Graphene History, Technical Applications and Production – A Brief Review

ABSTRACT

The review paper gives a brief overview of the historical use of carbon materials like graphite and charcoal and graphene and its production.
It reviews the application of graphene for industrial application such as energy storage, electronics, biomedical, and environmental fields, including and sustainable methods for producing graphene from waste products, addressing both the need for advanced materials and the growing problem of plastic pollution. It reviews various graphene production techniques such as catalytic carbonization, flash joule heating, and solid-state chemical vapor deposition for the production of graphene.

Keywords: Carbon, graphene, industrial application, production methods, plastic waste, upcycling, recycling

1. INTRODUCTION

1.1 A Brief History

Charcoal has been an indispensable tool throughout human civilization, with a rich diversity of applications worldwide. The true first use of charcoal is greatly debated, nonetheless, one of the first documented uses of charcoal in history was approximately 38,000 years ago in a charcoal painting produced in the Grotte Chauvet in southern France [1]. In the Tyrolean Alps, a mummified man dating back to roughly 3,500 BC was found with charred pieces of wood on his person. It is theorized that this charcoal was utilized by the man as fuel for fire production. Charcoal is a very efficient fire starter as it is light weight, inexpensive and withholds nearly double the energy content of wood making and it was a crucial resource for humans in past times [2]. Towards the middle of the neolithic age (7,000 to 1,700 Before Comon Era (BCE) in Europe, pottery was commonly decorated with motifs painted with charcoal. Eventually, around the third century BC, the Celts produced a method of using graphite to produce tempered pottery [3]. Other past applications of charcoal in Greece and Egypt have been recorded back to between 300-500 BC where it was used as for cooking, metal making and even as toothpaste. It is theorized that charcoal has been used medically since Hippocrates in ancient Greece however, the first recorded history of charcoal as a medical agent was in 1811 when French chemist Michel Bertrand survived a lethal dose of arsenic trioxide by consuming charcoal along with the lethal chemical. This medical practice is still used today, and now charcoal application has even spread to the beauty care industry [4].

In other parts of the world, like in ancient China, various carbonaceous materials were recognized and utilized. The descriptive terminology often lacked the precision of modern scientific classification. Terms like 石涅 (shinei), 石炭 (shitan, literally "stone coal"), 石墨 (shimó, literally "stone ink/graphite"), 乌金石 (wujinshi, literally "black gold stone"), and 黑丹 (heidan, literally "black elixir") were used to refer to dark, carbon-rich substances (though the primary focus of these terms was often on coal). This historical ambiguity makes it challenging to definitively distinguish between the uses of coal and graphite in ancient Chinese records. It's important to acknowledge that while the texts mention materials that could be graphite, in many cases, they are likely referring to coal. The clear separation between these materials is a relatively recent development in scientific understanding [5,6].

However, some historical texts offer compelling evidence for the early recognition and utilization of graphite-like materials. The *Shui Jing Zhu* (水經注), a geographical text compiled around 515 AD, contains passages that strongly suggest the knowledge and use of graphite. One passage states, "石墨可书，又燃之难尽，亦谓之石炭" (Shimó kě shū, yòu rán zhī nán jǐn, yì wèi zhī shítàn), which translates to "Graphite can be used for writing and does not burn out easily when set on fire, hence it is also known as coal." This description highlights two key properties associated with graphite: its ability to leave marks and its relative resistance to burning, especially when compared to wood. The text then connects graphite to the term "shitan" (stone coal), illustrating the aforementioned overlap in terminology [5,6].

Another passage from the *Shui Jing Zhu*, volume 15, mentions, "洛水之侧有石墨山，山石尽黑，可以书疏，故以石墨名山矣" (Luò Shuǐ zhī cè yǒu Shimó Shān, shān shí jìn hēi, kě yǐ shū shū, gù yǐ Shimó míng shān yǐ), translating to "By the side of the Luo River, there is a Graphite Mountain. The stones on this mountain are all black and can be used for writing, hence the mountain is named Graphite Mountain." This passage provides a geographical marker and directly links the name of the mountain to the writing properties of its black stones, strongly indicating the presence and recognition of graphite in this region during that period. These textual examples suggest that while the precise scientific differentiation between coal and graphite may not have existed, the Chinese had identified and utilized a material with characteristics closely matching those of graphite for practical applications, centuries before the scientific revolution in the West [5,6].

Despite the evident rich history of charcoal application via humans, there is a great lack of records of ancient production methods. Spanning through medieval times, it is believed that rectangular and/or circular pit kilns were the main apparatus used to produce charcoal. In general, these kilns were typically built by first digging a hole in the ground and then filling the hole with wood. Since these pit kilns were created underground, they are no longer visible as they have been continuously covered over time. Due to the lack of remaining pit kilns, much of the kiln process is theorized to follow a similar procedure to that of mound kilns that originated around 1,400 CE [7,8,9]. In the past charcoal was produced from wood through a process known as pyrolysis. This process involves the thermal decomposition of biomass, primarily wood, in an environment where the supply of oxygen is strictly limited [1]. The absence of sufficient oxygen prevents the complete combustion of the wood, instead leading to its transformation into a carbon-rich solid.

