Review

General overview of graphene: Production, properties and application in polymer composites

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ABSTRACT

Graphene is a new and exciting material that has attracted much attention in the last decade and is being extensively explored because of its properties, which have been described with so many superlatives. Production of graphene for large scale application is still a major challenge. Top-down graphene exfoliation methods from graphite, such as liquid-phase exfoliation which is promising because of low cost and high scalability potential will be briefly discussed. We also analyze the challenges and possibilities of using graphene as a nanofiller in polymer composites which has resulted in enhanced electrical, mechanical and thermal properties. In this review, we take a panoramic approach to give insight on the different aspects of graphene such as properties, graphite-based production methods and also examples of graphene application in polymer composites and which will be beneficial to both novice and experts.

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Contents

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1. Introduction

Graphene was successfully exfoliated just over a decade ago [1]. The discovery of free standing graphene by Andre Geim and Konstantin Novoselov at the University of Manchester in 2004 led to the award of the Nobel Prize in Physics 2010 "for groundbreaking experiments regarding the two-dimensional material graphene" [2,3]. Since then, there has been tremendous interest from academia, industries and government institutions in exploration of graphene properties, production methods and potential applications [4–6].

Graphene is a two-dimensional single layer of sp^2 bonded carbon atoms arranged in a hexagonal lattice. These carbon atoms are bonded together at the length of 0.142 nm [7], as shown in Fig. 1. In other words, graphene is a building block for all graphitic materials. It can be wrapped into 0-dimensional fullerenes, rolled into 1-dimensional carbon nanotubes and stacked into 3-dimensional graphite, as summarized in Fig. 2.

The exceptional interest in graphene is not surprising given the various excellent mechanical and chemical properties exhibited by graphene, such as high surface area (2630 $m^2 g^{-1}$) [8], excellent thermal conductivity (5000 $W m^{-1} K^{-1}$) [9], high electron mobility at room temperature around 250,000 $cm^2 V^{-1} s^{-1}$ at electron densities of $2 \times 10^{11} cm^{-2}$ [10], very high Young's modulus 1 TPa [11], very high light transmittance ~98% [12], excellent gas impermeability despite only being single atom thick, chemical stability, anomalous quantum Hall effect (QHE) etc. [1,13–18]. Due to these properties, graphene has found a wide range of potential applications, from medical to paper to electronics to composite materials etc. [19–23]. Graphene can also be modified to generate a band gap that can lead to application in the semiconductor industry for developing devices such as transistors [21,24–26]. Due to all these unique properties, graphene has been often called a "supermaterial" or "miracle material" in the world of materials science.

Before the successful exfoliation of free standing graphene in 2004, scientists believed that two-dimensional materials could not exist independently because of their being thermodynamically unstable at finite temperature, and, therefore, would be expected to decompose, crumple or collapse into other stable carbon allotropes [27,28]. However, graphene is able to remain stable because of the atomic scale ripples that occur on the surface, acting to minimize surface energy [29].

2. Scope of review

The interest in graphene research from 2004 has increased exponentially. Several reviews about graphene have been published all with a different focus [15,27,28,30–34]. In this review, rather, we shall consider a panoramic approach of the synthesis methods of graphene (particularly from graphite), and some properties and application in polymer composites. When needed, the reader will be directed to a more detailed reference.

In the synthesis section, we consider only the methods that use graphite as a raw material. The second part briefly looks at the main properties of graphene. The last part includes a few examples of graphene application in polymer composites and how their properties are enhanced by graphene fillers. The economic aspect of graphene is also briefly considered.

3. Fabrication of graphene

One of the major challenges of graphene since it was discovered has been finding a fabrication method that can not only produce high quality graphene but also at large scale. Utilization of graphene by various industries depends mostly on finding fabrication methods for large scale production. The current lack of viable large scale production method has hindered large scale industrial application of graphene despite its excellent properties. Some of the methods that have been reported so far range from mechanical and chemical exfoliation of graphite include [1,20], epitaxial growth of graphene on silicon carbide (SiC) [35,36], titanium carbide (TiC) [37], tantalum carbide (TaC) [38], and different metal substrates, such as Ni, Cu, Pt, Ru, Ir, Co etc. [39–42], and graphene formed from un-zipping of carbon nanotubes [43–45], solvothermal synthesis [46], organic synthesis [47], chemical vapor deposi-
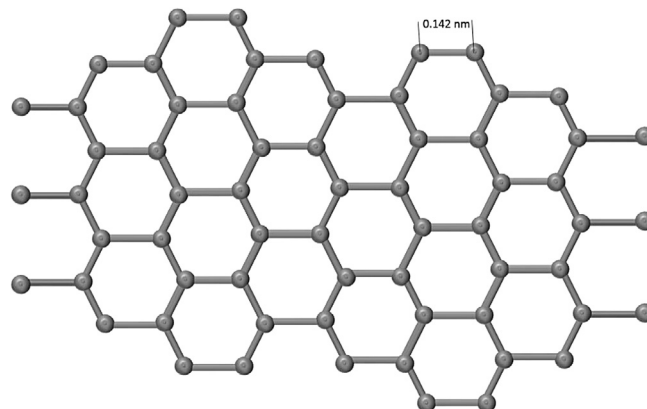

Fig. 1. Carbon atoms bonded in a honeycomb lattice, showing C—C bond length of 0.142 nm in graphene structure.
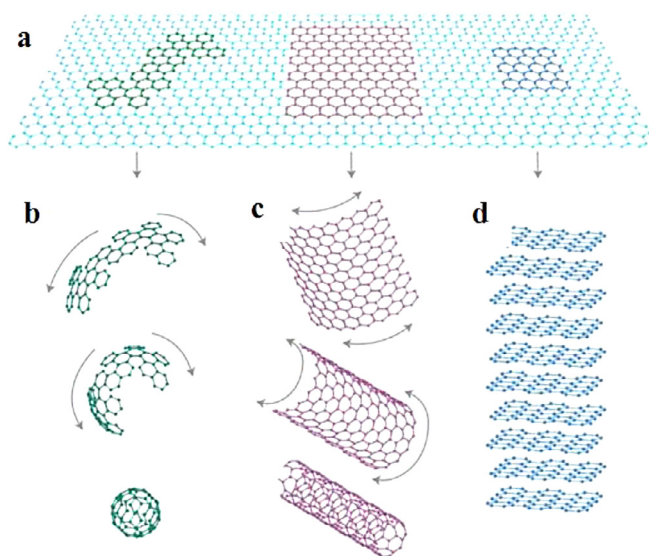
Fig. 2. Allotropes of carbon: a) 2-D graphene b) 0-D fullerene, c) 1-D carbon nanotube d) 3-D graphite. Reproduced with permission from Ref. [27]. Copyright: 2007 Nature Publishing Group.

tion methods (CVD) [48–50], and synthesis of graphene from graphite oxide *via* oxidation of graphite [22,51–54]. Some of these methods are depicted in Fig. 3, and each method can be utilized depending on the application and desired quality of graphene.

Graphite is a highly anisotropic natural mineral [56] that has been known for hundreds of years and is used as a lubricant, for electrodes and pencil lead. The thermal and electrical conductivities of in-plane graphite are about a thousand times higher than out-of-plane, which is also a similar scenario with strength and modulus [57]. Graphite is made up of single sheets of stacked graphene held together by the weak van der Waals forces. These sheets can be peeled off by application of a force that exceeds these forces. Since graphite is low cost and readily available, production of graphene based on exfoliation of graphite may be considered to have huge potential for large scale application [58].

One other method that has been reported for production of graphene is from biomass [59–62]. This is also an interesting method given the nature of biomass, i.e. its low cost, sustainability and non-toxic nature. Therefore, it is probably safe to say that it already has potential for scalability [62]. Given that the biorefinery industry is already well established, graphene production could, in principle, easily be integrated into a biorefinery facility. However, prior to this eventuality, a lot of effort is needed from the research community to develop and optimize the methodology for high quality graphene production from biomass.

Graphene derivatives such as graphene oxide, graphane, graphene fluoride *etc.* have shown interesting functional properties that could be utilized in various applications [63–65]. In this review however, only graphene oxide is considered. Detailed discussion regarding graphene derivatives can be found in the following publications [65–69].

This section will continue by briefly summarizing some of the main methods that have utilized graphite as a raw material for graphene production.

3.1. Micromechanical cleavage

Micromechanical cleavage (MC), also known as micromechanical exfoliation or the Scotch tape method is an old method that has been around for decades and extensively used in fields such as

crystallography [70]. Amongst the graphene research community, micromechanical cleavage is one of the most popular methods for graphene production – not surprising given that it led to the 'birth of graphene' [1]. The MC method is a simple method that does not require any special equipment. The only 'equipment' required basically is an adhesive tape. Graphite flakes are placed between the adhesive tape and the surface is peeled off continuously. This continuous peeling of graphite causes the cleaved thin flakes to adhere to the surface with almost an atomically clean flat surface [71]. To get few-layer and even single-layer graphene sheets, a clean tape is used to peel off the first flakes that stack to the surface and this continuous repeating process, i.e. peeling and replacing with a new tape breaks the flakes into thinner and thinner flakes until smooth single layers are achieved [72].

