# Graphene-based materials and their composites: A review on production, applications and product limitations

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## ABSTRACT

Recent years have perceived many innovations in research and advancement of graphene, the thinnest two-dimensional atomic material. Graphene-based materials and their composites possess promising applications in wide range of fields such as, electronics, biomedical aids, membranes, flexible wearable sensors and actuators. The latest studies and progression in this subject area often produce inconsistent or inconclusive results. This review article assesses and summarises published data so as to provide a critical and comprehensive overview of state of the art. Firstly, the distinct structural nature of the graphene materials available is elucidated, as well as different production techniques available thus far. The assessment then discusses the various composites focusing different sub-functional regimes such as mechanical and collective functional applications such as energy, electronics biomedical, membranes and sensors. The utilisation of graphene and its derivatives in the manufacture of nanocomposites with different polymer matrices has been reconnoitred. Finally, a conclusion and perspective are given to discussing the remaining challenges for graphene nanocomposites in functional science and engineering.

## Nomenclature and abbreviations

| | |
|---|---|
| $ | American dollar |
| ± | Represents the standard deviation |
| ~ | Approximately |
| ˚C | Degree Celsius |
| μm and nm | Micrometre and Nanometre |
| 2D and 3D | 2-dimentional and 3-dimentional |
| a.u. | Arbitrary units |
| ASTM | American society for testing and materials |
| Atm | Atmospheric |
| Cm and mm | Centimetre and millimetre |
| $cm^{-1}$ | The wavenumber/per centimetre |
| CMG | Chemically modified graphene |
| CO | Carbon monoxide gas |
| DC, dc | Direct current |
| DI | Deionised |
| eV | Electron volt |
| frGO | Functionalised reduced graphene oxide |
| G | Gram(s) |
| GNS and GNP | Graphene nanoplatelets |
| Gr | Graphene |
| H | Hour(s), Time |
| Kg/kg | Kilogram |
| L or l and ml | Litre(s) and millilitre |
| Ltd. | Limited (A business incorporated under the laws of England) |
| MGr and MGrS | Modified graphene and modified graphene sheets |
| $MI/m^3$ | The units of the energy dissipated in the composites over the loading |
| Min | Minute |
| Mmol and ppm | Millimole and Parts per mole |
| Mol | Mole |
| MPa and GPa | Megapascal and Gigapascal |
| $M_w$ | Molecular weight |
| N | Newton |

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| S.cm$^{-1}$/<br>S.m$^{-1}$ | Siemens per centimetre/Siemens per metre |
|---|---|
| T$_g$ | Glass transition temperature |
| TrGO | Thermally reduced graphene oxide |
| vol.% | Volume percentage |
| Wt.% | Weight percentage |
| Λ | Wavelength |
| Π | Pi |
| σ and ρ | Electrical conductivity and Electrical resistivity |

*For graphene family, general nomenclature suggested by Bianco *et al.* [1].

## 1. Introduction

The arena of nanoscience, nanotechnology and nanocomposites has bloomed in recent times and the importance of this subject matter increase in the variety of applications as automotive, aerospace, packaging, electronics, biotechnology, flexible sensors, and many other applications [2–4]. In this regard, the innovations polymer nanocomposites based on graphene materials have become a most significant addition. Graphene is a 2D structure of carbon atoms with hexagonal crystalline structure with sp$^2$ bonds. It has a high surface area (highest, adsorption and surface reactions), electron mobility, thermal conductivity and mechanical strength. With highest surface area compared to any other material of this kind, it enhances the interaction between the sheets and polymer material. It has applications in various fields including electronics and biomedical [5,6]. Graphene-based composite materials are of material scientist's interest today, for their structural fabrications would result in better properties leading to newer applications. Extensive research and development have materialised on graphene reinforced polymer composites in the last two decades. Adding graphene as a reinforcing agent in a polymer matrix has improved the overall performance and properties of such composites, which has been reported by almost all of these researchers who worked in this area [7]. The primary interest of utilising graphene materials has come due to its unique excellent mechanical, thermal, electrical and physicochemical properties, notably its thin physical existence [8,9]. These promising properties have generated widespread efforts to apply graphene in all fields of technologies [10–12]. In the following sections, we summarise latest outcomes in graphene (and its derivatives) production techniques, properties and inventions in their composites area. Furthermore, as an important part of this review, we also conclude environmental applications and toxicity and safe handling protocols to mitigate associated health implications while using graphene nanomaterials; this will give useful information for the research of this area. The growth of this research section can be evident from the publication record shown in Fig. 1.