During pyrolysis, the wood is heated to high temperatures, causing its organic compounds to break down. This thermal decomposition releases volatile gases and liquids, such as tar and oils, leaving behind the relatively pure carbon material we know as charcoal. The composition of the released gases and liquids is dependent on the specific type of wood used and the conditions of pyrolysis, but the primary output of the process is a solid carbonaceous material.

Mound kilns as shown in Figure 1, are an above ground version of pit kilns in which wood was piled into a domelike structure around a pole and then covered with an earth layer usually consisting of materials such as dirt, sand, stone, grass, straw, etc.

This earth layer prevented the presence of oxygen in the burning process thus generating a pyrolysis system defined as a process that promotes thermal degradation in the absence of oxygen [10]. A mound kilns can be as large as approximately 10 m in diameter and over 3 m tall [11]. The entire process of carbonization takes approximately one t o3 weeks base on the size of the mound Kilns. Cooling typically required several days to provide viable charcoal [11,12].

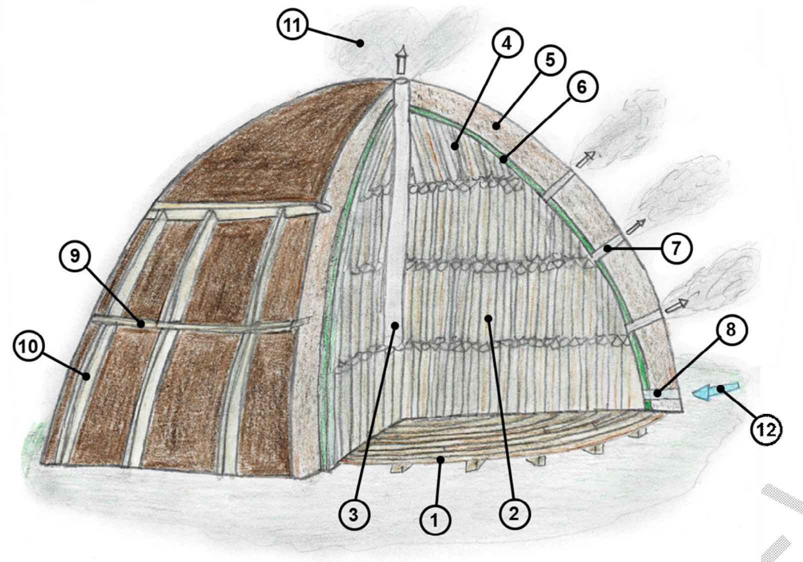

Fig.1. Mound Kiln: 1) Wooden supporting bed, 2) Stacked wood, 3) Heart (Kern or Quandel), 4) Wooden cap out of stacked wood, 5) Outer layer made of soil, 6) Inner layer made out of brush, leaves or pine twigs, 7) Draft holes, 8) Air Intake, 9) Horizontal outer layer support, 10) Vertical outer layer support, (11) Smoke exiting [13].

To fulfill the demand of the preindustrial steel industry a retort process is used for the industrial production of charcoal. This process uses a sealed chamber that is filled with wood. An external heat source is then applied to the chamber while the air inlet and emissions outlet are monitored. The process of carbonization requires around eight to twelve hours instead of weeks and yields about 30-32% [1].

The increase in steel manufacturing required to manufacturing charcoal as carbon source on a large scale and demand could not keep up with production. To supplement charcoal carbon source for industry applications, other large-scale processes have been developed, such as the coking process as part of steel manufacturing that uses coal as raw material and the production method to produce black carbon using natural gas as raw material [8,11,15].

2.0 A BRIEF GRAPHENE HISTORY

It is important to clarify that, despite its high carbon content, charcoal, coke or black carbon is not graphene. Graphene, as previously discussed, is a single layer of carbon atoms arranged in a hexagonal lattice, possessing exceptional properties due to its two-dimensional nature. Charcoal, on the other hand, is a macroscopic, three-dimensional material resulting from the partial decomposition of wood. While it contains carbon, its structure is far more complex and disordered than the highly ordered atomic arrangement of graphene. Charcoal often has a porous structure that develops from the wood cells that are burned, and the carbon itself exists in an amorphous or turbostratic form instead of the well-defined single-layer structure of graphene. Therefore, the methods and properties of charcoal are distinct from those of graphene, even though both are primarily composed of carbon.

While charcoal is not graphene, it does share some similarities with graphite, another important allotrope of carbon. One notable similarity is the relative purity of their carbon content compared to other carbonaceous materials. Charcoal and other "biocarbon" –

materials derived from the pyrolysis of biomass – containing virtually no sulfur or mercury [1]. They are also typically very low in nitrogen and ash, making them cleaner in terms of impurities compared to fossil fuels.

In fact, due to the relative purity of their carbon content, many carbonized charcoals can be considered purer forms of carbon than some naturally occurring graphite's [1]. This purity, along with its high reactivity, enables charcoal to be a valued reductant in metallurgy.