Geim et al. [1] used a thick highly oriented pyrolytic graphite (HOPG) and scotch tape method to produce a free-standing graphene sheet by repeated peeling of graphite as described above. In order to transfer the flake to the substrate, the tape was then dissolved in acetone and an oxidized Si wafer was dipped in the solution were some flakes were deposited on the surface of the Si wafer. The adherence force between graphene and the oxidized Si substrate is believed to be due to van der Waals and/or capillary forces. They were able to exfoliate graphite to few-layer and even single-layer graphene sheets with lateral sizes up to 10 μm. They used these deposited flakes to study thoroughly the electrical and electronic properties of graphene [1].

Graphene is not the only material that can be produced with the Scotch tape technique, in fact other 2-dimensional materials can also be produced using this technique [73,74]. For example, Geim et al. [16] used the MC technique to exfoliate other 2-dimensional materials such as molybdenum disilicide, boron nitride, and the compound oxide of bismuth-strontium-calcium-copper ($Bi_2Sr_2CaCu_2O_x$).

Although the mechanical cleavage technique is a versatile and simple method for fabrication of defect free graphene, scalability is still the main challenge. Despite the drawbacks, micromechanical exfoliation still remains the popular choice for fundamental research because of the high quality of the produced graphene flakes. The majority of the new graphene properties discovered and the potential application in new device prototypes have been achieved using mechanically cleaved graphene flakes. It is clear that the MC method did not only start the graphene revolution but still remains the main tool for further exploration of graphene properties and potential applications.

3.2. Liquid-phase exfoliation

Liquid phase exfoliation (LPE) can be used to exfoliate graphite in different liquid media *via* ultrasound or shear forces to extract single to few-layer graphene sheets (Fig. 4). Graphite is held together by the weak van der Waals, therefore the first step to successful exfoliation of graphene is to overcome these forces. Wang et al. [75] estimated the surface energy of graphene to be 46.7 mN m^{-1}. Therefore, the suitable liquid medium should have similar surface energy in order to minimize the interfacial tension between the solvent and the graphene layers [76]. Some of the solvents that have been successfully used to exfoliate and stabilize graphene include, but not limited to, N-methylpyrrolidone (NMP) and N,N-dimethylformamide (DMF) [76–82].

LPE is a simple method that has huge potential for scalability [58,83]. The main principle of LPE is that graphite is dispersed into a suitable solvent and then exfoliated with the aid of ultrasonication or shear forces. During these processes, the growth and collapse of the micrometer-sized bubbles or voids in liquids due to pressure fluctuations, act on graphite and induce exfoliation into single and few-layer graphene sheets.

The main challenges in exfoliation of graphite in solvents, i.e. suitable solvents with a surface energy around 40 mN m^{-1} is that most of these solvents are not only expensive and corrosive but have also high boiling point and normally toxic. Therefore, there have been attempts to exfoliate graphite in low boiling point solvents such as acetone, ethanol, methanol, acetonitrile *etc.* [84–86]. For example, Zhang et al. [81] reported exfoliation of graphite in ethanol by solvent exchange from NMP. Graphene was first exfoliated in NMP then filtered and subsequently re-dispersed into ethanol. After several centrifugation and washing steps, a dispersion in ethanol of stable graphene with a low concentration of 0.04 mg cm^{-3} was achieved. However, the dispersion was not only low in concentration but also very unstable, observed by 20% sedimentation after just a week.

Another solvent that can be used for graphene exfoliation is water. Unfortunately, water cannot be used without modification because of its high surface tension of around 72 mN m^{-1} and also because of its hydrophilic nature that makes it incompatible with hydrophobic graphene/graphite. These challenges are normally overcome by using surfactants or polymers [52,78]. Various polymers, nonionic and ionic surfactants such as sodium cholate, 4-dodecylbenzenesulfonic acid, sodium deoxycholate, sodium dodecylbenzenesulfonate, polymer poly(vinyl pyrrolidone) have been successfully utilized to exfoliate graphite under high concentrations [76,87–92].

A thorough investigation of surfactant-assisted graphite exfoliation using ionic and nonionic surfactants was explored by Guardia et al. [93]. It was found that nonionic surfactants performed better than ionic to stabilize graphene (Fig. 5). Nonionic surfactants have a hydrophobic tail and a long hydrophilic part that creates a steric repulsion between the hydrophilic moieties in water, and this plays a significant role in stabilizing graphene [80]. As clearly seen in Fig. 5, triblock copolymer Pluronic P-123 achieved the best results. After two and four hours of sonication, a high concentration yield of 1 mg cm^{-3} and 1.5 mg cm^{-3}, respectively, was achieved. It is also important to note that most of the surfactant systems act as insulators, therefore, utilizing them results in compromising, or decreasing, the conductive properties of graphene [89].

Ionic liquids have also been shown to be promising candidates for high concentration graphene dispersions in LPE systems. Wang et al. [94] exfoliated graphite in 1-butyl-3-methylimidazolium bis (trifluoromethanesulfonyl)imide achieving a concentration of 0.95 mg cm^{-3} of 1–5 layers of graphene sheets after one hour of sonication. This was also reported by Nuvoli et al. [95], and showed that 24 h sonication of graphite in 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIM) yielded a high concentration of 5.33 mg cm^{-3} of thin sheets of graphene of about 2 nm despite having a really low yield of just 1–2 wt%. Bari et al. [96] reported a high concentration of graphene 5.8 mg cm^{-3} after just one hour

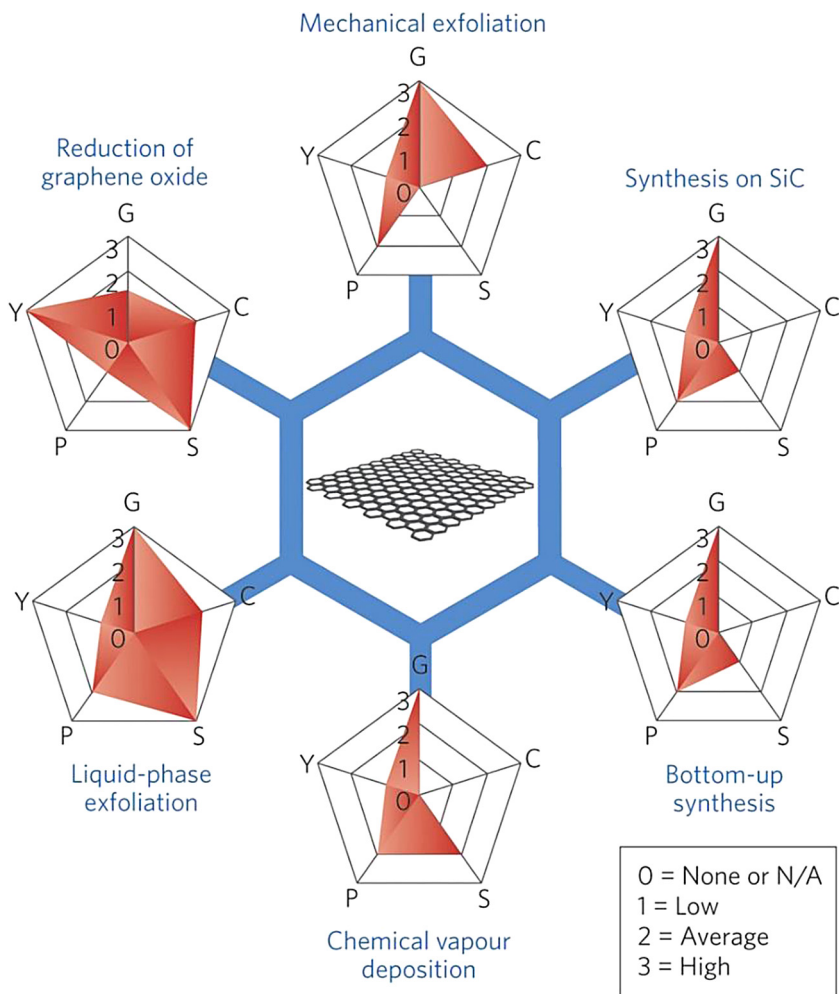**Fig. 3.** Some common production methods of graphene in relation to quality and scalability potential. Each method has been evaluated in terms of graphene quality (G), cost aspect (C; a low value corresponds to high cost of production), scalability (S), purity (P) and yield (Y) of the overall production process. Reproduced with permission from Ref. [55]. Copyright: 2015 Nature Publishing Group.
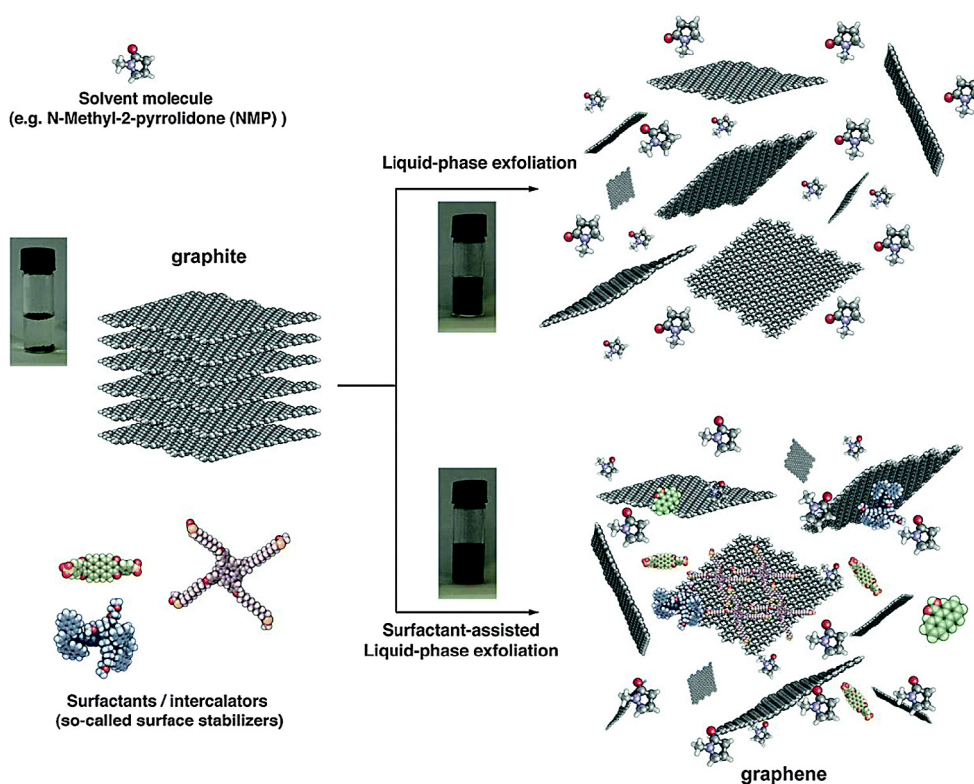
Fig. 4. Schematic representation of the liquid-phase exfoliation process of graphite in the absence (top-right) and presence (bottom-right) of surfactant molecules. Reproduced with permission from Ref. [58]. Copyright: 2014 The Royal Society of Chemistry.

