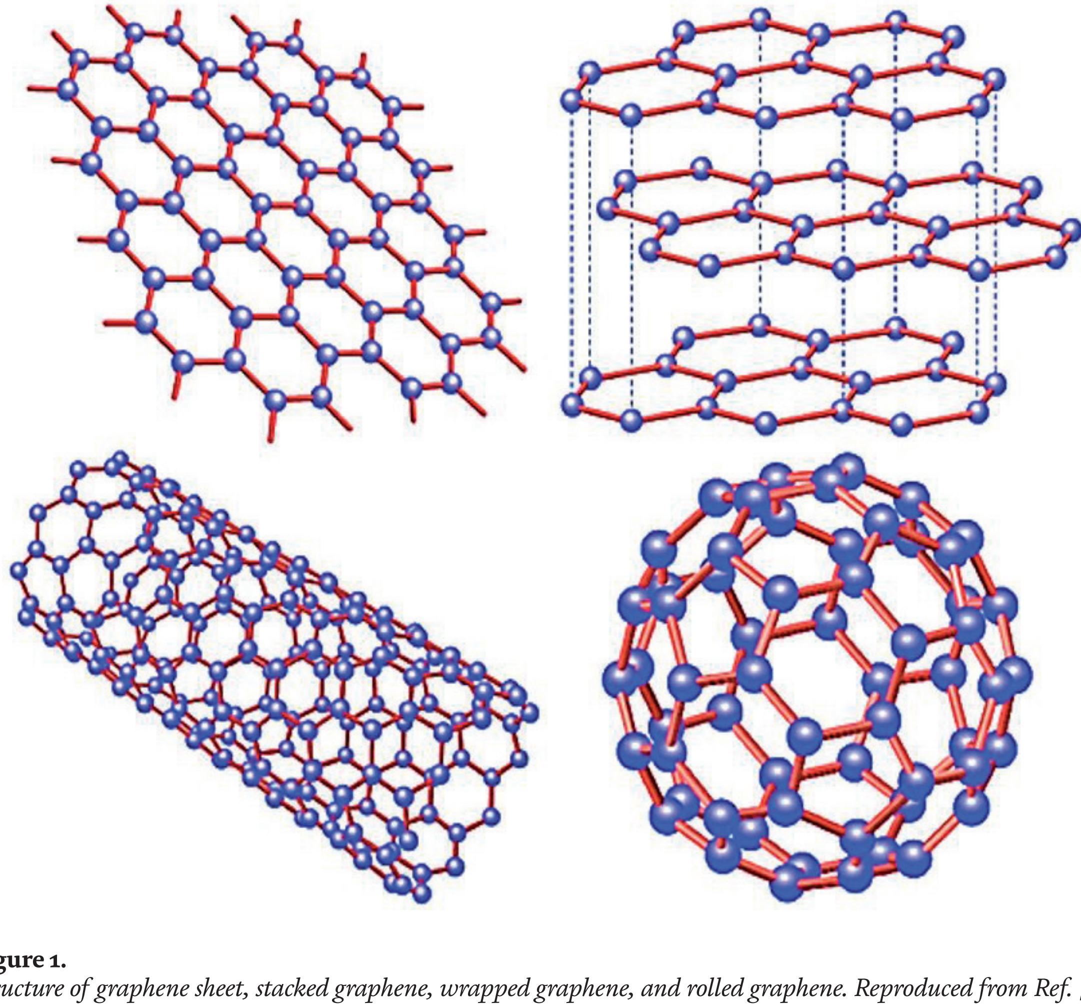

Figure 1.
Structure of graphene sheet, stacked graphene, wrapped graphene, and rolled graphene. Reproduced from Ref. [7].

2.2 Chemical vapor deposition (CVD) methods

Chemical vapor techniques use steam phase exfoliation. This method chemically extracts graphene sheets from graphite without passing through exfoliation stage. Horiuchi et al. [9] were the first people to produce graphene sheets using this method. They engaged the method to fabricate carbon nanofilms (CNF) using regular graphite sheets.

There are many types of CVD, depending on the precursors available, the structure needed, quality of material, and dimension, and there are many applicable CVD processes such as thermal, plasma-enhanced (PECVD), cold wall, reactive, hot wall [9], etc. Graphene thin films are formed on copper or nickel mostly by a chemical vapor deposition method.

2.3 Pyrolysis of graphene

The pyrolysis uses solvothermal technique to synthesize graphene from graphite by a bottom-up approach. Sodium ethoxide and ethanol were mixed in a molar mass ratio of 1:1 in a closed vessel with intense heat treatment and sonication; this process detaches graphene from graphite [10].

