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# **Graphene Nano Composites for High Performance Super Capacitor**

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# **Abstract**

Graphene-based nano composites have shown great promise as a material to improve the effectiveness of super capacitors because of its special combination of mechanical flexibility, chemical stability, high surface area, and superior electrical conductivity. An overview of current developments in the design and manufacturing of graphene nano materials for efficient super capacitor applications is given in this article. The effects of different synthesis techniques, including chemically vaporized depositing, also hydrothermal synthesizing, and electrochemical deposition, on the shape and characteristics of the final nano composites are examined. Additionally, the impact of several graphene fillers on the electrochemical stability of super capacitors is examined, including reduced graphene oxide, the material graphene oxide, and the nano sheets of graphene. Methods such as surface functionalization, electrode architecture optimization, and hybridized with other nano materials are also highlighted as ways to enhance the density of energy, power density, and stability during cycling by incorporating graphene the nano composite materials into super capacitor electrodes. All things considered, graphene-based nano composites have a great deal of promise to enable super capacitors to operate at higher efficiency, opening the door for their wider commercialization in a range of energy conversion and storage applications.

**Keywords:** Smart technologies, Super capacitors, Graphene Nanocomposite, carbon allotrope.

## **Introduction**

Super capacitors are regarded as some of the possible options for energy storage devices in the future generations. The significance of these devices has been demonstrated by their diverse applications, such as powering hybrid electric/electric automobiles and other electronic systems that depend on electrical energy to function. The most adaptable and often used devices for delivering electrical energy quickly and in environments requiring a long shelf life are super capacitors. Consequently, there are enormous market demands for the development of super capacitors, and sustained improvement is required for both their effective advancement and commercialization [\(Huang](#page-22-0) *et al.*, 2019). In addition to integrating many alternative power sources into electrical systems, storage mechanisms for energy (ESS) are very appealing for improving energy efficiency. Specified energy, power, lifetime, dependability, and protection are the most important factors to take into account while selecting an energy storage system [\(Yadlapalli](#page-23-0) *et al.*, [2022\)](#page-23-0).

 In order to meet the demands of the smart technologies that are becoming an essential element of modern life, creative inventions are always searching for efficient as well as effective materials. One such technology is the super capacitor, which has consistently drawn the interest of academics and technologists due to its many applications in areas such as industrial power supply, storage backup systems, energy management, and the emergency exits of Airbus A380 etc. However, due to their superior energy storage efficiency in recent times, super capacitors (SCs) have garnered a lot of attention. This is because they store energy by the accumulation of ions that are charged from the double layer of electric current (EDL). The quest for clever and innovative materials to

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significantly improve the electrochemical energy storage capacity of SCs is also ongoing among material scientists. The two most common charge storage techniques used in super capacitors are pseudo capacitance and EDL capacitance. The efficiency of devices that participate in the charge accumulation process between electrodes and electrolyte depends on their surface area. In the case of an EDL type of process, energy storage occurs through the electric separating of ionic as well as electronic charges at the electrode and electrolyte interfaces for energy storage. As opposed to this, the energy storage effects of a pseudo capacitance process are produced at the electrode surfaces by a faradic (redox) process. Moreover, the energy storage process in EDL SCs is facilitated by the electron transfer mechanism, which is initiated by the ion accumulation in EDLs. On the other hand, all of the weight and volume are essential for charge storage in the case of pseudo capacitors. Because conducting polymers have both ionic and electronic conductivities, they are the ideal material for these two types of electrochemical devices. By doping other ionic or non-ionic compounds or fillers, these conductivity of the polymers that conduct can be further enhanced (Pal *et al.*[, 2021\)](#page-22-1).

### **Super Capacitor**

An electrical energy storage device that is solid state and capable of storing charges is a supercapacitor. Since it gets beyond many of the drawbacks of batteries, it is a breakthrough in the realm of energy storage. An overview of the many kinds of super capacitors and electrode materials and electrolytes, and super capacitors' future is given in this paper. Super capacitors have a large storage capacity, which makes them useful in hybrid cars and other applications as well as portable electronics like MP3 players and cell phones [\(Sharma and Kumar, 2020\)](#page-23-1).

Super capacitors are one of the electrical storage technique undergoing extensive developments in the last years. In the energy-power spectrum, capacitor takes an intermediate place between [batteries](https://www.sciencedirect.com/topics/engineering/battery-electrochemical-energy-engineering) and dielectric capacitors, delivering higher power densities than the former and higher energy densities than the latter. Typical values of energy and power densities of commercially available super capacitors are in the range of 4–5 Wh/kg and 10–20 kW/kg, correspondingly, but recent developments suggest that these figures can be overcome in the foreseeable future. Super capacitors (SCs) are regarded as one of the newest developments in energy storage technology. Their combined qualities of having a high energy density from batteries

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and a high power density from capacitors allow them to bridge the disparity between the two technologies. Carbon nanotubes (CNTs), activated carbons, porous graphite, and graphene are among the high-surface-area carbon-based nanostructures that are most frequently used as EDLC super capacitor electrode materials. But up until now, these carbon-based electrodes' very poor characteristic capacitance and high energy density have prevented their widespread use in practical systems. When compared to EDLCs, pseudo capacitors made of conducting polymers, metal hydroxides, or other metal oxides show noticeably greater specific capacitances. The insufficient electrical conductivity of commercially available redox capacitors continues to hinder their implementation. Pseudo capacitors continue to face challenges from inadequate electron transport and substantial material degradation during redox processes. As a result, in an effort to overcome these issues, numerous researchers have recently focused on developing hybrid materials that can combine the benefits of both carbon-based and pseudo capacitive materials in a way that works together for super capacitor applications [\(Yadav and Devi, 2020\)](#page-23-2).