of bath sonication dispersed in 1,3-Bis(phenylmethyl)imidazolium bis(trifluoromethylsulfonyl)amide.

The general challenge for all LPE systems, be it in surfactants, polymers, solvents or ionic liquid stabilized systems, is that it is very difficult to control the sizes of produced graphene flakes [97]. It has been shown that graphene concentration can be increased with an increase in processing time but this is at the cost of lateral graphene sheet sizes as well as purity of graphene [79,98,99]. The longer it is exposed to shear or cavitation forces the greater the defects and smaller the average sheet size becomes [98,100]. Therefore, it is critical to find the right balance between the processing parameters that can lead to not only high concentration of graphene dispersions but also reduce the amount of defects induced in graphene. It is also important to develop ways to control the size of the flakes during exfoliation other than having random sizes in dispersions. Despite the challenges presented by LPE, its simplicity, cost-effective and potential for scale-up, makes it a versatile method for exfoliation of graphite to graphene.

3.3. Graphene via graphite oxide

The popular method for production of graphene is *via* the reduction of graphite oxide or graphene oxide (GO) to reduced graphene oxide (RGO) [98,22,54]. The popularity of this method is due to low-cost, high scalability potential, excellent yield and ability to disperse functionalized graphene in various solvents.

This method involves intercalation of graphite with an oxidant, which introduces functional oxygen groups on the surface of graphene sheets. These functional groups help to disperse and stabilize graphene oxide in water [28,52]. Fabrication of graphite oxide is normally achieved by the so-called Hummers method [101], which is the most widely used protocol for oxidation of gra-

phite. After oxidation, graphite oxide is dispersed in water and subjected to sonication resulting in individual dispersed graphene oxide sheets in water. A comprehensive study of graphite oxidation was conducted by Tour et al. [102]. They identified three main steps involved in converting graphite to GO (Fig. 6). Graphite is first intercalated with sulfuric acid, then oxidized to form graphite oxide and finally dispersed in water. Potassium permanganate
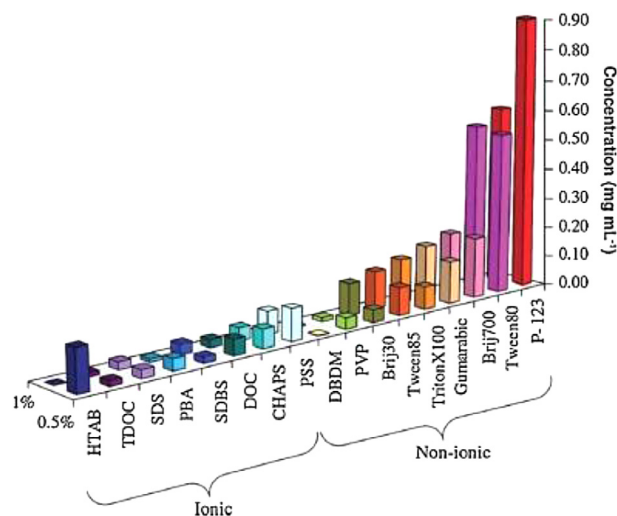

Fig. 5. Concentration of graphene in aqueous dispersions achieved by the use of different surfactants, as estimated from UV–Vis absorption measurements. Two surfactant concentrations are shown: 0.5% and 1.0% wt/vol. Reproduced with permission from Ref. [93]. Copyright: 2011 Elsevier.
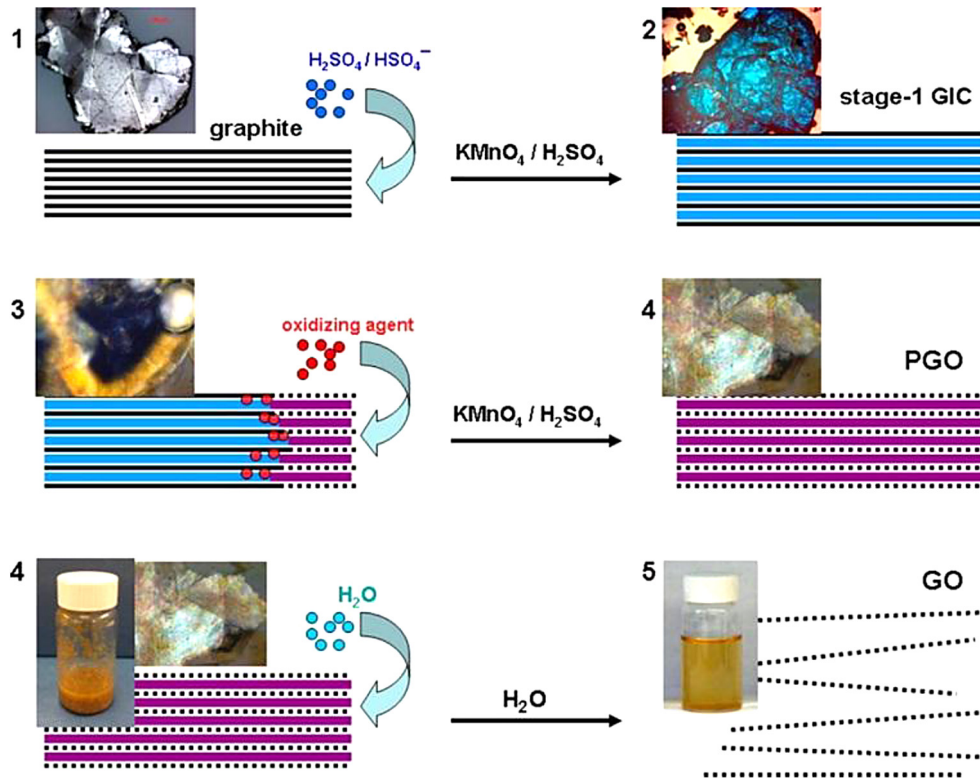
Fig. 6. Schematics of conversion of graphite into graphene oxide with corresponding sample appearance at each stage. The three steps signify formation of the two intermediate products (stage-1 GIC and PGO) and the final GO product. The solid black and dotted black lines represent graphene layers and single layers of GO, respectively; while the wide blue lines represent H_2SO_4/HSO_4^- intercalant; wide purple lines represent a layer of the mixture of H_2SO_4/HSO_4^- intercalant with the reduced form of oxidizing agent. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Reproduced from Ref. [102].
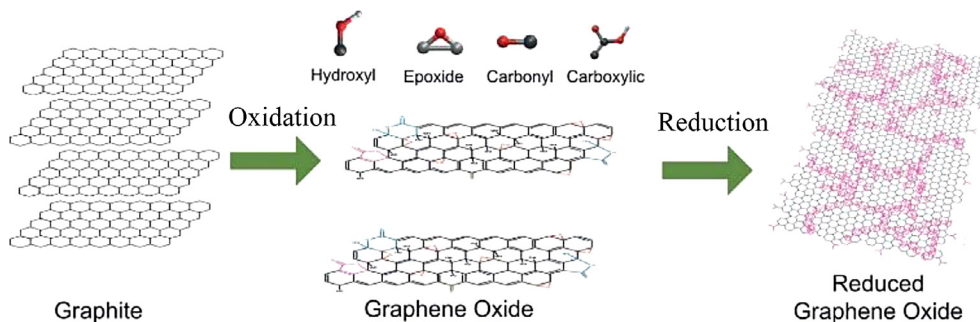