2.4 Other techniques

2.4.1 Unzipping CNTs

One of the most recent techniques of fabricating graphene is a type of synthesis that uses multiwall carbon nanotubes (MWNT) as initial material. This method is commonly known as "**CNTs' un-zipping.**" MWNTs can be unzipped longitudinally using lithium and ammonia intercalation, followed by intense acid and heat treatment, which induces exfoliation immediately [11].

2.4.2 Thermal decomposition of ruthenium crystal

Graphene single layers can be grown on single crystal ruthenium (Ru 0001) surface at ultra-high vacuum (4.0×10^{-11} Torr) [11]. It was discovered that graphene could form on the crystal surface. This can be achieved by heat breakdown of ethylene (pre-adsorbed on the crystal surface at room temperature) at 1000 K or by controlled segregation of carbon from the bulk of the substrate [12].

2.4.3 Thermal decomposition of SiC

Thermal disintegration of silicon on the surface plane of a single crystal of 6H-SiC to produce graphene recently gained researchers' awareness. It takes less time to achieve and become popular techniques of graphene growth recently [13].

3. Graphene oxide

Graphene oxide (GO) is a product of graphene obtained by oxidizing graphene. It has a single monomolecular layer containing oxygen functionalities such as carboxyl, carbonyl, epoxide, or hydroxyl groups [14]. These added functionalities expand the separation between the layers and make the material hydrophilic (meaning that they can be dispersed in water). Layers of graphene stacked on top of each other form graphite, with an interplanar spacing of 0.335 nm. The separate layers of graphene in graphite are held together by van der Waals forces. GO are synthesized mostly based on widely reported Hummers method in which graphite is oxidized by a solution of potassium permanganate in hydrogen tetraoxosulfate (IV) acid [15].

The diagram in **Figure 2** illustrates the processes and stages involved in moving from graphite to graphene, graphene to graphene oxide, and graphene oxide to reduced graphene oxide [14, 16]. Many scientists are confused about the difference between carbon derivatives (**Figure 3**).

Graphene oxide is dispersible in water and other organic solvents like ethanol, 1-propanol, acetone, methanol, ethylene glycol, pyridine, etc. as well as in different matrixes. This property of GO was due to the presence of the oxygen functionalities.

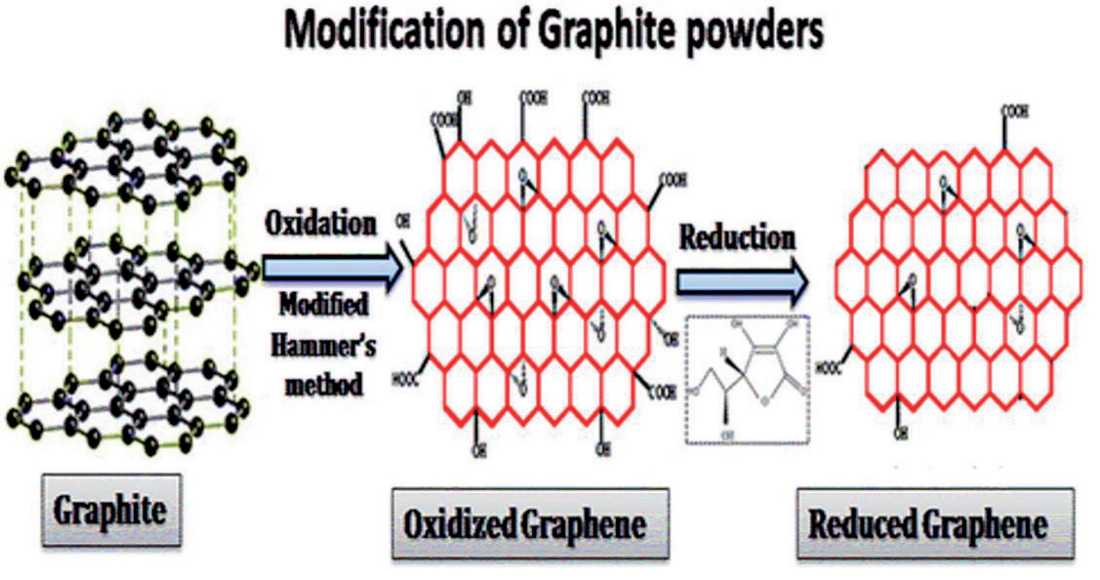

Figure 2.
Stages of synthesis of GO and rGO. Reproduced from Ref. [8].