While both graphite and graphene are allotropes of carbon, meaning they are different structural forms of the same element, their properties and dimensionality differ significantly. Graphite is a naturally occurring mineral composed of stacked layers of graphene. These layers are held together by weak van der Waals forces, allowing them to slide past each other easily, which accounts for graphite's softness and its use as a lubricant. Each individual layer within this structure is a sheet of graphene, a single layer of carbon atoms arranged in a hexagonal lattice. Graphene, unlike graphite, is a two-dimensional material with exceptional strength, conductivity, and flexibility. The isolation of individual graphene layers from graphite was only achieved relatively recently, marking a significant breakthrough in materials science.

Graphene, a once purely theoretical material, is a single atomic sheet of graphite completely composed of hexagonally arranged carbon atoms as shown in Figure 2.

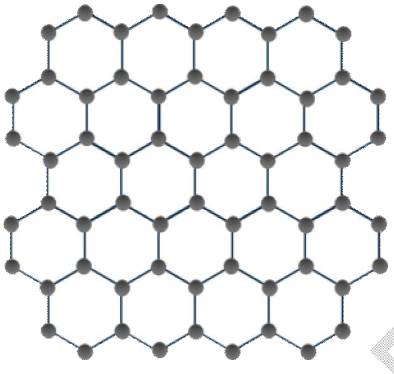

Fig.2. Graphene Model [15]

The history of graphene began with experiments performed on graphite which later led to the conceptualization and discovery of graphene. In the 1840s, Schafhacult, a German scientist, declared that Graphite Intercalated Compounds (GIC) could be produced by positioning small molecules such as acids or alkali metals in-between carbon layers of graphite followed by exfoliation using nitric or sulfuric acid [16]. The resulting product was found to withhold superconducting properties [17,18]. In 1859 Benjamin Brodie performed a study with the goal of determining the molecular weight of graphite. This study involved an experiment in which a strong acid such as sulfuric or nitric acid is exposed to graphite in the presence of an oxidant like potassium chlorate. Brodie claimed the resulting product was "carbonic acid" from which he discovered what he believed to be a new type of carbon referred to as "graphon" with a molecular weight of 33. This product Brodie observed was a suspension of small graphene oxide crystals produced via intercalation of the graphite sheets followed by surficial chemical oxidation [17,18,19]. Approximately forty years later, a scientist named Staudenmaier performed a similar experiment to Brodie's in which the potassium chlorate was added in portions throughout the experiment as opposed to all at once. Brodie and Staudenmaier's experiments were significant as they were one of the first documented studies to prompt the delamination of graphite into single planar sheets despite their lack of knowledge of doing so [17,18]. Their methods are still referred to for graphene oxide production.

Later studies branching from these experiments focused on proving that the "carbonic acid" obtained floating atomic planes. In 1948, Ruess and Vogt attempted to do so through Transmission Electron Microscopy (TEM) on a dry droplet of graphene oxide suspension [17,18,20]. Boehm, Clauss and Hofmann continued a similar study in 1962 in which they reduced graphene oxide in diluted alkaline solution with either hydrazine, hydrogen sulfide or iron salts [21]. This process produced a solution of carbon sheets with few hydrogen and oxygen atoms from which they claimed to have successfully identified monolayers of reduced graphene oxide via TEM. This determination later faced scrutiny as the identification method relied on relative TEM contrast which would not pass current standards. Nonetheless, Boehm and Hoffmans study is generally accepted as the first observation of graphene sheets it follows proper logic and graphene sheets should have been present in their suspension. Boehm later coined the term graphene in 1986 with the definition now known [22].

The concept of epitaxial growth, the growth of crystalline material on a substrate to produce a well-ordered crystal, also made major advancements in the study of graphene [23]. Early studies of epitaxial growth of graphene report its growth on substrates such as ruthenium, rhodium, and nickel [17,18]. In 1975, Bommel and their research group demonstrated epitaxial growth of graphite on the insulating substrate silicon carbide [24]. Epitaxial growth of graphene is a method still used in many graphene production procedures.

In 1997, the term graphene was officially accepted in the scientific field as the International Union of Pure and Applied Chemistry adopted the term in the compendium of chemical technology with the generalized definition of being a single planar sheet of carbon or graphite [22]. Around this time researchers began to develop experiments aimed at estimating the electrical properties of graphene. One of these scientists is Yoshiko Ohashi who successfully cleaved graphite crystals to approximately 20 nanometers thick, estimated to be 60 layers of graphene sheets. The electrical properties of the cleaved graphite were then assessed [25]. A research group led by scientists Geim and Novoselov was able to successfully obtain graphene samples with a thickness down to a few atomic layers and even some samples that were a single layer thick through exfoliation with scotch tape [26]. This achievement made it possible to develop a much better understanding of high-quality graphene itself and its true electronic properties through testing of the samples produced [17,18,22].