### 1.1. Concept of graphene materials

Graphene, the thinnest material in existance, has high thermal conductivity, quantum hall effect, mechanical good with high Young's modulus (1 TPa) and intrinsic strength of 130 GPa, high optical transmittance and high electronic transport, barrier and flame retardant properties owing to their zero bad gaps [5,13–17] as a single sheet. With gate voltage, it exhibits ambipolar electric field effect. A model of non-interrelating massless Dirac fermions had shown that a single layer of graphene absorbs 2.3% light and the breaking strength of the material was found as 42 Nm$^{-1}$ [18]. Graphene is the basic structure of all other carbon allotropes as depicted in Fig. 2.

It is well noted that graphene and its derivatives' potential applications are mainly driven by progressive production of different graphene materials (GO, rGO, fGO, frGO and mG) with particular focus on specific applications and this is expected to be continued for at least a couple of decades as it is meeting promising applications and requirements. There are a range of processes and techniques (Fig. 3) have been advanced, and most of them will be covered in the following section and categorise promising as well as scalable methods.

Graphene oxide (GO) has been popularly used as nanofiller for fibre reinforced polymer composites [20–22]. GO can be chemically coated onto the surfaces of either carbon fibre or carbon fabric to augment the interfacial bonding properties through surrounding polymer matrix of the composites [6-7,23,24]. By coating them onto the fibre would enhance the bonding strength due to the increase of surface friction of the fibre and the ultimate fibre pull out strength would be increased. However, the process may be too complicated and costly due to the treatment of each fibre is needed. Hung *et al.* [20] coated the GO on the surface of fabrics by an electrophoretic deposition method, to boost the interlaminar shear strength of composites. The process is relatively simple and faster. The UTS and Young's modulus of the composites were improved at the low-temperature condition, which is service temperature range of typical aircraft flying at tropopause layer.

Recently, GO is also used as a dielectric material for the purpose of energy storage. A thin layer of GO film is inserted between carbon fabric layers which act an electrode to form a structural capacitor. Due to the increasing demand for unmanned air vehicles (UAVs), the energy storage capacity and weight of battery always limit their fight duration. GO film can be an effective medium to storage energy in the range between 15 and 1500 V, to support the power for the UAVs, in which the energy is captured from the solar panels attached onto the surface of structures [8]. In this design, the UAVs can support energy by themselves during the flight mission.

## 2. Modern preparation methods: an overview of synthesis, reduction and functionalisation of graphene derivatives

Most of the research studies have not used graphene in its pure form (pristine graphene) due to its limited yield from the preparation point of view. Moreover, graphene derivatives such as GO, rGO and frGO have become more commonly available and showcase similar properties to that of graphene. Though, because of heteroatomic irregularity as well as an impurity and structural defects, it is deceptive to denote such materials as graphene, which most researchers do and should be corrected with a proper and standardised nomenclature in the future. Interestingly, not much has been progressed in the synthetic procedures or modifications of synthetic techniques used to produce rGO since Boehm *et al.* first described the reduction of GO suspension with a several of chemical reducing agents [53,54] besides by thermal reduction [25].

### 2.1. Synthesis

Micro-mechanical exfoliation, chemical vapour deposition (CVD), liquid phase reduction of graphene oxide and epitaxial growth are the four different synthetic methods of graphene [9]. They are grouped as a top-down or bottom-up approach. Among these methods, low cost and high throughput material are obtained through direct liquid phase exfoliation. Hummers and Offeman 1958 had defined a method to produce graphene oxide from graphene which is still used as a major method [26]. The graphene and their derivatives are produced via major techniques as shown in Fig. 4.

There are different methods to synthesise graphene oxide/graphene, with the quality and quantity of the yield depending on the method. Fig. 4 shows various methods to prepare graphene oxide and its derivatives, but for this work, the source material will be graphite, oxidised to exfoliate graphene oxide layer from the bulk.

### 2.1.1. Liquid phase exfoliation

Graphite oxide was first ever prepared by Brodie [32] through oxidation of graphite with potassium chlorate (KClO$_3$) in a graphite and nitric acid (HNO$_3$) mixture. Staudenmaier further extended Brodie's work by varying the acidity of the graphite and HNO$_3$ mixture and