Because of their easy synthesis, high conductivity, and low cost, conducting polymers are commonly employed as materials for electrodes for pseudo capacitors. Up to 2000 F g-1, conducting polymers, in particular poly aniline (Lim *[et al.](#page-22-2)*), have extraordinarily high theoretical capacitance. A tiny amount of poly aniline (Lim *[et al.](#page-22-2)*) could, however, contribute to the capacitances because the electrochemically accessible active surface area of PANI is highly dependent on both PANI conductivity and counter ion diffusion. As a result, PANI electrode experimental values are substantially lower than theoretical values. Furthermore, major volume variations would be experienced by the PANI species during cycles, and cycling stability is another issue that needs to be resolved. The readers are provided with an overview of the current state of PANI/graphene nano composites as super capacitor electrode materials through the presentation of recent advancements. PANI/graphene nano composites are synthesized and fabricated using various techniques, and their electrochemical performances are determined by multiple parameters that are also examined. There are also some suggested future prospects for PANI/graphene nano composites as well as issues that need to be resolved when combining PANI with graphene to create high-performance super capacitors [\(Huang](#page-22-3) *et al.*, 2018).

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To investigate graphene oxide's interactions with poly aniline, also known as PANI, and poly pyrrole (PPy), graphene oxide-based nano composites were created in the presence of aniline and pyrrole compound. In addition, the lack of functional groups containing oxygen was observed to result in a greater binding energy for poly pyrrole – graphene oxide compared to poly aniline– graphene oxide [\(Chauhan](#page-21-0) *et al.*, 2016). Smart capacitors (SCs) store energy through two types of capacitive nature: pseudo capacitance, which is caused by quick and reversible redox processes, and electric double-layer (EDL) capacitance, which results from the quick rush of the various electrostatic charges at the interior surface of the electrode and hydrolyte [\(Raghavendra](#page-23-3) *et al.*, [2020\)](#page-23-3).

### **Graphene supercapacitors**

Graphene's remarkable physical and chemical properties, along with its two-dimensional structure, have made it one of the most sought-after nano materials in recent years. Formally speaking, all  $sp<sup>2</sup>$  carbon allotropes, such as graphite, carbon nanotubes, and fullerenes, are thought to have originated from it. In the chemical, physical, and biological contexts, the material graphene and its related compounds hold great promise as innovative functional materials for use in electrical, energy-storage, liquid crystal, and other applications (Tian *et al.*[, 2019\)](#page-23-4).

From the 1870s to the present, the development of super capacitors has gone through many important processes: In the late 1950s, some scientists proposed replacing double-layer electrochemical capacitors made of metal sheets with capacitors made of porous carbon materials, and It has been proven by practice. In other words, electrochemical capacitors have made rapid progress at this time. In the 1950s of the 20th century, work on super capacitors began.

The US businesses General Electric Company (GE) and the Standard Oil Corporation of Ohio (SOHIO) carried out the initial trials in the 1950s and 1970s. About 1F was the capacity obtained by these initial electrochemical super capacitors. SOHIO was the patent holder of this kind of super capacitor in 1971. With an extremely high effective series resistance [\(Tekin](#page-23-5) *et al.*), Panasonic introduced the "Gold Cap," the first super capacitor, to the commercial marketplace in 1982. For military use, the Pinnacle Research Institute (PRI) created the first electric double-layer capacitors (EDLC) super capacitor in 1982. There was already a low ESR on this initial EDLC super capacitor. T

he world's first commercial super capacitor came out in 1971, which marked that super capacitors have begun to enter the market operation stage; in the 1980s, In the 1990s, due to the introduction of pseudo capacitive electrode materials, the energy density of super capacitors has been greatly improved, reaching a farad level that has never been reached before. Only then did the so-called electrochemical capacitors be called true super capacitors. Name; In the 1990s, the development prospects of super capacitors were valued by Western developed countries, and they have proposed major projects related to it.

In 1879, Helmholtz discovered the properties of double-layer capacitance and proposed the concept of electric double layer. However, the use of double-layer super capacitors for energy storage has only been in recent decades. In 1957, Becker (General Electric Co. GE) proposed using capacitors with a specific capacity close to the battery as energy storage components. In 1968, Sohio (The Standard Oil Company) used high specific surface area carbon materials to produce electric double layer capacitors. In 1978, Japan's Osaka Company produced gold capacitors, which were the earliest commercialized and mass-produced carbon electric double layer capacitors. In 1979, Nippon Electric Company, Limited began producing super capacitors and used them in starting systems for electric vehicles. In 1980, Japan's Panasonic Corporation studied super capacitors using activated carbon as electrode material and organic solution as electrolyte. After this, super capacitors began to be industrialized on a large scale. Following a decade, in 1992, Maxwell's Laboratories launched a variety of EDLC supra capacitors with reduced ESR, dubbed "Boost Cap," with a nominal capacity of 1 k F, onto the commercial market.

New hybrid-super capacitors have been developed. Since 2007, It was decided to build new hybrid super capacitors. Comparing this type of super capacitor to traditional EDLC super capacitors, it should be possible to achieve higher nominal voltage as well as higher volume and gravimetric energy density. Today's super capacitors can provide charging and discharging currents in the tenth to hundredth of an amp range and have capacities ranging from several thousand to several thousand farads [\(Libich](#page-22-4) *et al.*, 2018).

## **Advantages and Disadvantages of super capacitors (SCs)**

SCs have several disadvantages but also some benefits that set them apart from conventional storage devices. It seems sense to employ them in tandem when weighing the pros and downsides. The energy and power density values, as well as the charging duration, are linked to the benefits and drawbacks of different electrochemical storage devices. Many studies have compared the performance analysis of SCs with other storage devices, and the results have demonstrated that it makes sense in many ways to use SCs in addition to other storage devices. . Hybrid PV–battery SC storage systems for energy have been the subject of investigation about these superiorities. To clarify the probable future trend of SCs, it is important to thoroughly examine the commercial organizations and product circumstances, the market framework, and recent advancements in the industry.