3.0 GRAPHENE APPLICATION

The excellent physical properties of graphene, such as a high theoretical surface area, electron mobility, electrical conductivity, and its optical properties, make it attractive to many fields. In addition to this, graphene is non-toxic and inexpensive making it a highly researched replacement material for several applications that currently require materials that are expensive, difficult to harvest and/or cause damage to the earth upon harvesting. The quality of the graphene produced dictates its potential to effectively function in its application as different qualities provide different properties. Depending on the graphene production method utilized, the graphene quality will vary. Additionally, the quality of graphene produced from the same method may also differ if slightly different materials are used during production [27]. In some studies, it has been shown that the properties of graphene can be tailored towards the desired properties for the application through chemical and/or physical processes [28,29]. Nonetheless, regardless of the quality of graphene, its properties show massive potential to innovate numerous technologies at a lower cost and with less destruction of earth.

3.1 Graphene Use in Energy Storage

Graphene utilization in supercapacitors is one of the most common applications considered in graphene studies. Supercapacitor producers stive to increase the energy density of the product so that it can serve as a power source for longer periods of time. One method of increasing the duration of power usage is to increase the energy storage capacity of the supercapacitor which can be done by increasing the capacitance. In theory, if the electrode surface area is increased, the capacitance will increase, improving the supercapacitor's energy density. Graphene is known to have a high surface area thus it has potential to be a proper fit as an electrode material in supercapacitors, however; the surface area of graphene must be ion-accessible to improve the capacitance. Due to this, the graphene stacking configuration plays a vital role in its overall effectiveness as an electrode material within supercapacitors. In addition to this, the pore size and volume of the graphene are also crucial factors of its overall effectiveness as an electrode material. Specifications such as these are why supercapacitors made with graphene electrodes are not yet widely available, however, studies are still being conducted to discover methods to optimize the performance of graphene [30].

Solar cells are another application considered for graphene. Currently, solar cells rely on the use of metal or transparent conducting oxides. These materials have been observed to decrease the degree of sunlight permitted to enter and be captured by the cell. In addition to this, they lack flexibility, their harvesting often has destructive impacts on the environment, and they tend to be more expensive than the theoretical doped graphene replacement. Doped graphene is suggested to perform higher than metal or transparent conducting oxides in these properties, but its sheet resistance is much higher, decreasing its overall efficiency as a solar cell. It has been proposed that if the sheet resistance is decreased to a similar value of that achieved by transparent conducting oxides, solar cells can be produced at a lower cost and impact on the environment which could be pivotal for the ever-growing demand for clean energy sources [28].

3.2 Graphen Usage in High Frequency Electronics

Graphene is also being studied for application in semiconductors in high-speed electronics. Graphene has a high carrier mobility which can allow devices to operate at higher frequencies leading to a superior performance than that of the current silicon-based semiconductors. One factor preventing graphene from being a viable replacement for silicon in semiconductors within high-speed electronics is its lack of a bandgap which is responsible for providing an on/off state. This lack of a bandgap makes graphene a good fit for analog devices but not necessarily for high-speed electronics. Therefore, studies involving graphene application in high-speed electronics typically focus on methods to induce a bandgap within the graphene [31]. A study by Randviir et al., suggests that a one-degree twist in the graphene sheet may provide the bandgap necessary but further studies must be conducted for evaluation [29].

Organic Light Emitting Diodes (OLEDs) are frequently used in high-speed electronics to provide a display screen. OLEDs typically contain tin doped indium oxide in the transparent conductive electrode. This material has been noted to be undesirable for this application due to its brittle nature, poor transparency around the infrared region, excessive cost and it is a limited resource. Graphene may be a sufficient replacement for this material as it is flexible, inexpensive and its vibrational properties contribute proficient optical properties. Nonetheless, the high sheet resistance of graphene hinders its success as a replacement material. Therefore, if studies reveal a method to decrease the sheet resistance of graphene, the performance of both OLEDs and solar cells themselves may improve at a lower cost [32].

3.3 Graphene Usage in Electrochemical Systems

Graphene has rapidly emerged as a highly versatile material in the field of electrode technology due to its exceptional electrical conductivity, high surface area, and unique two-dimensional structure. Its applications span a diverse array of devices, and their performance is often enhanced when compared with other conventional materials [33]. A crucial factor determining the performance of graphene-based electrodes is the number of graphene layers, with single- or few-layer graphene typically exhibiting the best performance due to its superior charge carrier mobility.

Graphene's adaptability has led to its integration into numerous electrochemical systems:

3.3.1 Solar Cells

In solar cell applications, graphene, particularly when produced via Chemical Vapor Deposition (CVD), presents itself as a compelling alternative to Indium Tin Oxide (ITO), owing to its superior flexibility and stability. Huang et al. specifically notes that solar cells based on reduced Graphene Oxide (rGO) often suffer from lower efficiency due to higher sheet resistance. To counter this limitation, various strategies have been developed, including doping and compositing graphene with Carbon Nano Tubes (CNT)s to improve conductivity. The versatility of graphene is further evident in its application in both organic solar cells and dye-sensitized solar cells (DSSCs) [33].

3.3.2 LEDs:

Graphene's inherent flexibility also makes it highly suitable for flexible Light Emitting Diodes (LEDs). It can serve as both an electrode and a substrate for the epitaxial growth of inorganic semiconductors, allowing the development of efficient and flexible LED devices. The patterning capability of graphene also facilitates the creation of LED arrays. Additionally, the ability to modify graphene's work function, which determines how electrons move at the interface, has been proven to be important to optimize the performance of organic LEDs (OLEDs).