Fig. 7. RGO synthesis steps from oxidation to reduction. Graphite can be oxidized using different approaches. This introduces various functional groups on the surface and edges of the sheets, which act as defects. These defects can be partially removed by suitable reduction processes. Reproduced with permission from Ref. [116]. Copyright: 2012 Elsevier.

reacts with sulfuric acid to form an active oxidizing agent, dimanganese heptoxide (Mn_2O_7) [103]. This aggressive chemical treatment of graphite destroys the sp^2 structure of graphene and introduces functional groups such as hydroxyl (-OH) or epoxide (C-O-C) in the basal plane and carbonyl (C=O) and carboxylic (-COOH) on the edges [104–108] (see Fig. 7). These functional groups help to disperse graphene in water homogenously. We note that the Hummers' method utilizes chemicals such as sodium nitrate, concentrated sulfuric acid and potassium permanganate [101], which are in turn not environmentally friendly. Since these materials are processed at high temperatures, there is a high risk of an explosion during processing. Besides, sodium nitrate produces toxic nitrous gas, thus making this method unsuitable for large scale application. Several efforts have been made to improve the Hummers' method, for example, by eliminating the use of sodium nitrate [109].

Graphene or reduced graphene oxide is obtained from graphene oxide by a reduction process. Different methods exist for the reduction of GO and there is a lot of research going on in this area [110–115]. This step is very important, because the chosen method affects the quality and properties of the produced graphene and the potential areas of application.

Oxidation of graphite *via* Hummers' method introduces defects to the graphene sheets. Some of these defects can be partially removed by the reduction processes. However, none of the current known methods is able to restore and remove fully all graphene defects introduced by oxidation [117]. The three main methods that are utilized for the reduction of graphene oxide are chemical, thermal and microwave. In chemical methods, GO is chemically treated with reducing agents such as hydrazine hydrate, hydroiodic acid, sodium borohydride, amino acid, dopamine, ascorbic acid *etc.* [54,111,113–115,118,22,119–122]. GO can also be thermally

Table 1
Examples of reduction processes of GO to RGO with corresponding C/O ratio and conductivity.

Reduction methods/conditions	C/O ratio	Conductivity, σ (S m^{-1})	Cited reference
Hydrazine hydrate, 100 °C, 24 h	10.3	2420	[54]
Thermal, H$_2$ gas, 700 °C, 30 min	28.6	8100	[123]
L-Ascorbic acid/NH$_3$, 95 °C, 15 min	12.5	7700	[115]
Plasma assisted, CH$_4$ gas, 700 °C, 20 s	9.2	34,500	[131]
150 mM NaBH$_4$ solution, RT, 2 h	8.6	45	[113]
NaBH$_4$, 80 °C, 1 h	4.8	82	[104]
NH$_3$BH$_3$, 80 °C, 12 h	14.2	19,300	[122]
Thermal, 1000 °C, C$_2$H$_2$, 30 min	50.2	142,500	[124]
DMF + 0.6 M H$_2$SO$_4$, 1 h	8.4	1223	[132]
Zn/HCl, RT, 1 min	33.5	15,000	[133]
HI/AcOH, 40 °C, 40 h	11.5	30,400	[118]

treated at high temperature to thermally reduced graphene (TRG) [123–126]. The oxygen containing functional groups are decomposed to CO$_2$ and H$_2$O. Microwave irradiation has also been efficiently used to reduce graphene oxide to few-layer graphene [127–130]. Most of the materials used in chemical reduction methods that are effective, such as hydrazine, are very toxic and dangerous, especially in large volumes. Thermal and microwave treatment eliminate the need for chemical treatment but high local temperatures on the surface in excess of 1000 °C can be detrimental, for example, on flexible substrates. A detailed analysis of reduction methods was conducted by Pei et.al. [117], Pumera et al. [110] and also briefly by Khaled et al. [80]. A summary of some of these methods is provided in Table 1, together with corresponding C/O ratio and electrical conductivity. The reader is referred to Refs. [110,117] for more comprehensive reviews on the various reduction methods of graphene oxide.

The potential of the GO route for graphene production is really huge, low cost and scalability being the main advantages, but the introduction of functional groups on the surface of graphene sheets hinders applications where the pristine properties of graphene are paramount. Although some of these can be removed *via* reduction steps, the properties and quality of the RGO is still far from that of pristine graphene. Therefore, it is important to find ways in which one can easily control the amount of functional groups introduced on the surface of graphene by oxidation as well as finding more efficient methods for the reduction of GO. Besides, before this method can be considered for large scale production, there remains a dire need to find more environmentally acceptable ways of oxidizing graphite, and at high efficiency, with less toxic chemicals and less waste material.

3.4. Graphene from mechanical milling of graphite

The first known study of graphene production by graphite milling was made by Antisari et al. [134]. They managed to produce few-layer graphene sheets with high aspect ratio by milling graphite dispersed in distilled water for 60 h. It was also demonstrated by Zhao et al. [135] that graphene can also be produced from graphite by a ball milling technique using different liquid media. They used a planetary mill at low speed to mill graphite flakes dispersed in anhydrous N,N-dimethylformamide (DMF) solvent for 30 h. The low milling speeds were implemented in order to prevent the destruction of graphite flakes and enhance the shear force being exerted on graphite. By using TEM and AFM, they were able to estimate that the graphene sheets exfoliated in DMF *via* ball milling were around three layers. The quantity and quality of produced graphene flakes depended on parameters such as speed of rotation, diameter of milling ball, milling time, type of graphite used, concentration of graphite in the solvent and centrifugation

speed. In another study [136], the same authors were able to show that the same method can be used to exfoliate graphite in various organic solvents to form stable colloidal dispersions of graphene sheets such as N-methylpyrrolidone (NMP), ethanol, tetramethyluren (TMU), acetone, formamide and tetrahydrofuran (THF).

It was also demonstrated by Peipei et al. [137] that by co-processing graphite with cellulose in a ball mill, graphene-like sheets can be produced. Subsequently, the production of graphene from graphite *via* ball milling in the presence of melamine was also investigated [138,139]. The maximum concentration of graphene managed to be produced by using DMF as a stabilizing agent was 0.13 mg cm^{-3} in less than 1 h.

Cao et al. [140] also utilized the ball milling method to exfoliate graphite with dry ice for 48 h in the presence of carbon dioxide to produced graphene oxide nanoplatelets (GONPs) that were later combined with poly(p-phenylenediamine) to produce the composites. The resulting GONPs showed a high specific surface area of 589.7 m^2 g^{-1}. This reported value was much higher than was achieved by Jeon et al. [141] for edge-selectively carboxylated graphite (389.4 m^2 g^{-1}), also produced by milling graphite in dry ice.

It is evident from the above that mechanical milling of graphite is a simple, low-cost and effective method providing control over a wide range of parameters during processing and shows potential for large scale production [142,143]. However, long processing times, high energy consumption, low graphene yield, as well as induced defects in the final products, still hinders this method for wider applicability [143–145].

3.5. Electrochemical exfoliation of graphite

Electrochemical exfoliation is a well-known technique that has been around for many decades. The most popular application of electrochemical methods is found in the metal industry, in particular for the production of aluminum. It has also found wide application in industrial chemicals for the production of peroxoacids, chlorates *etc.* [146]. Coincidentally, carbon materials have been extensively used as electrodes in electrochemistry [147,148]. Due to their excellent electrical properties, in particular, graphite and graphene have been utilized as electrodes in devices such as supercapacitors, batteries, solar cells *etc.* [148]. As already mentioned earlier, graphite can be intercalated to form graphite intercalate compounds (GIC). One of the methods utilized for this process is electrochemistry. Ever since the graphene revolution started in 2004, a lot of interest has been generated to find methods other than mechanical exfoliation for synthesis of graphene. In recent years, some researchers have successfully used the well-known electrochemical method to exfoliate natural graphite [149–153].