The advantages of super capacitors over batteries and fuel cells, namely their extended cycle life and high power density resulting from fast charging and discharging, have drawn significant attention from both academia and industry. Super capacitors can store three to thirty times less charge than batteries because they can produce power in a volume that is hundreds or thousands of times greater than that of batteries. For applications that require an energy supply for longer periods of time, connection with cells is required. Because of this, super capacitors are suitable for applications where large storage capability is not needed but energy bursts are needed. They can also be added to battery-based energy storage systems (ESSs) to separate the device's power and energy functions, improving the device's sizing while meeting its power and energy requirements and possibly extending its lifespan (Pan *et al.*[, 2019\)](#page-22-5).

Super capacitors, or SCs, are thought to be a viable solution to the conflict between the rapidly expanding electrically powered devices and the incapacity of batteries to discharge at high rates efficiently. They are among the most promising prospects in the field of electrochemical energy storage. Electrical double-layered super capacitors (EDLCs) store energy through the electrostatic binding of electrolyte ions on the outer layer of the electrode active materials as a result of the

Remittances Review June 2024, Volume: 9, No: 3, pp.401-424 ISSN : 2059-6588(Print) | ISSN 2059-6596(Online) generated electric potential. This method differs from the idea of chemical reactions that are used to harvest the electrical power used in the batteries and fuel cells (Islam *et al.*[, 2022\)](#page-22-6).

## **Properties of Graphene**

Excellent physical-chemical, electrical, visual, thermal energy, and mechanical properties are provided by graphene's unusual atomic depth and hexagonal crystalline configuration of  $sp<sup>2</sup>$ bonded carbon atoms. You may think of graphene as just one layer of graphite, however instead of graphite's metallic characteristic, graphene shows a distinctive zero band gap and a semi-metal property. At room temperature, graphene, which exhibits a significant transport velocity from ~10,000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> along with at low temperature, 200,000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which corresponds to the resistivity of  $10^{-6}$  Ω. At low temperature, graphene's charge carriers have zero rest weight near their Dirac point, with an extremely high carrier density that ranges up to 1013 cm−2. (Lv *[et al.](#page-22-7)*, [2019\)](#page-22-7).

## **Graphene Oxides**

Graphene oxide is the graphene layer integrated with various oxygen-rich functional groups, such as the carboxyl group, hydroxyl, and epoxy groups. One possible explanation for the perforated cell membranes is that graphene oxide's sharp edges. Krishnamoorthy et al. (2012) suggested that individual E. coli cells might be encased in aggregated graphene nano sheets, therefore isolating them from their surrounding microbial environment. Using a polyamide membrane with graphene oxide integrated, E. coli growth was successfully suppressed. Graphene oxide embedded in a polyamide nano composite membrane induced a 1-hour drop in the colonies forming units (CFU) of Escherichia coli of 64.5%. Membranes made of graphene oxide nano composite also showed remarkable permeability (Wen *et al.*[, 2019\)](#page-23-6).



### **Graphene Based Polymer Nano Composite**

Carbon single planar sheets with sp2-bonded carbon atoms tightly arranged in a honeycomb pattern make up graphene, an allotrope of carbon. The basic component of other significant carbon allotropes is the honeycomb structure. Composed of many graphene sheets layered on top of one another and spaced apart by 3.37 Å, the graphite is a 3 dimensional carbon allotrope. By rolling graphene sheets, carbon nanotubes (CNTs) are a type of 1-D carbon allotrope [\(Othman](#page-22-8) *et al.*, [2019\)](#page-22-8).

### **Pollutant Removal Mechanism of Various Graphene-Based Membranes**

RO, adsorption, flocculation, exchange of ions, ultra-filtering, oxidation, the sedimentation process, the membrane and sophisticated oxidation procedures are among the wastewater treatment methods [\(Fatima](#page-22-9) *et al.*, 2024). The use of nano filtration to purify wastewater is becoming more popular, although it is still constrained by issues with swelling and interlayer spacing, which are critical to maximizing membrane performance [\(Ummer](#page-23-7) *et al.*, 2023). Depending on the solvent, the interlayer gap may change. Maximum membrane performance is achieved in liquids with higher solubility.

Through the use of a semipermeable membrane and membrane separation technology, a mixture can be selectively separated as it passes through. The goal of separation can be accomplished by the separation membrane's ability to efficiently regulate the transmission rate of tiny particles or ions, i.e., to let some molecules or ions pass through while effectively blocking others from doing so Energy-saving, highly efficient, environmentally benign, compact, and reusable are some of the benefits of membrane separation technology (Ullah *et al.*[, 2024\)](#page-23-8). In order to effectively treat chromite (hexavalent chromium) wastewater, membrane separation methods requires the selection of appropriate membrane materials. For oil-contaminated wastewater treatment processes, polycarbonate/multi walled Nanotube carbon composite materials are

Advanced nanotechnology, diverse nano materials, and membrane separation technology are combined. Materials for ultrafast molecular separation membranes are compact, thin, and come from a variety of sources. It is applicable to the water treatment industry as well as other sectors and has the ability to extract nano molecules from liquids or other solutions. It is a viable way to address energy and environmental issues (Du *et al.*[, 2019\)](#page-21-1).