3.3.3 Field-Effect Transistors

Graphene is employed in Field Effect Transistors (FET)s as both the source/drain electrodes and the semiconducting channel itself. However, graphene's zero bandgap (meaning there is no energy barrier for electrons to jump over) leads to low on/off ratios, which makes it challenging to control the flow of electricity in these devices. Research has been done to address this, including a tunneling FET design using materials like hexagonal Boron Nitride (h-BN) or Molybdenum Disulfide (MoS_2) as a barrier to overcome this limitation, leading to more effective and controllable devices.

3.3.4 Electrochemical Sensors

Reduced graphene oxide is prominent in the fabrication of highly sensitive and selective electrochemical sensors. The high surface area of rGO is one reason for its success in detecting various analytes. The review also highlights electrochemical reduction of graphene oxide as a greener alternative to the chemical reduction which uses hydrazine. In addition, the review compared the electrochemical and chemical reduction methods. It was found that electrochemical reduction creates superior sensing performance because chemical reduction results in varying amounts of oxygen on the graphene, which decreases performance. Furthermore, graphene-metal nanoparticle composites are used to improve performance, by using the good catalytic activity of metal nanoparticles along with graphene's high surface area.

3.3.5 Lithium-ion Batteries

Graphene and its composite materials are widely investigated as electrode materials for Lithium Ion Battery (LIB)s. Graphene offers benefits in addressing issues with traditional electrodes including poor conductivity, material degradation, and large volume change during charging/discharging cycles when using other material electrodes. Strategies include doping graphene, combining it with CNTs, and using graphene to encapsulate nanoparticles, all to improve the cycling performance and rate capability of LIBs.

3.3.6 Supercapacitors

Graphene's high surface area and electrical conductivity are ideal for supercapacitor applications. The review mentions the use of methods like potassium Hydroxide (KOH) activation and laser scribing to obtain graphene for flexible supercapacitors. Moreover, combining graphene with metal oxides or other carbon materials can also improve the overall performance of supercapacitors.

3.4 Bio-Medical Field

Biosensors are a device that is applied internally or externally to detect internal changes in enzymes, DNA, proteins etc. Currently biosensors are expensive as they rely on costly nanoparticles. The application of graphene to biosensors is proposed to decrease their cost. Additionally, it has been observed that graphene application in biosensors improves their precision and sensitivity due to graphene's sensitive thermal, electrically conductive, and chemical behavior [34]. In a study conducted by Reucha and their colleagues, a paper-based biosensor was produced with a nanocomposite composed of graphene, polyvinylpyrrolidone and polyaniline to detect cholesterol. The biosensor was used to test cholesterol indirectly by detecting hydrogen peroxide, the product of cholesterol after oxidization, and direct testing via human serum. The results of these tests indicate that the nanocomposite composition improved the electrochemical sensitivity of the hydrogen peroxide detection, and, under ideal conditions, it displayed a high sensitivity and an ability to detect low quantities of cholesterol [35].

Graphene has also shown prospective implementation into medical scaffolding materials, substances used as structural basis for cell or tissue growth. Historically, polymer polyurethane has been used as the basis for scaffolding material as it is biologically compatible and obtains satisfactory mechanical properties. Nonetheless, it lacks sufficient electroconductivity, a problem that may be resolved through the addition of graphene within the polyurethane. Testing done on polyurethane scaffolding material embedded with dispersed graphene indicates an improvement in mechanical properties and thermal and electrical conductivity. Evaluations also displayed that the scaffolding material provided proper cell adhesion and growth all while maintaining a nontoxic nature [36].

Graphene has also been projected for further application within the medical field in areas such as drug delivery and therapy technology in the future [37]. Despite graphene's promising application to several areas of the medical field, it is important that further research is conducted to verify the nontoxic nature of graphene.

3.5 Environmental Field

Prospectively, graphene may become a major contribution to the environmental field due to its sorbent properties such as high flexibility, mechanical strength, theoretical surface area, and mendable surface chemistry. Most studies that aim to assess graphene's sorption ability focus on substances that are common water pollutants such as dyes, oil, and heavy metals. Current studies often aim to increase the trapping capacity of graphene by producing a Three Dimensional (3D) graphene macrostructure with an increased quantity of pores and decreased density derived from a Two Dimensional (2D) graphene nanosheets [38]. Spongy graphene is a 3D derivation of 2D graphene oxide. Analysis of spongy graphene found that it is capable of adsorbing petroleum products and toxic substances such as toluene up to 86 times its own weight (Bi et al., p.4421, 2012). In addition to this, approximately 99 % of the adsorbates can be removed from the spongy graphene via heat treatment. Typically, this regeneration via heat treatment can be conducted over 10 times [39].

Plastic waste presents itself as a compelling precursor for graphene production primarily due to its abundant carbon content, and it's cheap. As polymers, plastics are fundamentally long chains of repeating carbon-based units, with some unsaturated carbon making them a readily available source of the core element required for graphene synthesis.