The mechanism of electromechanical exfoliation is well illustrated in Fig. 8. This process involves reduction and oxidation processes at the cathode and anode, respectively, in the presence of an aqueous or organic electrolyte [154]. One of the electrodes is graphite based and the other auxiliary is usually platinum. The exfoliation process is usually commenced by application of a positive current to the electrodes. The graphite based electrode will undergo oxidation and the negatively charged ions from the electrolyte will be intercalated into the graphite layers. To facilitate the exfoliation process, application of a negative potential is subsequently applied [155]. The choice of electrolyte is vital for successful graphite exfoliation and active research is continuing in this field to find the best aqueous and non-aqueous based electrolytes that can be used efficiently to achieve effective electrochemical exfoliation of graphite.

Electrochemical exfoliation is showing itself to be a fast growing method for the production of graphene sheets, and it is easy to see why [98]. Unlike the Hummers' method that utilizes aggressive oxidants, the electrochemical method takes advantage of the
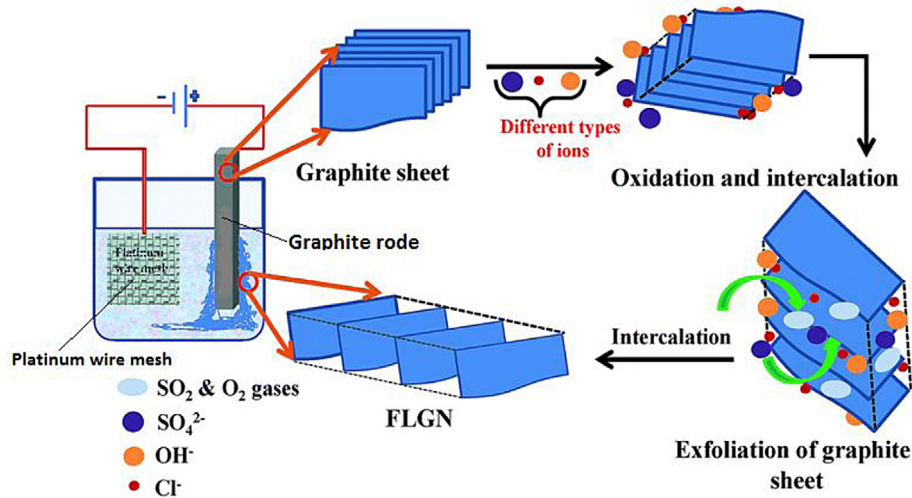
Fig. 8. Schematic diagram of the mechanism of electrochemical exfoliation of graphite. The electrodes used were graphite rode and platinum wire mesh for the anode and cathode, respectively. Reproduced with permission from Ref. [156]. Copyright: 2007 The Royal Society of Chemistry.

electrical conductivity of graphite to intercalate charged ions, and the subsequent electrochemically initiated reaction with the electrolyte to provide the exfoliation mechanism. Another advantage of this method over the chemical and mechanical methods is the possibility of mass production of graphene at a much lower cost [157].

One of the drawbacks of the electrochemical exfoliation of graphite is the need for an unbroken voltage bias to the electrode, which can be problematic in some instances. Since exfoliation does not only occur on the surface of the graphite electrode, but rather throughout its complete thickness, exfoliation of thick graphite layers is a common result. The higher the surface area that is exposed to the electrolyte the higher the possibility of having large junks of graphite in the final product. Unless it can be successfully addressed, this limitation will continue to be a big hindrance for the electrochemical exfoliation method to become a viable option for large scale graphene production.

The potential of graphene will only be reached if viable options for large scale graphene production with controlled properties are found. In this section of the review, some of the promising methods based on graphite exfoliation have been discussed. The advantages and drawbacks of these methods are summarized in Table 2.

4. Properties of graphene

The rapid interest in graphene research arose from the unusual properties exhibited by graphene. These properties have made it a fascinating material with huge potential for application in different industries and devices. It is important to note that most of the excellent properties that have been reported are in regard to single layer defect-free graphene. Most of the methods discussed above are unable to produce pristine graphene that can exhibit all these

Table 2
Comparison of graphite based graphene production methods.

Method	Advantages	Drawbacks
Micromechanical cleavage	• High quality flakes • Simple preparation method • Low-cost and easy • No special equipment needed	• Low yield • Labor intensive (not scalable) • Uneven films • Dimensions dependent on initial crystal size
Graphene *via* graphite oxide	• High dispersability • Scalable method • High processability • High yield • Relatively inexpensive	• Poor electrical/electronic properties • Fragile stability of the colloidal dispersion • Potentially explosive process • Time consuming • Use of toxic chemicals • Small area flakes • Reduction to graphene is only partial
Liquid-phaseexfoliation	• High Quality • Good Scalability • Low Temperature • Relatively inexpensive	• Small area graphene flakes (<5 μm) • Low yield of thin graphene layers • Limited dispersability • Limited processability
Mechanical milling of graphite	• Simple technique • Control over the various process parameters • Relatively inexpensive	• Long processing times • Induces defects • Low graphene concentration • Low yield
Electrochemical exfoliation	• High yield • Cost effectiveness • High processability • Environmentally benign • Scalable • Fast production • Good electronic properties	• Slight oxidation • Inhomogeneous flake thickness

superlative properties. In this section, some of these exciting properties will be briefly discussed.

4.1. Electronic properties

The graphene revolution started with the study of electrical and electronic properties of graphene [1]. These properties are much dependent on the number of graphene layers in graphene sheets. The properties shown by single layer, bilayer or trilayer are very different materials. One of the earlier works of Novoselov et al. [16] on graphene, showed the potential application in transistors due to the possibility of varying charge carriers from holes to electrons. This electron-hole dependence is only applicable to single layer graphene sheets, but, if the number of layers begin to increase, the dependence becomes weaker due to the electrical field screening by other layers.

The quantum Hall effect of graphene for both electron and hole carriers has been found to be due to the extremely high electron mobility of graphene at various temperatures and under exposure to magnetic fields [16,158]. At room temperature this can exceed 2000 $cm^2 V^{-1} s^{-1}$ for mechanically produced graphene. Typically, the classic integer quantum Hall effect occurs at $4e^2/h$, where e is the electron charge and h is Planck's constant, but in graphene it occurs at only half integers. It is believed that this effect is due to the unique graphene band structure.

The electron mobility of graphene is dependent on temperature and substrate used. Bolotin et al. [10] showed graphene suspended and annealed on Si/SiO_2 to have a staggering mobility of more than 200,000 $cm^2 V^{-1} s^{-1}$, which happens to be the largest reported value of any kind of semiconductor material.

4.2. Mechanical properties

Carbon based materials have naturally exhibited excellent mechanical properties. Diamond, for example, is the hardest known natural material, while carbon nanotubes have been known to have the highest tensile strength. Graphene is no different in respect to its extreme mechanical properties. Lee et al. [11] showed graphene to be the strongest material known by nanoindentation using an AFM, with a tensile strength of 130 GPa. They also showed single layer graphene to have a breaking strength of more than 200 times that of steel, and Young's modulus of 1 TPa. However, these values are believed to be dependent on the purity of graphene sheets. Frank et al. [159] measured the Young's modulus of single layer graphene using AFM to be 0.5 TPa.

Dikin et al. [160] prepared graphene oxide paper that showed the elastic modulus to be around 32 GPa and fracture strength around 120 MPa. To improve the mechanical properties of these graphene papers, divalent ions and polyallylamine [161,162] were introduced between the layers by chemical cross linking. A summary of some of the mechanical properties of graphene is presented in Table 3. It is clearly evident that the thickness of graphene sheets has a major effect on the properties.

4.3. Optical properties

Despite being only one atom thick, graphene is able to absorb 2.3% of white light [50]. Bilayer graphene absorbs white light up to 4.6%. Basically, the absorption of white light was found to be increasing nearly linearly with the increase in graphene layers, each layer absorption $A = 1 - T = \pi\alpha = 2.3\%$, where $\alpha \sim 1/37$ is the fine structure constant. Graphene can also be identified by optical microscopy on a Si/SiO_2 substrate due to interference. Individual graphene layers can be identified by different contrast as shown in Fig. 9(a) and (b) [164]. In the UV region, from 900 down to 300 nm the absorption spectrum of graphene is featureless, and

Table 3
Summary of measured mechanical properties of graphene by AFM.