## **Functionalization Procedures for Higher Performance Super Capacitor**

Graphene usually enhances charge dissociation, charge transport, and the mechanical characteristics of polymers when combined with a polymeric matrix. But for graphene and its derivatives to adequately mix with the polymer chains, they need to go through a functionalization step. There are numerous functionalization choices available to enhance the Graphene-polymer interaction. The two primary groups of techniques that these approaches fall into are non covalent and covalent schemes (covalent coupling of polymeric chains to G materials)



**Fig 2.** Schematic illustration of covalent and non-covalent functionalization approaches of graphene.

# **Preparation of Chemically Modified Graphene Oxide**

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Utilizing a modified Hummers technique, GO was created from expandable graphite. After dispersing 200 mg of GO in 100 mL of water that had been deionized and stirring it, an ultrasonic bath was used to sonicate the mixture for 30 minutes in order to create the chemically altered GO (CMGO). After the GO suspension was mixed for six hours with the addition of about one gram of KOH, the suspension's color turned via yellow to black. At 8,000 rpm, the suspension was centrifuged next. 1 g of KOH was incorporated while stirring, and the resulting residue was re dispersed in water that was deionized. Three iterations of this process were conducted. The suspension turned entirely dark black when the GO was finally fully functionalized with KOH, transforming it into CMGO.

## **Chemical Reduction of GO and CMGO**

In an oil bath with a temperature of 95°C, the GO was distributed in deionized water. Every time there was a reaction, the compound hydra the monohydrate form (1:5, GO/hydrazine) had been added and heated. Filtered and rinsed with water, the smaller amount of GO was baked for 24 hours at 80°C to dry it out. By using the identical reaction conditions for RGO on CMGO, the less CMGO (RCMGO) specimen was also produced. Labeled RGO into the mix-6, RGO-24, and RCMGO-24, respectively, were the samples of GO decreased for 6 hours, CMGO reduced for 24 hours without KOH treatment, and GO reduced for 24 hours [\(Rajagopalan and Chung, 2014\)](#page-23-9).



## **Applications of Graphene Based Materials**

Due to its exceptional structural and functional characteristics, graphene-based materials are used in many different cutting-edge applications. Graphene is being employed in a wide range of application industries, from aerospace to agriculture, as an outcome of decades of intensive research. Graphene-based materials find surprising applications in sensors, Li-ion batteries, solar cells, super capacitors, microbial fuel cells, and micron-sized membrane for wastewater treatment. Additionally, graphene nanoparticles are being employed for bio-imaging, prospective cancer therapeutics, gene therapy, tissue engineering, artificial bones, DNA sequencing, and medication delivery systems. Additionally, the high stiffness to weight ratio capabilities of grapheneincorporated fiber-reinforced composites are notably occupied the automotive, marine, and aerospace industries.

### **1. Graphene Applications in Bio-Medicine**

Three separate research groups led by Drndic, Dekker, and Golovchenko simultaneously developed effective graphene uses in biomedicine. DNA translocations across graphene membrane nano pores were demonstrated by Drndíc. The devices were made of graphene membranes ranging in thickness from 1 to 5 nm and featuring nano pores sculpted by electron beams with a diameter of 5 to 10 nm. Because the graphene membranes were so thin, the authors saw more obstructed currents than they would have with conventional solid-state nano pores. Ionic current noise levels, on the other hand, were orders of magnitude higher than those observed in silicon nitride nano pores. By applying a thin coating of 5 nm  $TiO<sub>2</sub>$  to the device, these oscillations were lessened.

As an outstanding electrical conductor, graphene differs from conventional solid-state nano pore nano materials that are insulators. Electrical sensing and control at the pore level are now possible because to the use of graphite as a material for membranes in a new class of the nano pore devices. DNA translocation via graphene nano pores was the subject of another study [\(Nguyen and](#page-22-11)  [Nguyen, 2016\)](#page-22-11). Graphene nano materials potential in regenerative medicine promises to revolutionize tissue repair and regeneration [\(Tehseen](#page-23-10) *et al.*).

### **2. Applications of Graphene Material and their Polymer Composites**

Many fields have begun to use composites because graphene reinforcement can give polymers multifunctional features. The performance of polymer nanocomposites based on graphene is essentially defined by three primary attributes [\(Haidri](#page-22-12) *et al.*, 2024).

1. Matrix polymer chains are nano scale imprisoned.

2. The considerable change in characteristics of inorganic constituents at the nanoscale, as revealed by multiple investigations, is related to their size

3. Arrangement of nanoparticles

## **Characterization of Graphene Based Material**

The materials must be thoroughly characterized using defined and verified characterization methodologies in order to perform an accurate hazard assessment. Considering the range of GBMs that are now on the market, all toxicology and pharmacological investigation s need to provide an overview of the physical and chemical features. The most often used methods for chemical characterization are elemental analysis, X-ray photoelectron spectrum (XPS), Raman spectroscopy, FTIR (Fourier transform infrared) spectral analysis, X-ray diffraction (XRD), and thermo gravimetric analysis (TGA). Information on the morphology and size of the material can be obtained using atomic force microscopy (AFM), electron microscopy with scanners (SEM), and transmission electron microscopy (TEM). An alternate assay based on macrophages has been proposed as the limulus amoebocyte lysates (LAL) assay, which is frequently used to determine the endotoxin concentration of nano- and biomaterials, is interfered with by GBMs, according to recent investigations. Endotoxin contamination can obscure or cause biologic effects of biomaterials to be misinterpreted, which would make them unsuitable for medical application.







# **Synthesis of Graphene-Nano Particle (GNP) Composites**

Graphene nano materials (NP) have been investigated for numerous possible uses. Interest in incorporating different metals, metal oxides, and semiconductors to create composite materials with improved characteristics increased following the discovery of graphene. On the other hand, there are a few problems that must be resolved in order to produce graphene NP composites. This comprises graphene sheet separation, non-uniform NP dispersion on the graphene sheets, and NP interaction[\(Dasari](#page-21-3) *et al.*, 2017).



**Fig 4.** Schematic illustration of the synthesis of hierarchically porous biomass-derived graphene-based materials (Jung *et al.*[, 2018\)](#page-22-13) available under a an open access CC BY license .