Utilizing plastic waste as a precursor offers several significant benefits. Firstly, it provides a cost-effective alternative to traditional graphene precursors like graphite. It is often considered a low-value or even negative-value material, requiring expenditure for disposal. Transforming this waste into graphene not only avoids disposal costs but also generates a valuable product, creating a closed-loop system. Secondly, employing plastic waste as a feedstock directly addresses the growing global issue of plastic pollution. By diverting plastic from landfills and the environment, this approach contributes to a more sustainable and circular economy.

While plastic waste might be a promising precursor, it's important to note that other carbon-rich materials can also be utilized such as food waste and other carbon containing waste products. For instance, Rice University's flash Joule heating method has also demonstrated the versatility of this technique by successfully using carbon containing waste as an alternative precursor [40].

4.0 VARIOUS GRAPHENE PRODUCTION METHODS

The generation of graphene has been approached through various methods, broadly categorized as top-down, bottom-up, and Chemical Vapor Deposition (CVD) techniques.

4.1 Top-Down Method

In the top-down method of graphene production, graphene layers are obtained by physical separation of bulk graphite into individual graphene layers. Mechanical exfoliation, a classic example demonstrated by the "Scotch tape method," physically peels off graphene layers from graphite. Liquid-phase exfoliation utilizes sonication, shear mixing, microfluidization, or ball milling in liquid media to separate graphene sheets. The oxidation-reduction method involves oxidizing graphite to graphite oxide, exfoliating it, and then reducing it to form rGO. While scalable, this method often introduces defects into the graphene structure.

Examples of the top-down method include but aren't limited to mechanical and chemical exfoliation, electrochemical and laser ablation. Chemical and mechanical exfoliation are the top-down methods most frequently used due to their simplicity and practicality. The concepts used in the top-down methods make it easily applicable for large scale production. Nonetheless, the graphene produced using this method is often of low quality due to structural defects, decreasing the performance of its properties and thus its overall worth as a material [27].

4.1.1 Mechanical Exfoliation

Mechanical exfoliation, a top-down method, requires a longitudinal or transverse stress of approximately 300 nN/μm^2 to be applied to the graphite to overcome the van der Waals forces holding the graphene sheets together [41]. It was the first recognized method of graphene production discovered by Geim and Novoselov [26], later coined the “Scotch Tape” method [27]. The removal agents successfully used in this method have been done by means of electric field, ultrasonication, transfer printing technology and scotch tape. The size and thickness of the graphene flakes obtained depend on the form of graphite chosen, such as pyrolytic, natural, or mono-crystal graphite [42]. In theory, this method is easy, but obtaining valuable graphene flakes of proper size, thickness and without major defects is difficult [27]

4.1.2 Chemical Exfoliation

Chemical exfoliation (CE) is a two-step process beginning with reducing the van der Waals forces between graphene sheets by turning the graphite into Single-Layer Grapheene (SLG) and Multi-Layer Graphene (MLG) [41]. MLG and SLG can be created through several methods, but the most common method chosen for subsequent chemical exfoliation involves soaking the graphite in a solution of sulfuric and nitric acid. This method causes the acid to penetrate the graphite creating alternating layers of graphene and intercalant. Then exfoliation of the MLG is performed via rapid heating to cause the intercalants to evaporate or by ultrasonication, the application of soundwaves to a fluid containing the GIC [43,44]. The thickness of the graphene derived from a single round of this process can range from a few to a few hundred layers. To obtain SLG this process must be repeated using different intercalation and exfoliation chemistry and processes [44].

4.2 Bottom-Up Method

Bottom-up approaches focus on building graphene from atomic or molecular precursors. Epitaxial growth involves heating silicon carbide substrates under vacuum or inert gas conditions, causing silicon atoms to evaporate and leaving behind carbon atoms that reorganize into graphene. Laser-Induced Graphene (LIG) directly converts polymers into 3D porous graphene using laser irradiation. Flash Joule heating (FJH) employs rapid electrical heating to transform carbonaceous materials into graphene.

The bottom-up method involves the deposition of a starting material in a controlled environment in regard to factors such as temperature, pressure, and flow rates of inlet and outlet gases [27]. The major advantage of this method is that the controlled nature of the process allows the process to be tailored to acquire graphene of specific structures and thus specific properties [45]. Additionally, this method is generally acknowledged to produce high quality graphene with good electronic properties and limited structural defects [27]. Conversely, the bottom-up method is often expensive, produces a lower yield than up-down, and difficult to scale up thus decreasing its practicality to be applied large scale [46].

4.2.1 Chemical Vapor Deposition

Chemical vapor deposition (CVD) grows graphene on metal substrates like copper or nickel by decomposing volatile carbon precursors. This method is known for its ability to produce large-area graphene films with precise control over the number of layers, although it often requires expensive equipment and strict preparation conditions.

CVD requires a chamber maintained at elevated temperatures with a metal substrate film that functions as a reaction catalyst by reducing the energy barrier and determines the mechanism of graphene deposition. The metal substrate is a transition metal such as platinum, ruthenium, iridium, cobalt, titanium, copper, or nickel [45]. Most commonly, nickel films 100-500nm thick or copper films of 25-100μm thick are used as they are inexpensive and produce relatively high-quality graphene [46]. Regarding the graphene deposition mechanisms for each, carbon dissolves into the nickel film at elevated temperatures and then diffuses out at reduced temperatures while carbon deposits on the surface of copper films [27]. The graphene generated on copper films tends to contain more monolayers while nickel generates more multilayers [47,48].