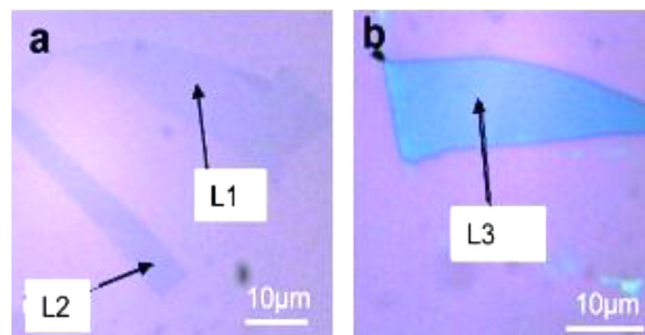| Graphene layers	Mechanical properties		Cited references
	Young's modulus, E (TPa)	Intrinsic strength, σ (GPa)	
One	1	130	[11]
One	1	131	
Two	1.04	125	[163]
Three	0.98	101	

Fig. 9. (a) Microscopic images of a single layer (right), bilayer (left), and (b) multilayer (n ∼ ∞) of graphene. Reprinted with permission from Ref. [164]. Copyright: 2010 American Chemical Society.

the maximum absorption peak can be seen to be at around 270 nm [50].

4.4. Thermal properties

The thermal conductivity of graphene is dominated by phonon transport, i.e. diffusive and ballistic conduction at high and low temperatures respectively [8]. However, due to the low carrier density of non-doped graphene, the electronic thermal transport in graphene is negligible [165]. The intrinsic thermal conductivity of graphene is about 2000–6000 $Wm^{-1} K^{-1}$ for suspended graphene sheets at room temperature [166,167] and ~600 $Wm^{-1} K^{-1}$ for suspended graphene on SiO_2 substrate [168]. These values are very much dependent on the defects of graphene such as edge scattering [169], isotopic doping [170], and sample fabrication residues [171] that causes phonon scattering and localization. Therefore, the higher values of thermal conductivity are achieved by graphene produced by MC method due to high quality of the sheets.

Balandin et al. [9] measured the thermal properties of a suspended graphene sheet. They produced graphene *via* mechanical exfoliation and the measured thermal conductivity was in the range of 4800–5300 $Wm^{-1} K^{-1}$, which is higher than that of natural diamond, ~2200 $Wm^{-1} K^{-1}$ [172] and ~3000 $Wm^{-1} K^{-1}$ [173] for multi-wall, and ~3500 $Wm^{-1} K^{-1}$ [174] for single wall carbon nanotubes at room temperature. At these values, the thermal conductivity of graphene is more than ten times higher than that of copper. It was also determined by Cai et al. [175] that chemical vapor deposited graphene exhibited values of up to 3000 $Wm^{-1} K^{-1}$, lower than earlier reported for mechanically produced graphene. In spite of that, these excellent thermal properties of graphene can be exploited to manufacture devices such as thermal sensors, heat dissipators and composites with excellent thermal conductivity. The reader is referred to [167,169,176–178] for a more comprehensive coverage of the thermal properties of graphene.

4.5. Chemical properties

Pure graphene sheets are mostly unreactive. Functionalization of the surface is required to make them reactive with other

material. Graphene sheet chemistry is dominated by its surface, while in the form of graphene nanoribbons by its edges. Thickness also plays a crucial part in graphene reactivity. For instance, it has been determined by Sharma et al. [164], by using the relative disorder (D) peak in the Raman spectroscopy, that single layer graphene is almost 10 times more reactive than bi- or multi-layer graphene. Using the spectroscopic test, they compared the reactivity of graphene edges with bulk materials. It was found that the reactivity of edges is at least two times higher than the reactivity of the bulk single graphene sheet.

One way to functionalize graphene sheets is *via* nitrene chemistry [179], i.e. introducing reactive species covalently linked to the graphene surface, such as hydroxyl, bromine, carboxyl, amino *etc.* The resulting functionalized graphene nanosheets can be controlled to be electrically conductive, and readily dispersible in different solvents. These sheets can be easily processed and utilized in various applications such as nanohybrids and for fabrication of polymer composites.

5. Graphene/polymer nanocomposites

Graphene and its derivatives have been extensively used as fillers in composites because of their excellent resultant properties. The properties of polymer-graphene composites depend on filler dispersity, filler and matrix bonding, ratio of filler to matrix and the quality of graphene filler and polymer matrix. These factors can be altered by the fabrication processes and methods. The advantage of graphene compared with other fillers is that it allows for large changes in the properties of composites at very low percolation thresholds due to the ultrahigh aspect ratio of graphene. This section briefly discusses a few examples were graphene has been used to enhance the properties of polymer composites. However, before we discuss the examples, we shall take a look into how graphene and polymer are incorporated together to form composites.

5.1. Fabrication methods of graphene/polymer nanocomposites

There are three main methods for incorporation of graphene into polymer matrices that are commonly used, *in situ* polymerization, melt intercalation and solution mixing. When considering the type of method to pick, it is important to understand the interaction dependence of graphene and polymers on hydrophobicity, molar mass, polarity, reactivity *etc.* These three main methods will now be briefly discussed.

5.1.1. In-situ polymerization
In the *in-situ* polymerization method, a monomer and graphene fillers are mixed together, in some cases in the presence of catalyst (s). This step is normally followed by polymerization initiation by heat or radiation [180]. Utilization of epoxy in in-situ polymerization is a good example where this method has been extensively applied [181,182]. Some examples of polymer/graphene composites that have been fabricated using this method include graphene/polystyrene (PS) [180,183], graphene/polyaniline (PANI) composite [184], and graphene/silicone composites [185]. The main advantages of this method are that there is a strong interaction between the filler and the polymer matrix that leads to a faster stress transfer, and so enables a rapid formation of a homogeneous dispersion, that, in turn, facilitates a homogeneous distribution of the filler in the polymer matrix [186]. In-situ polymerization provides excellent miscibility for high filler loading in polymer matrices. However, the polymerization process itself usually increases the viscosity of the mixture and thus further processing becomes difficult, and this eventually restricts the loading fraction [186].

In some cases, this method requires the use of solvents, and this adds the need for further purification steps for solvent removal [187].

5.1.2. Melt intercalation technique
In the melt intercalation method, graphene is mixed with the polymer matrix in the molten state, meaning that no solvent is required in this technique. Basically, homogeneous mixing of graphitic materials and polymers is achieved by high shear mixing at elevated temperatures. This method has found extensive application for preparation of thermoplastic composites. Some examples of the application of this method for graphene/polymer composites include exfoliated graphite/polypropylene nanocomposites [188], polystyrene/graphite nanosheet composites [189], polyethylene terephthalate (PET)/graphene nanocomposites [190] *etc.* The main drawbacks of this method are that the dispersity and distribution of the fillers in the matrix are quite poor when compared with other methods. Besides, the utilization of high shear forces induces defects and breakage of graphene sheets [191].

5.1.3. Solution mixing
Solution mixing is the most commonly used technique for polymer composite fabrication amongst all of the methods discussed. This is because of its simplicity, potential for large scale application, and it does not require specialized equipment. The idea is that the polymer is solubilized in a suitable solvent and graphene is allowed to swell, i.e. increase the curvature of its curvilinear surface. Solubility and dispersity of graphene can be a challenging problem in polymer solution. To alleviate this problems, graphene sheets need to be functionalized to provide easy dispersability in different solvents, such as organics. Poly(vinyl alcohol) (PVOH)/graphene oxide (GO) composites were easily fabricated due to the high solubility of PVOH [192]. In some cases especially involving organic solvents, homogeneous mixing is achieved via sonication or shear mixing. Other examples where this method has been used include poly(methyl methacrylate) (PMMA)/graphene [181], graphite oxide nanoplatelets (GONPs)/ polycaprolactone (PCL) [193], graphite oxide nanoplatelet/ polyurethane (PU) composite [194] *etc.* This method should be used with caution, as re-aggregation of the sheets usually occurs during solvent evaporation. It is important to find ways to functionalize graphene sheets to prevent against aggregation by increasing the solubility of graphene in respective solvents.

5.2. Examples of graphene/polymer composites

5.2.1. Graphene/epoxy composites
Since their discovery in 1936, epoxy based materials have become one of the most utilized materials because of their excellent properties [195] and are found in applications ranging from aerospace, electronics, automotive, adhesives *etc.* [182,195–197]. Graphene has been incorporated into epoxy based materials to enhance various functional properties.

Graphene's excellent mechanical properties make it is a good candidate for reinforcement in nanocomposites. Bortz et al. [198] investigated the effect of graphene concentration on the mechanical properties of graphene/epoxy nanocomposites. The tensile modulus of unmodified epoxy increased by ~12% at only 0.1 wt% loading of graphene oxide. Wajid et al. [199] used solution mixing to fabricate graphene/epoxy composites. The strength and modulus increased by 38% and 37% respectively at only 0.46 vol% graphene loading. By using a simple such solution mixing technique, Galpaya et al. [200] fabricated a graphene oxide/epoxy nanocomposite with enhanced mechanical properties. At only 0.1 wt% addition of graphene oxide, fracture toughness increased by ~50%. The

graphene oxide sheets in the composite disturbed and deflected the crack propagation. The elastic modulus increased by ~35% from the neat epoxy with only 0.5 wt% loading of graphene oxide. Shen et al. [201] investigated the tribological properties of epoxy nanocomposites reinforced with graphene oxide at low loading (0.05–0.5 wt%). The wear resistance significantly increased with the additional of graphene oxide, such that, at 0.5 wt% loading, the specific wear rate was reduced by 90.0–94.1% compared to the neat polymer.