For the synthesis of graphene, several methods have been developed. Nonetheless, the techniques that are currently most frequently employed are thermal chemical vapor deposition, or CVD, synthesis, chemical exfoliation, mechanically cleaving (exfoliation), and chemical synthesis. There are also reports of additional methods, like microwave production and unzipping nanotubes. While few-layer graphene was shown to be able to be produced by mechanical exfoliation using an AFM cantilever, the technique was limited by the graphene's thickness, which fluctuates to about 10 nm, or thirty-layer graphene.



**Fig 5.** Flow sheet for the synthesis of graphene.

# **1. Bottom-Up Approach**

A summary is provided of the characteristics, average thickness, and size of the sheets of graphene generated by the various bottom-up techniques, along with the benefits and drawbacks of each technique [\(Bhuyan](#page-21-4) *et al.*, 2016).



**Table 2.** Summary of synthesis of graphene by bottom up method.

## **Chemical Vaporization Method (CVD)**

CVD is the process of using chemical processes to deposit material as a thin coating from vapour species onto surfaces. Many intricate variables, such as the system configuration, reactor arrangement, gas feedstock, gas ratios, reactor pressure, gas pressures that are partial, reaction temperatures, growth time, temperature, etc., control the process and kinds of the different possible reactions of chemicals that take place in a CVD reactor. One popular bottom-up method for synthesizing single- and few-layer graphene sheets is chemical vapor deposition (CVD). In 1966, it was first reported that extremely crystalline graphite films could be grown on Ni substrates using thermal CVD on metals [18]. Later, only one layer of graphene was deposited on the Pt surface via a CVD technique employing hydrocarbon breakdown at 530 °C. The processing parameters (temperature, stress, wall/substrate, nature of the precursors, depositing period of time, gas flow state, activation method) can be used to classify these methods into seven main categories based on these characteristics. The categories include nature of the precursor, depositing time, wall/substrate temperature, pressure, gas and flow rate.

### **Epitaxial Growth**

Epi means "above" in Greek, and taxis means "an ordered manner." These two roots are the source of the word epitaxy. According to the substrate's structure, it denotes the formation of a crystal layering on a crystalline substrate. "Epitaxial layer" refers to the layer that has been deposited. A viable technique to generate high-quality graphene in large quantities with consistent thickness is surface Si depletion-induced epitaxial graphene growth on SiC substrates. Among its benefits is the ability to construct electrical devices direct on semi-insulating SiC since the graphene layer need not be transferred to a different substrate. For this technique, commercially available SiCs up to 6 inches in diameter provide epitaxial conditions and come in p-and n-type semiconducting, semi-insulating, and other poly types, allowing for a variety of device designs [\(Sulaiman](#page-23-11) *et al.*, 2023). This process produces clean, ordered graphene because of the high temperature. Surface the graphitization process of SiC had been reported previously, produced graphene layers by means of the sublimation procedure. The method was initially carried out in a vacuum rather than an Ar atmosphere, however growth is usually carried out in an Ar high pressure atmosphere to enhance the epitaxial graphene film's homogeneity (Chen *et al.*[, 2021\)](#page-21-5).

#### **Spray Pyrolysis**

An appealing, affordable, and scalable method for material preparation is the aerosol-spray synthesis approach, which has shown a lot of promise. Simple, quick, continuous, and affordable methods can be used to create particles with intricate chemistry and architecture. The planning and manufacturing process of electrode materials for energy storage applications are highlighted here, along with recent developments in the commercially feasible aerosol-spray-pyrolysis approach. In terms of material manufacturing for high-performance energy-storage devices, aerosol-spray

Remittances Review June 2024, Volume: 9, No: 3, pp.401-424 ISSN : 2059-6588(Print) | ISSN 2059-6596(Online) pyrolysis is incredibly versatile and represents a significant advancement in multidimensional structure design (Nie *et al.*[, 2018\)](#page-22-14).

# **2. Top-Down Approach**

Exfoliating the layers that make up graphite, the 3D crystal from which graphene is derived, will yield graphene. There are two methods to achieve the exfoliation mechanism: chemical and electrochemical exfoliation, which involves introducing huge alkaloid ions through the graphite layers in a solution-dispersed graphite, and mechanical exfoliation, which involves applying an upward force which generates longitudinal research or diagonal stress on the surface of graphite [\(Gutiérrez-Cruz](#page-22-15) *et al.*, 2022)



**Table 3.** Summary of synthesis of graphene by top down.

## **Mechanical Exfoliation**

Over 285 nm of  $SiO<sub>2</sub>$ , the material being used is (100) Si. Graphene and WSe<sub>2</sub> were the two distinct bulk layered materials examined in this study. The sample is manually exfoliated using sticky tape. Following that, an in-house system operated the exfoliation process. A velocitycontrollable motor and two fixed stages make up the apparatus. Stage 1 is attached to the samples, and stage 2 is pushed onward by the motor while a piece of tape that is sticky is adhered to both the sample and stage 1. With double-sided adhesive, we are able to adhere the substrate to stage 2.

### **Micromechanical Cleavage**

Few top-down techniques, such as the scotch tape method, are available for mechanically exfoliating graphite. These techniques typically result in low yields or severely disrupted morphology in FLG, as is the situation with graphite that has been ball-milled. A pencil lead mechanically ablation on a rough glassy surface is one of the greatest yield techniques we published a few years ago. Aiming to separate the ablated (exfoliated) products, the glass surface was simultaneously ultrasonically sonicated in ethanol (water) to aid in the ablation process [\(Pirzado](#page-23-13) *et al.*, 2019).