Prior to graphene CVD, nickel and copper films must be pretreated to remove oxides, control the grain size of the metal, and reduce the occurrence of lattice mismatch. The films are first cleaned through ultrasonic conditions using acetone and/or alcohol for 30 minutes followed by washing with distilled water [47,48]. After cleaning, the films are then annealed, usually in the same apparatus that the CVD process will occur in. In general, nickel films are annealed at 800°C -1100°C in a gas mixture of argon and hydrogen [46]. In Cui et als experiment the nickel film is annealed in a quartz tube at 1050°C in a mixture of argon and hydrogen gas at a ratio of 150/25 cm^3 per minute for thirty minutes [47]. Copper films are usually annealed at 800°C-1060°C in hydrogen gas. In Sharma et.al., experiment, the copper film is annealed in hydrogen gas at a volumetric rate of 100cm^3/minute for thirty minutes at 1020°C [48].

To begin the CVD process, an inlet of carbon gas enters the furnace operating at an elevated temperature containing the metal substrate film. The operating conditions vary depending on the thickness and type of foil. In Sharma et al. experiment, in which copper foil is used, the operating conditions are 1020°C, 90cm^3 argon, 2.5 cm^3 hydrogen gas, carbonaceous gas at fluctuating rates for 90 minutes. The graphene crystals on the copper foil are then coated with Polymethyl Methacrylate (PMMA) and the copper is etched away with 50 mg/ml ferric nitrate solution. The graphene and PMMA layer are then transferred to a Silicon Dioxide / Silicon (SiO_2/Si) substrate. The PMMA is then removed with acetone after which the graphene is treated with diluted nitric acid to remove residual ferric nitric acid. The graphene is then allowed to air dry [48]. In contrast, Cui et.al. experiment utilized nickel foil and operated at 1050°C in the presence of carbonaceous gas for 120 minutes. After subsequent cooling of the nickel and graphene layer, the nickel is etched away ferric chloride and hydrochloride followed by washing with deionized water [47].

The carbonaceous gas used for graphene (CVD) can be derived from plastic waste. The plastic waste is pyrolyzed, submitted to elevated temperatures in the absence of oxygen, which causes the plastic to thermally degrade into heavy hydrocarbon residues such as gas and oil [10]. The gas produced from the furnace in which plastic pyrolysis occurs is then transported to the furnace with the metal substrate film for graphene CVD.

4.2.2 Catalytic Carbonization

Catalytic carbonization is the process of converting organic substances into carbon-based materials through the application of a catalyst. In summation, graphene, the carbon-based material, is produced via catalytic conversion of plastic waste, the organic component, and a degradation agent, the catalyst, through a two-stage pyrolysis process [49].

First, the collected plastics are finely chopped into flakes with the approximate dimensions of 11.21 mm by 5.75 mm [50]. The plastic shreds are then washed with distilled water and soap solution to remove grease and oil, after which the plastics are permitted to dry. The plastics are then uniformly mixed in a mixer with a degradation agent at an approximate mass percentage of 0.05%. The degradation agent acts as a degrading catalytic template for plastic pyrolysis by improving the formation of light hydrocarbon and aromatics produced by the pyrolyzed plastic responsible for generating graphene. In summation, the degradation agent supplies a pathway for the generation of the graphene skeleton [51].

The degradation agent used in the production of graphene can affect both the quality and quantity of the graphene produced. The use of Zinc Oxide, (ZnO), produces a yield of about 13% multilayer graphene nanosheets with disturbed pore distribution and a rough morphology. Montmorillonite clay provides a yield of roughly 15 % one-to-two-layer graphene nanosheets. The morphology is smooth with a more uniform pore distribution relative to ZnO based graphene. These graphene nanosheets are found to have good supercapacitor performance [51]. Bentonite clay generates a yield of approximately 15 % graphene nanosheets that are generally described as containing defects. However, these defects cause an increase in energy density making this form of graphene nanosheets a proper fit for the electrodes of energy storage capacitors and Li-ion batteries [50]. Aluminum Oxide, (Al_2O_3) produces graphene nanosheets of 3-4 nanometers thick with uniform alignment making it a good fit for thermoelectric materials [52].

Ensuing the mixing of the plastic with the degradation agent, the mixture is placed in a primary pyrolysis chamber with a bed composed of transition metal(s) such as nickel, iron or stainless steel [53]. It is important that the bed is composed of transition metals as they have a high activity for carbon and the transition metal bed is where the graphene synthesis will occur [53].