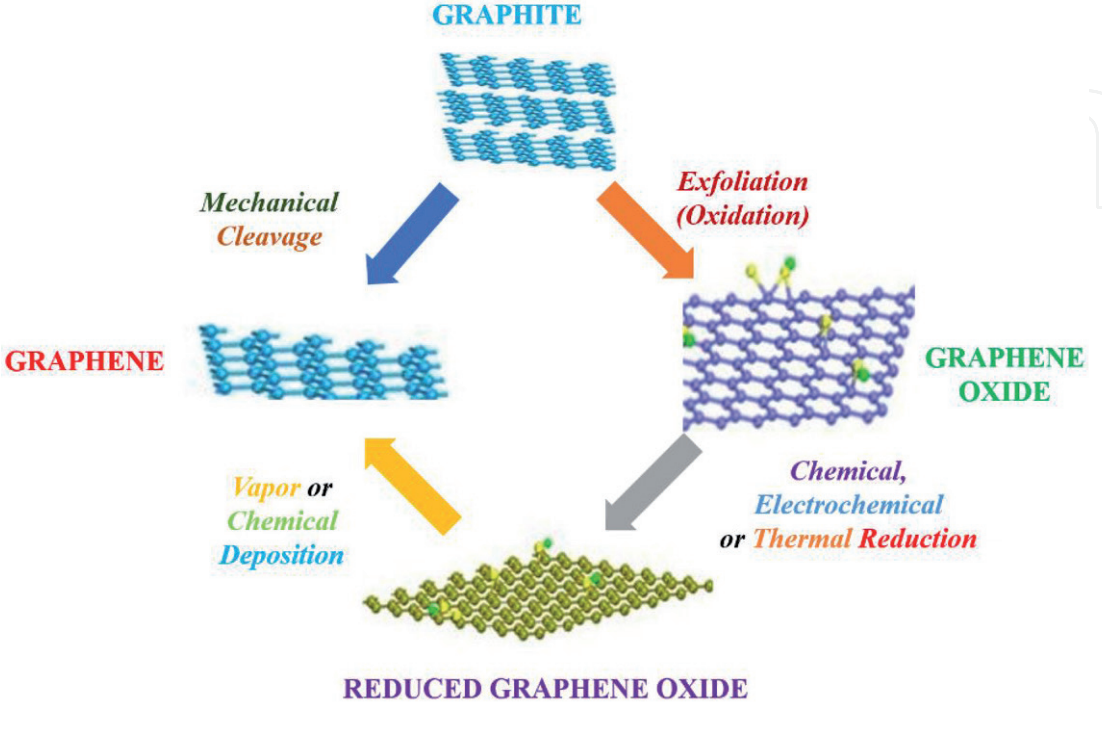

Figure 3.
Cycle synthesis of graphene/GO/rGO. Reproduced from Ref. [33].

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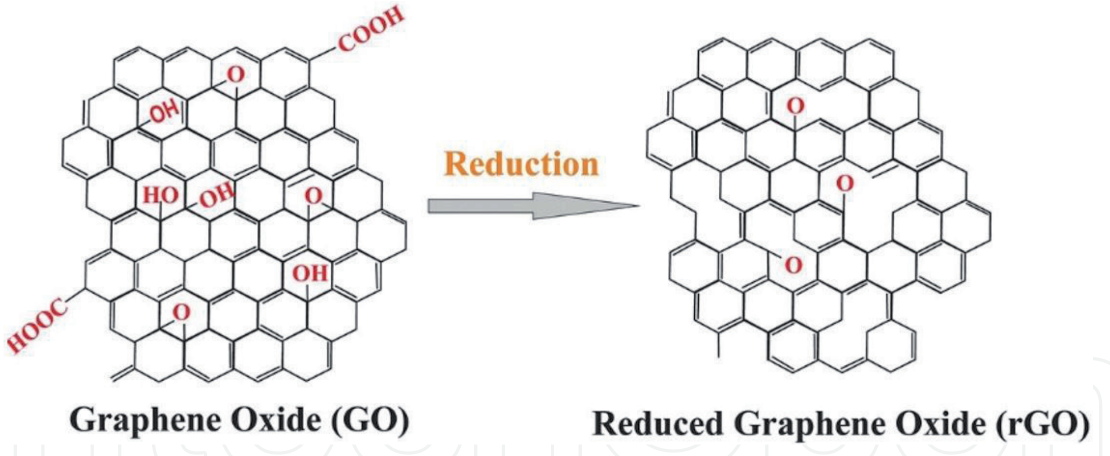

Figure 4.
Diagram of reduced graphene oxide (rGO). Reproduced from Ref. [34].

3.1 Reduced graphene oxide (rGO)

Reduced graphene oxide (rGO) is a graphene oxide (GO) in which its oxygen content is reduced either by thermal, chemical, or any other methods. Graphene oxide is reduced to improve the honeycomb hexagonal lattice distorted during oxidation from graphene to graphene oxide and also enhance its electrical conductivity [14, 34]. It is also observed that once most of the oxygen groups are removed, the reduced graphene oxide obtained becomes indispersible in a solvent due to its tendency to create aggregates (**Figure 4**).