Electrical conductivity in nanocomposites is achieved by the formation of a continuous network of the conductive fillers [202,203]. Therefore, because graphene has a very high aspect ratio, the percolation threshold is achieved at very low graphene loading [204]. Wajid et al. [199] used sonication and shear mixing methods to disperse graphene into the epoxy matrix and achieved the percolation threshold at 0.088 vol%. In another study, the composites were fabricated by incorporation of functionalized graphene into the epoxy matrix by an *in-situ* process [182]. The percolation threshold was reached only after 0.52 wt% loading of graphene, and electrical conductivity increased from 1^{-10} to 1^{-2} S cm^{-1} by ~9 vol% loading of reduced graphene oxide. Zhao et al. [205] conducted a thorough investigation into the properties of epoxy composite filled with epoxide-functionalized graphene (G-EP). The tensile strength and Young's modulus increased by 116% and 96%, respectively, compared to the polymer at only 1 wt% loading of G-EP. The percolation threshold was reached at only 0.33 wt% loading, and electrical conductivity increased from about 1^{-17} to 1^{-2} S cm^{-1} at ~2 vol% loading. Thermal conductivity also improved by 189 % at 10 wt% G-EP loading.

For a more comprehensive review on graphene/epoxy nanocomposites, the reader is referred to a review by Rasheed et al. [206].

5.2.2. Graphene/cellulose composites

Graphene has been incorporated in cellulose composites to enhance mechanical and electrical properties. GO and cellulose were dissolved in N-methylmorpholine-N-oxide (NMMO) monohydrate to prepare the composite films [207]. Despite being brittle, the produced graphene/cellulose composites showed improved thermal and electrical properties. Nguyen et al. [208] used reduced graphene oxide sheets (RGO) and amine-modified nanofibrillated cellulose (A-NFC) to produce composites with enhanced properties. These composites showed good electrical conductivity of up to 71.8 S m^{-1} and tensile strength of up to 273 MPa. Graphene-cellulose paper (GCP) membranes are used to fabricate flexible supercapacitors [209]. These composites displayed high electrical conductivity stability with a decrease of only 6% after being bent 1000 times. The capacitance of these supercapacitors per geometric area is 81 mF cm^{-2}, which is equivalent to a gravimetric capacitance of 120 F g^{-1} of graphene, and these supercapacitors did not lose any capacitance after 5000 cycles. Manman et al. [210] reported cellulose/graphene composite hydrogels prepared from ionic liquids (IL). They used Vitamin C to prepare RGO directly in IL. These hydrogels showed enhanced mechanical and thermal properties. At only 0.5 wt% doping of RGO in cellulose composite, the Young's modulus was improved more than four times.

5.2.3. Graphene/polyaniline (PANI) composites

Wang et al. [184] prepared a PANI/graphene composite paper (GPCP) *via in-situ* anodic electropolymerization (AEP). This graphene/polyaniline composite was shown to have a tensile strength of 12.6 MPa and a stable large electrochemical gravimetric and volumetric capacitance of 233 F g^{-1} and of 135 F cm^{-3} respectively. The mechanical strength was also shown to have improved by 43%.

In another example, flexible graphene/polyaniline hybrid material, for use as a supercapacitor electrode, was synthesized by an *in-situ* polymerization-reduction/dedoping-redoping process [211]. This composite showed a high specific capacitance, as high as 1126 F g^{-1} compared to 115 F g^{-1} for pure PANI. Wang et al. [212] reported a composite of fibrillar polyaniline (PANI) doped with graphene oxide sheets. For a mass ratio of aniline/graphite oxide of 100:1, the composite displayed a high electrical conductivity of 10 S cm^{-1} and specific capacitance of 531 F g^{-1}.

5.2.4. PVA/graphene nanocomposites

Zhao et al. [213] reported the preparation of graphene nanosheets and poly(vinyl alcohol) (PVOH) *via* a facial aqueous solution. In their study, they showed that it is possible to increase the tensile strength by as much 150% by only 1.8 vol% loading of graphene, and at the same time elongation breakage decreased by more than 100%.

Liang et al. [214] also studied poly(vinyl alcohol) (PVOH)/-graphene nanocomposites. In this study, they used water as a solvent to fuse GO into the PVOH matrix. At only 0.7 wt% GO loading, tensile strength increased by 76% and Young's modulus by 62%.

5.2.5. Polyurethane (PU)/graphene composites

Lee et al. [215] reported the study of waterborne polyurethane (WPU)/graphene sheets (FGS) nanocomposites prepared using an *in-situ* method. The electrical conductivity of the nanocomposites was increased 10^5-fold compared with that of pure WPU. This was attributed to high dispersity and homogeneity of graphene sheets in the WPU matrix. They obtained a percolation threshold of graphene sheets at only 2 wt%.

Liang et al. [216] used thermoplastic polyurethane (TPU) to fabricate nanocomposites with three differently processed graphene samples. They were able to show that the rate of thermal degradation for thermoplastic polyurethane/isocyanate modified graphene composites are much higher than that of the sulfonated graphene and reduced graphene based TPU nanocomposites. The TPU/-graphene nanocomposites doped with only 1 wt% sulfonated graphene showed enhanced infrared-triggered actuation performance. The tests showed that the composite could contract and lift a 21.6 g weight up to 3.1 cm with 0.21 N of force when exposed to IR. The mechanical properties of this composite were also increased. The tensile strength of TPU/sulfonated graphene nanocomposites with 1 wt% graphene was increased by 75% at a strain of 100%, and the Young's modulus was enhanced by 120% [216]. However, IR-triggered actuation performance of isocyanate modified graphene/TPU nanocomposites showed inferior results.

5.2.6. Poly (vinylidene fluoride) (PVDF)/graphene composites

PVDF/graphene nanocomposites were prepared by a simple solution mixing followed by compression molding from graphite oxide and exfoliated graphite (EG) [217]. GO based composites displayed higher thermal stability than EG based composites. However, the mechanical properties of both composites outperformed those based on only PVDF. A lower percolation threshold of 2 wt% was obtained for GO/PVDF composites compared to EG/PVDF composites, having above 5 wt%. The difference is attributed to the higher aspect ratio of GO compared with EG. With the addition of 2 wt% of GO, the storage modulus of neat PVDF increased from 1275 MPa to 1859 MPa, while with EG it increased to 1739 MPa. At a 4 wt% filler loading, the storage modulus for GO/PVDF and EG/PVDF was increased to 2460 and 2695 MPa, respectively.

5.2.7. Graphene/Polyethylene terephthalate (PET) nanocomposites

The melt intercalation technique was used to prepare PET/-graphene composites by Zhang et al. [190] Transmission electron microscopy analysis showed that graphene nanosheets were evenly distributed in the PET matrix. This criterion was confirmed by the high electrical conductivity values they got from the PET/-

graphene composites. The threshold percolation was only 0.47 vol% loading, and with graphite 2.4 vol%. A high electrical conductivity of 2.11 S m^{-1} was achieved with the addition of only 3.0 vol% graphene.

5.2.8. Polycarbonate (PC)/graphene nanocomposites

Kim et al. [218] studied PC composites doped with graphite and functionalized graphene sheets (FGS) by the melt intercalation technique. In this study, they used melt rheology to study the viscoelastic properties of the composites. They annealed the composites for 10,000 s and observed that the composites manifest a solid-like state above the percolation threshold, which was around 1 wt% for the FGS, while around 3 wt% for graphite loading. In terms of electrical properties, FGS/PC showed lower percolation threshold as compared to graphite/PC composites. Both graphite and FGS fillers lead to improved PC composites stiffness and dimensional stability. The composites also exhibited good barrier properties. The permeability of nitrogen and helium of the PC composites is significantly reduced by incorporation of both FGS and graphite. Moreover, FGS showed potential for application in gas separation processes as it was more effective against molecules with large kinetic diameter.

5.2.9. Poly(amido amine) (PAMAM)/graphene composites

Ramanathan et al. [181] studied the mechanical, thermal and electrical properties of graphite/PMMA composites. PAMAM and graphitic nanoplatelets (FNPs) were mixed together in THF *via* sonication and shearing. The glass transition temperature (T_g) of the fabricated composites increased by 30 °C with 1–5 wt% filler loading. When FNPs were replaced with functionalized graphene sheets (FNPs) as nanofillers, the composites exhibited enhanced properties, because the FNPs contain a higher percentage of wrinkled single-layer sheets, and thus have a high aspect ratio which, in turn, increases the filler-matrix bonding. With only 0.05 wt% loading, T_g increased by 30% for the PAMAM/FGS composite, while a loading of 1 wt% led to a T_g of 40 °C. The modulus at room temperature increased by 66% at only 1 wt% loading of graphite nanoplatelets, and as high as 133% at 5 wt% GNP loading.