In the pyrolysis chamber, the plastic mixture undergoes slow pyrolysis, in which nitrogen gas is fed into the chamber at an estimated rate of temperature change of 0.1-1°C/s for a minimum of thirty minutes. In Pandey et al.'s study, the maximum temperature reached was 400°C with a temperature change of 5°C/minute [50]. In the studies done by Garg et al. And Karakoti et al., slow pyrolysis was not performed. Instead, the plastic mixture was placed in the pyrolysis chamber at 400°C for two hours [51,52]. Whether or not slow pyrolysis was the chosen route, the product produced from this step is called carbon residue. The carbon residue then undergoes secondary pyrolysis. In Pandey et al.'s study, this step was done at a temperature change of 10°C/minute to 750°C whereas Garg et al.'s study performed it at 850°C and Karakoti et al.'s study maintained a temperature of 920°C for three hours [50,51,52]. The reduced graphene nanosheets produced from secondary pyrolysis are then crushed in a ball mill to produce a fine powder, other than in Pandey et al.'s study in which the carbon residue was ball milled prior to secondary pyrolysis. In all studies, the reduced graphene nanosheets are then washed with a varying combination of 5 % Hydrogen Chloride (HCl), Ethanol (CH_3CH_2OH) and distilled water followed by drying [50,51,52].

4.2.3 Flash Joule Heating

Flash joule heating is the process of transporting a current through a material to prompt the material to internally generate heat, ultimately causing the material to sinter. This method of sintering provides a much higher rate of heat generation than the traditional furnace, therefore, flash joule heating is considered faster and more efficient than furnace sintering [54].

The first step of flash joule heating plastic waste to produce graphene is to grind the plastic into a powder with a commercial grinder and then uniformly mix the plastic powder with carbon black at a weight percent 5 %. The mixture is then loaded into a quartz tube situated between two copper electrodes. Then alternating flash joule heating is performed on the apparatus in which currents of 120 V and 60 Hz are applied to the apparatus for 8 seconds. This stage produces an intermediate flash graphene which is then converted into high quality flash graphene, referred to as turbostratic flash graphene, by submitting it to a direct flash joule heating in which a single 500 ms direct current pulse is sent through the apparatus. The energy consumption for converting 1 gram of plastic waste to flash graphene is estimated to be about 23 kJ thus the overall electricity cost is approximately $125 per ton of plastic waste [55]

Flash joule heating may also be applied to the ash produced from pyrolyzed plastic. To do so, the plastic ash is compressed in a quartz cylinder. Then copper wool and copper electrodes are placed on each end of the quartz cylinder. The initial resistance of the material is observed to be approximately 15 Ω. The quartz cylinder is then placed in a desiccator. Then pulses of 50V, 70 V, 90 V and 160 V are sent through the apparatus for 450ms each until the final resistance of 1 Ω is acquired. Following, flash joule heating the flash graphene is removed from the quartz cylinder and ground with a mortar and pestle. This process provided 85-90% weight yield [56].

One significant challenge associated with using plastic waste in FJH is its inherent poor electrical conductivity. Effective Joule heating requires the material to conduct electricity sufficiently to generate heat. To overcome this limitation, a common strategy is to pre-mix a certain amount of conductive material, typically carbon black, with plastic waste before the FJH process. Carbon black, being a highly conductive form of carbon, acts as a "starter" material, allowing the electric current to flow through the mixture and initiate the heating process, which then facilitates the conversion of the plastic into graphene.

5.0 GRAPHENE ANALYSIS EQUIPMENT

The subsequent analysis of graphene required after production to evaluate the degree of quality requires a combination of several forms of equipment. The analysis method most frequently performed on graphene is Raman spectroscopy, as it can evaluate numerous properties. Raman spectroscopy is commonly applied to evaluate the bulk and structure properties of graphene such as defects, defect density, doping, degree of doping, strain, stacking order and the number of layers of graphene [57]. Another analysis method frequently employed to evaluate bulk and structure properties is atomic force microscopy (AFM). AFM utilizes a sharp tipped cantilever to analyze the topography of graphene. The AFM then provides a 3D image that can be used to decipher the number of layers of graphene present, thickness, and surface roughness. Despite AFM's potential as a reliable tool, it requires a high degree of experimental skill to provide accurate results [58]. The surface morphology and structure of graphene may be evaluated using scanning electron microscopy (SEM) and/or transmission electron microscopy (TEM). SEM provides a 3D image while TEM provides a 2D image. Often, both methods are performed to provide an opportunity to compare results [51,56]. Finally, the functional groups present in graphene are often examined with Fourier Transform Infrared Spectroscopy (FTIR) [58].

Overall, studies on graphene typically utilize several forms of equipment to develop a well-rounded understanding of the characteristics of the graphene produced. Additionally, the results provided from the various analysis methods can be used to cross reference the values acquired to determine the potential accuracy of the results.

6.0 CONCLUSION

The production of graphene requires complicated technical processes to produce industrial-like quantities. Most reviewed techniques are at the laboratory stage and do not yield the high quantities industrial production needs for the enhancement of today's products.

Graphene production from waste materials is currently at its beginning stage. Further research into more efficient and sustainable production methods is needed in order provide a highly anticipated technical product by eliminating and utilizing waste materials at the same time.

7.0 COMPETING INTERESTS

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

8.0 DISCLAIMER (ARTIFICIAL IMTELLIGENCE)

The author hereby declares that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during writing or editing of manuscripts.

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