### **Liquid Phase Exfoliation**

Similar to bulk  $MoS<sub>2</sub>$ , liquid phase exfoliation begins with flakes that have arbitrary sizes, shapes, and layer counts. That being said, the quality is lesser and the quantities are significantly bigger. Exfoliating  $MoS<sub>2</sub>$  in solution can be done in two ways, roughly. Sonication, shearing, churning, grinding, and bubbling are examples of mechanical exfoliation techniques. A small amount of chemistry might still be present, but the essence is entirely physical. Examples of surfactants that can be added to the solutions to stop the exfoliated granules from recombining include sodium deoxycholate (SDC), bile salt, and chitosan (Sun *et al.*[, 2017\)](#page-23-14).

#### **Electrochemical Reduction**

There has been a thorough analysis of the electrochemical degradation of GO.Other approaches using electrical chemistry techniques like cyclic voltammetry [\(Cvetek](#page-21-6) *et al.*) can be used to avoid the presence or functionalization of RGO sheets when combined with the reducing agent during chemically reduced processes, as well as the degeneration of the lowest plane during the procedure for reduction during thermal reduction [\(Agarwal and Zetterlund, 2021\)](#page-21-7).

#### **Thermal Exfoliation Reduction**

The material experiences a notable decrease in weight and an increase in volume upon heat reduction of GO. Currently, research is being conducted to identify the beginning temperature (325 °C at conventional atmospheric pressure) at which exfoliation begins to decrease. In terms of the percentage of carbon weight and lattice defect, reduction temperature is the most important factor influencing the degree of purity of reduced graphene oxide. Following the analysis, the graphene lattice's optimal temperature—350 °C at standard atmosphere pressure—is shown to have the highest content with the least amount of defects. Infrared spectroscopy using the Fourier transform, thermo gravimetric investigation, and thermal decomposition kinetics have all been used to examine the thermal reduction process. Based solely on temperature and the thermal breakdown kinetics of GO, it has been discovered that a rate of reaction is concentration-independent [\(Sengupta](#page-23-15) *et al.*, 2018).

### **Chemical Exfoliation**

Significant decrease in weight and material volume expansion result from the thermal reduction of GO. The current study looks at the temperature at which exfoliation starts to decrease, which is shown to be approximately 325 °C at the standard pressure of the atmosphere. The most important factor is reduction temperature, which regulates the lattice defect and weight ratio of carbon in reduced graphene oxide. The research results in the graphene lattice's maximum content and lowest defect at the ideal temperature, which is determined to be 350 °C at the average pressure of the atmosphere. Thermal degradation kinetics, thermogravimetric analysis, and infrared spectroscopy with the Fourier transform have all been used to evaluate the thermal reduction process [\(Perveen](#page-22-16) *et al.*)

#### **Electrochemical Exfoliation**

 Electrochemical exfoliating is also very interesting for the commercial use of graphene because of its potential for scaling up. The electromechanical exfoliation method has several advantages over other procedures, including ease of use, environmental friendliness, reduced processing time, and milder conditions at which it can be performed. Typically, this technique uses

proliferation of graphene/graphene at a large quantities graphite [\(Kumar](#page-22-17) *et al.*, 2021).



**Figure 6.** Schematic of the most common graphene production methods. Each method has been evaluated in terms of graphene quality (G), cost aspect (C; a low value corresponds to high cost of production), scalability  $(S)$ , purity  $(P)$ , and yield  $(Y)$  of the overall production process (self generated).

## **Conclusion**

It has been summarize that a single covering of atoms of carbon organized in a lattice that is hexagonal makes up the two-dimensional substance known as graphene. It has exceptional mechanical, thermal, and electrical qualities. Materials called graphene nano composites are created by combining graphene with other materials to create hybrid structures, such as metals, polymers, oxides of metals or other carbon-based compounds. Graphene oxide (GO) is chemically reduced using a variety of methods, such as chemically vaporizing deposition (CVD), liquid-phase exfoliation, mechanical exfoliation, and chemical reduction. The resulting nano composites' form, structure, and characteristics are influenced by the production method selected. Effective charge transfer between the super capacitor electrodes is made possible by graphene's high electrical conductivity, which also increases the nano composite's overall conductivity. Because of its

enormous surface area, graphene exhibits enhanced electrode-electrolyte interaction, leading to better capacitance and energy storage.

The use of graphene improves the nano composite's mechanical characteristics and guarantees mechanical stability over charge-discharge cycles. The chemical inertness of graphene helps to stabilize the nano composite and slows down its breakdown over time. Flexibility is a property of graphene nano composites, which makes them appropriate for wearable and flexible electronics applications, depending on the matrix material and production technique used. The high specific capacitance, quick charge-discharge rates, and extended cycle life of graphene nano composites have prompted much investigation into their potential for use in super capacitors. Lithium-ion batteries fuel cells and other devices that store energy could benefit from the application of graphene nano composites in addition to super capacitors. Environmental, gas, and biosensor are just a few of the sensing applications that graphene nano composites are well-suited for due to their high sensitivity and surface area. In conclusion, research into perfecting the characteristics, fabrication processes, and various uses of graphene nano composites in energy storage and other fields is underway. These efforts are expected to yield greater performance super capacitors.