4. Applications of graphene/GO/rGO

Graphite and its derivate recently gained science and engineering awareness due to its numerous applications. The discovery of graphene is rightly regarded as a milestone in the world of material science; as can be seen in the worldwide attention, the material has received in the fields of electronics, photonics, capacitors/supercapacitors, biosensing, etc. They are used in numerous applications as illustrated below. In this book, applications of graphene and its derivatives are discussed in detail. These applications include photocatalysis, electronics, gas sensing, graphene-based heterogeneous electrodes for energy storage devices, etc. In addition, sound devices based on graphene is also explained in this book.

4.1 Electronics

GO are used in electronic fabrications as initial materials. Electronic devices such as graphene effect transistors (GFETs) and field effect transistors (FETs) are graphene-based [17]. Reduced graphene oxides (rGO) are used as chemical sensors [18]. Functionalized graphene oxide in conjunction with glucose oxidase deposited on electrode material is used as an electrochemical glucose sensor [19]. They are widely used in the manufacturing of electronic devices like light-emitting diodes (LEDs) and solar cells. Reduced graphene oxide dispersed in a solvent can be used in the production of the transparent electrode, which is an alternative transparent electrode like FTO and ITO [20].

4.2 Energy storage

Reduced graphene oxide nanocomposites have a high surface area and good conductivity, which suited them for use in supercapacitors and lithium-ion batteries with good energy storage capacity. GO-based supercapacitors and lithium-ion batteries possess high-energy storage capacity, long life span, and good cycle stability.

4.3 Water purification

As far, back as the 1960s [21], scientists have started studying graphite oxide usage in desalination of water. In 2011, some group of researchers employed the principle of reverse osmosis using GO to achieve the same goal [22]. It was discovered that graphite allows water to pass through but retain some larger ions [23]. Its narrow mono- or bilayer capillaries allow water but restrain heavy ions.

Moreover, in the year 2015, a group of scientists also purified water using graphene tea by removing 95% of heavy metal ions in water solution [24].

It was reported that in 2006, engineers fabricated graphene-based thin film powered by solar energy that possesses the quality of filtering dirty and salty water. These films are non-heavy and can be easily produced on a large scale [24].

4.4 Biomedical applications

Graphite and its derivative like GO are widely used in the biomedical field as a constituent in the drug delivery system. Magnetite stacked with GO and doxorubicin hydrochloride (DXR) drug adsorbed onto the system is used as anticancer treatment by targeting it to a specific site to kill cancer cells.

4.5 Biosensors

Graphene oxide and reduced graphene oxide have been incorporated into many gadgets. These GO-/rGO-based gadgets are fabricated with the quality to identify biologically significant molecules. GO/rGO uses fluorescence resonance energy transfer (FRET) characteristics to work effectively as a biosensor.

4.6 Elemental storage

All elements that form part of GO or rGO functional groups can be effectively stored in their sheets and extracted later for use and are also being explored for their applications in hydrogen storage.

4.7 Plasmonics

Recently, the science of plasmonics discovered that near field infrared optical microscopy [25] and infrared spectroscopy [26] of graphene provide accommodations for plasmonic surface mode [27].

4.8 Lubricant

Scientists recently found out that graphene lubricants perform better than regularly used graphite lubricants. A graphene lubricant applied to a ball and bearing roller or steel ball and steel disc lasted for 6500 cycles, while our usually used graphite lubricants lasted only for 1000 cycles [24].

4.9 Radio wave absorption

A heavenly crammed graphene layer deposited on glass substrates absorbs radio waves of the wavelength range of 125–165 GHz bandwidth by 90% [24]. In our modern houses, graphene serves as roof, door, and window coatings to safeguard houses from radio wave interference [28].

4.10 Nanoantennas

A nanoantenna called graphene-based plasmonic nanoantenna (GPN) operates on a wavelength of millimeter within the radio wavelength range. This nanoantenna is better than our conventional antennas because its operational surface plasmon polaritons wavelength is much smaller compared to the wavelength of electromagnetic waves propagating at the same frequency. Our conventional antenna operational frequencies range from 100 to 1000, which is very huge compared to GPNs [29].

4.11 Sound transducers

Graphene has been predicted as a good candidate for the manufacturing of electrostatic audio microphones and speakers due to their lightweight, which provides moderately good frequency response [30]. In 2015 an A model audio ultrasonic microphone and the speaker was fabricated; it operates at a frequency range of 20–500 kHz [31]. Its performance operation was up to 99% efficiency, good and uniform frequency output throughout the audible range [32].

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