## **References**

- <span id="page-21-7"></span>Agarwal, V. and P.B. Zetterlund. 2021. Strategies for reduction of graphene oxide–A comprehensive review. Chemical Engineering Journal 405: 127018.
- <span id="page-21-4"></span>Bhuyan, M.S.A., M.N. Uddin, M.M. Islam, F.A. Bipasha and S.S. Hossain. 2016. Synthesis of graphene. International Nano Letters 6: 65-83.
- <span id="page-21-0"></span>Chauhan, N.P.S., M. Mozafari, N.S. Chundawat, K. Meghwal, R. Ameta and S.C. Ameta. 2016. Highperformance supercapacitors based on polyaniline–graphene nanocomposites: Some approaches, challenges and opportunities. Journal of Industrial and Engineering Chemistry 36: 13-29.
- <span id="page-21-5"></span>Chen, Z., C. Xie, W. Wang, J. Zhao, B. Liu, J. Shan, X. Wang, M. Hong, L. Lin and L. Huang. 2021. Direct growth of wafer-scale highly oriented graphene on sapphire. Science Advances 7: eabk0115.
- <span id="page-21-6"></span>Cvetek, D., M. Muštra, N. Jelušić and L. Tišljarić. 2021. A survey of methods and technologies for congestion estimation based on multisource data fusion. Applied Sciences 11: 2306.
- <span id="page-21-3"></span>Dasari, B.L., J.M. Nouri, D. Brabazon and S. Naher. 2017. Graphene and derivatives–Synthesis techniques, properties and their energy applications. Energy 140: 766-778.
- <span id="page-21-1"></span>Du, Y.C., L.J. Huang, Y.X. Wang, K. Yang, J.G. Tang, Y. Wang, M.M. Cheng, Y. Zhang, M.J. Kipper and L.A. Belfiore. 2019. Recent developments in graphene‐based polymer composite membranes: Preparation, mass transfer mechanism, and applications. Journal of Applied Polymer Science 136: 47761.
- <span id="page-21-2"></span>Fadeel, B., C. Bussy, S. Merino, E. Vázquez, E. Flahaut, F. Mouchet, L. Evariste, L. Gauthier, A.J. Koivisto and U. Vogel. 2018. Safety assessment of graphene-based materials: focus on human health and the environment. ACS nano 12: 10582-10620.

Volume: 9, No: 3, pp.401-424

ISSN : 2059-6588(Print) | ISSN 2059-6596(Online)

- <span id="page-22-9"></span>Fatima, R., U. Basharat, A. Safdar, I. Haidri, A. Fatima, A. Mahmood, Q. Ullah, K. Ummer and M. Qasim. 2024. AVAILABILITY OF PHOSPHOROUS TO THE SOIL, THEIR SIGNIFICANCE FOR ROOTS OF PLANTS AND ENVIRONMENT. EPH-International Journal of Agriculture and Environmental Research 10: 21-34.
- <span id="page-22-15"></span>Gutiérrez-Cruz, A., A.R. Ruiz-Hernández, J.F. Vega-Clemente, D.G. Luna-Gazcón and J. Campos-Delgado. 2022. A review of top-down and bottom-up synthesis methods for the production of graphene, graphene oxide and reduced graphene oxide. Journal of Materials Science 57: 14543- 14578.
- <span id="page-22-12"></span>Haidri, I., N. Fatima, M. Abdullah, A. Ilyas, A. Parveen, R. Afzal, M. Shahbaz, M. Batool and M. Qasim. 2024. SYNTHESIS CHARACTERIZATION AND APPLICATIONS OF NANOPARTICLES IN ENVIRONMENTAL DETOXIFICATION. EPH-International Journal of Agriculture and Environmental Research 10: 43-57.
- <span id="page-22-10"></span>Haidri, I., M. Qasim, M. Shahid, M.M. Farooq, M.Q. Abbas, R. Fatima, W. Shoukat and Q. Ullah. 2024. Enhancing the Antioxidant Enzyme Activities and Soil Microbial Biomass of tomato plants against the stress of Sodium Dodecyl Sulfate by the application of bamboo biochar. Remittances Review 9: 1609-1633.
- <span id="page-22-0"></span>Huang, S., X. Zhu, S. Sarkar and Y. Zhao. 2019. Challenges and opportunities for supercapacitors. Apl Materials 7.
- <span id="page-22-3"></span>Huang, Z., L. Li, Y. Wang, C. Zhang and T. Liu. 2018. Polyaniline/graphene nanocomposites towards highperformance supercapacitors: A review. Composites Communications 8: 83-91.
- <span id="page-22-6"></span>Islam, M.S., Y. Shudo and S. Hayami. 2022. Energy conversion and storage in fuel cells and supercapacitors from chemical modifications of carbon allotropes: State-of-art and prospect. Bulletin of the Chemical Society of Japan 95: 1-25.
- <span id="page-22-13"></span>Jung, S., Y. Myung, B.N. Kim, I.G. Kim, I.-K. You and T. Kim. 2018. Activated biomass-derived graphenebased carbons for supercapacitors with high energy and power density. Scientific reports 8: 1915.
- <span id="page-22-17"></span>Kumar, N., R. Salehiyan, V. Chauke, O.J. Botlhoko, K. Setshedi, M. Scriba, M. Masukume and S.S. Ray. 2021. Top-down synthesis of graphene: A comprehensive review. FlatChem 27: 100224.
- <span id="page-22-4"></span>Libich, J., J. Máca, J. Vondrák, O. Čech and M. Sedlaříková. 2018. Supercapacitors: Properties and applications. Journal of energy storage 17: 224-227.
- <span id="page-22-2"></span>Lim, S.S., J.-M. Fontmorin, P. Izadi, W.R.W. Daud, K. Scott and E.H. Yu. 2020. Impact of applied cell voltage on the performance of a microbial electrolysis cell fully catalysed by microorganisms. International Journal of Hydrogen Energy 45: 2557-2568.
- <span id="page-22-7"></span>Lv, C., C. Hu, J. Luo, S. Liu, Y. Qiao, Z. Zhang, J. Song, Y. Shi, J. Cai and A. Watanabe. 2019. Recent advances in graphene-based humidity sensors. Nanomaterials 9: 422.
- <span id="page-22-11"></span>Nguyen, B.H. and V.H. Nguyen. 2016. Promising applications of graphene and graphene-based nanostructures. Advances in Natural Sciences: Nanoscience and Nanotechnology 7: 023002.
- <span id="page-22-14"></span>Nie, P., G. Xu, J. Jiang, H. Dou, Y. Wu, Y. Zhang, J. Wang, M. Shi, R. Fu and X. Zhang. 2018. Aerosol‐ spray pyrolysis toward preparation of nanostructured materials for batteries and supercapacitors. Small Methods 2: 1700272.
- <span id="page-22-8"></span>Othman, N.H., M.C. Ismail, M. Mustapha, N. Sallih, K.E. Kee and R.A. Jaal. 2019. Graphene-based polymer nanocomposites as barrier coatings for corrosion protection. Progress in Organic Coatings 135: 82-99.
- <span id="page-22-1"></span>Pal, R., S.L. Goyal, I. Rawal and A.K. Gupta. 2021. Efficient energy storage performance of electrochemical supercapacitors based on polyaniline/graphene nanocomposite electrodes. Journal of Physics and Chemistry of Solids 154: 110057.
- <span id="page-22-5"></span>Pan, Y., K. Xu and C. Wu. 2019. Recent progress in supercapacitors based on the advanced carbon electrodes. Nanotechnology Reviews 8: 299-314.
- <span id="page-22-16"></span>Perveen, S., I.A. Bhatti, S. Jamil, A. Ghaffar, A. Faiz and R. Sulaiman. Carbon Dots: Synthetic Routes, Optical Properties, and Emerging Applications.

Volume: 9, No: 3, pp.401-424

ISSN : 2059-6588(Print) | ISSN 2059-6596(Online)

- <span id="page-23-13"></span>Pirzado, A.A., F. Le Normand, T. Romero, S. Paszkiewicz, V. Papaefthimiou, D. Ihiawakrim and I. Janowska. 2019. Few-layer graphene from mechanical exfoliation of graphite-based materials: Structure-dependent characteristics. ChemEngineering 3: 37.
- <span id="page-23-3"></span>Raghavendra, K.V.G., R. Vinoth, K. Zeb, C.V.M. Gopi, S. Sambasivam, M.R. Kummara, I.M. Obaidat and H.J. Kim. 2020. An intuitive review of supercapacitors with recent progress and novel device applications. Journal of energy storage 31: 101652.
- <span id="page-23-9"></span>Rajagopalan, B. and J.S. Chung. 2014. Reduced chemically modified graphene oxide for supercapacitor electrode. Nanoscale research letters 9: 1-10.
- <span id="page-23-15"></span>Sengupta, I., S. Chakraborty, M. Talukdar, S.K. Pal and S. Chakraborty. 2018. Thermal reduction of graphene oxide: How temperature influences purity. Journal of Materials Research 33: 4113-4122.
- <span id="page-23-1"></span>Sharma, P. and V. Kumar. 2020. Current technology of supercapacitors: a review. Journal of Electronic Materials 49: 3520-3532.
- <span id="page-23-11"></span>Sulaiman, R., A. Ghaffar, S. Perveen, D. Ashraf, I. Tariq and T. Shakir. 2023. Synthesis, Characterization, and Biomedical Applications of Zinc Oxide Nanoparticles. BME Horizon 1.
- <span id="page-23-14"></span>Sun, J., X. Li, W. Guo, M. Zhao, X. Fan, Y. Dong, C. Xu, J. Deng and Y. Fu. 2017. Synthesis methods of two-dimensional MoS2: A brief review. Crystals 7: 198.
- <span id="page-23-10"></span>Tehseen, P., U. Mahmood, F. Gulzar, R. Afzal, A. Ghaffar, I. Nawaz, I. Rafiq, M. Jabeen, A. Abbas and R. Saleem10. Journal of Population Therapeutics & Clinical Pharmacology.
- <span id="page-23-5"></span>Tekin, G., S. Yıltay and E. Ayaz. 2016. The effect of Brand image on consumer behaviour: case study of louiss Vuitton-Moet hennessy. International Journal of Academic Values Studies: 1-24.
- <span id="page-23-4"></span>Tian, J., L. Guo, X. Yin and W. Wu. 2019. The liquid-phase preparation of graphene by shear exfoliation with graphite oxide as a dispersant. Materials Chemistry and Physics 223: 1-8.
- <span id="page-23-8"></span>Ullah, Q., M. Qasim, A. Abaidullah, R. Afzal, A. Mahmood, A. Fatima and I. Haidri. 2024. EXPLORING THE INFLUENCE OF NANOPARTICLES AND PGPRS ON THE PHYSICO-CHEMICAL CHARACTERISTICS OF WHEAT PLANTS: A REVIEW. EPH-International Journal of Agriculture and Environmental Research 10: 1-9.
- <span id="page-23-7"></span>Ummer, K., W. Khan, M.A. Iqbal, M.Q. Abbas, R. Batool, R. Afzal, Q. Ullah, M. Qasim and I. Haidri. 2023. THE INTRICACIES OF PHOTOCHEMICAL SMOG: FROM MOLECULAR INTERACTIONS TO ENVIRONMENTAL IMPACT. EPH-International Journal of Applied Science 9: 23-33.
- <span id="page-23-6"></span>Wen, Y., J. Yuan, X. Ma, S. Wang and Y. Liu. 2019. Polymeric nanocomposite membranes for water treatment: a review. Environmental Chemistry Letters 17: 1539-1551.
- <span id="page-23-2"></span>Yadav, S. and A. Devi. 2020. Recent advancements of metal oxides/Nitrogen-doped graphene nanocomposites for supercapacitor electrode materials. Journal of Energy Storage 30: 101486.
- <span id="page-23-0"></span>Yadlapalli, R.T., R.R. Alla, R. Kandipati and A. Kotapati. 2022. Super capacitors for energy storage: Progress, applications and challenges. Journal of Energy Storage 49: 104194.
- <span id="page-23-12"></span>Yuan, L., J. Ge, X. Peng, Q. Zhang, Z. Wu, Y. Jian, X. Xiong, H. Yin and J. Han. 2016. A reliable way of mechanical exfoliation of large scale two dimensional materials with high quality. AIP Advances 6.