5.2.10. Polystyrene (PS)/graphene nanocomposites

Polystyrene/graphene composites have been extensively studied for various application. Stankovich et al. [22] reported PS/isocyanate modified graphene composites prepared using a solution blending method in DMF. They obtained a percolation threshold for the electrical conductivity at 0.1 vol% GO in PS. The low percolation value is due to the homogeneous dispersion and extremely large aspect ratio of graphene sheets. The PS/graphene composite showed an electrical conductivity of ∼0.1 to ∼1 S m^{-1} at 2.5 vol% loading.

Liu et al. [219] prepared a PS/GNP composite in ionic liquids. The electrical conductivity increased from 10^{-14} S m^{-1} for pure PU to 5.77 S m^{-1} with the addition 0.38 vol% GNP, which is 3–15 times higher than that of polystyrene composites filled with single-walled carbon nanotubes. They also studied the thermal stability of PS/GNP composite and pure polystyrene. The degradation temperature of the PS/GNP composite was about 50 °C higher than that of pure PS. This enhancement is due to the strong interaction of GNP and the polymer matrix at the interface, which leads to a decrease of polymer chain mobility near the interface and, hence, the increase in thermal stability.

5.2.11. Graphene/alginate composites

Alginate is a natural polysaccharide that can be extracted from seaweed and other moisture loving plant and cellular life forms, such as algae, and is composed of (1–4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) units [220]. The material is nontoxic, biocompatible, and formable [221], and therefore alginates have been used in food, paper and textiles as stabilizers and emulsifiers and also for biomedical applications [222,223].

To enhance the functional properties, alginates have been incorporated with fillers, including graphene, to fabricate composites. Wu et al. [224] investigated the adsorption properties of graphene oxide/calcium alginate (GO/CA) nanocomposite of ciprofloxacin (CPX) from wastewater. It was found to remove CPX to levels as high as 78.9% compared with only 30% using calcium alginate. In another study, GO was encapsulated in calcium alginate and formed into macroporous alginic beads for the adsorption of acridine orange dye [225]. The incorporation of GO into the CA matrix improved the overall adsorption kinetics and increased the effective pH range compared to CA beads alone.

Zheng et al. [226] synthesized graphene oxide/sodium alginate (GO/Na-alg) composites with multivalent cations that resulted in enhanced thermal and mechanical properties. The tensile of Na-alg increased from 33.6 MPa to ∼80.2 MPa. However, this was lower than that for Ca-alg/GO, Ba-alg/GO and Fe-alg/GO with the tensile strengths 122.3, 137.6 and 161.8 MPa respectively. The lower value with Na$^+$ cations was attributed to lack of crosslinking with the alginate chains. In another study [227], sodium alginate/graphene oxide fibers were prepared by wet spinning. At 4 wt% GO loading, the tensile strength and Young's modulus increased from 0.32 and 1.9 to 0.62 and 4.3 GPa, respectively. Li et al. [228] investigated the adsorption properties of GO/CA composites prepared by the sol-gel method for methylene blue removal. The ecofriendly composite showed a high adsorption capacity of 181.81 mg/g in a wide pH range and it is easily separated from the water solutions. The adsorption process was exothermic with increasing temperature.

5.2.12. Graphene nanocomposites for thermal interface materials

High power densities of modern devices in the electronics industry, for example, has created a need for more efficient ways to dissipate generated heat [229]. Poor dissipation of heat flux generated in these devices can deteriorate not only the performance but also shorten the lifetime of devices. Thermal interface materials (TMI) have been developed to minimize the thermal resistance between the heat sources and heat sinks by filling the interface surface irregularities such as air gaps and grooves [229–231]. Due to high intrinsic thermal conductivity and strong thermal coupling abilities, graphene has been used as a filler in TMIs [167,232–235].

Shahil et al. [232] prepared a graphene/epoxy composite for TMI application. Using a "laser flash" method, thermal conductivity of the composite was determined to have increased by 2300% at a graphene loading of 10% and this was attributed to the presence of high concentration of single and bilayer graphene sheets (∼10–15%) as well as the presence of flakes with large lateral size ∼1 μm. Renteria et al. [236] also studied the efficiency of Fe$_3$O$_4$ functionalized graphene nanocomposite in thermal applications. By using the external magnetic field, the fillers were able to be aligned on the interfaces during dispersion of thermal paste which led to an enhanced thermal conductivity by a factor of two than with the random oriented fillers at ∼1% graphene loading. Real-life computer testing with these materials incorporated as thermal dissipators showed that at 1% loading with oriented filler, the temperature was reduced by 10 °C [236].

In another study [237], Goli et al. demonstrated that the efficiency of thermal management in Li-ion batteries could be improved by incorporation of graphene fillers in phase change materials such as paraffin wax. It was shown that the thermal conductivity of material was increased by more than two orders of magnitude while keeping the latent heat storage constant, successfully decreasing the temperature increase in Li-ion batteries [237].
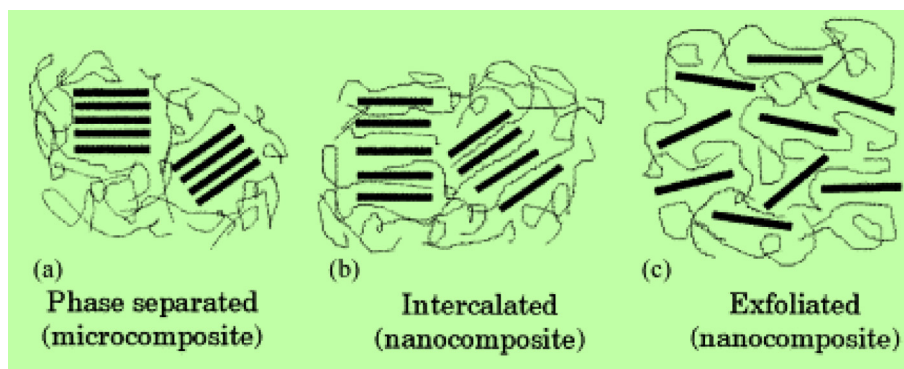
Fig. 10. Schematic representation of three morphological states of graphene based nanocomposites: (a) phase separated (b) intercalated (c) exfoliated. Adapted from Ref. [246] with permission from Elsevier.

5.3. Outlook of graphene/polymer nanocomposites

It is clear that graphene has a lot of potential as a filler to enhance the mechanical, electrical and thermal properties of polymer materials. However, a number of barriers must be overcome in order to reach the full potential of the resulting composites with acceptable properties for wider applications. The composites properties depend on the interaction between graphene and the polymer as well as graphene dispersion in the polymer matrix [187,238].

In order to achieve significant improvement of the polymer properties, nanoscale homogenous dispersion of graphene in the polymer matrix is essential [239]. Homogeneous dispersion minimizes the formation of concentrated local stresses and promotes uniform load transfer throughout the matrix [240–242]. However, achieving good dispersion is still a critical challenge, because graphene has a strong interaction between the layers due to the van der Waals force, and thus tend to agglomerate irreversibly or even to restack into graphite-like structures in the polymer matrix [187,243,244]. Therefore, the excellent potential in the composite cannot be fully realized. Functionalization of the graphene surface is normally implemented to enhance the dispersion capability of graphene. Unlike LPE produced graphene, reduced graphene oxide (rGO) or GO are often used as fillers in polymer composites. This is because GO contains oxygen functional groups such as hydroxyl, epoxy and carboxylic, which can easily interact with the polymer matrix [103,245]. rGO produced from the reduction of GO oxide also still contains a lot of these residual functional groups [110], which act to increase the interlayer spacing and reduce the interaction effects of the van der Waals force between the graphene layers [187].

Studies have shown that when layered materials such as graphene are used as nanofillers in polymer-based composites, three types of phases are possible: stacked, intercalated or exfoliated, as shown in Fig. 10 [245,246]. When the polymer is unable to intercalate between the graphene sheets, because of insufficient exfoliation of graphite in the case of LPE systems, or restacking of layers during reduction of GO, a phase separated composite is formed that consists of large stacked agglomerates of graphene sheets [247]. Superior properties can be achieved if there is a strong interfacial bonding interaction between graphene and the host polymer matrix. In the exfoliated structure (Fig. 10(c)), exfoliated graphene flakes have the largest possible interfacial contact with the polymer matrix. This significantly enhances the mechanical properties of the composites since, graphene develops a curved wrinkled surface that increases mechanical interlocking with the polymer chains [206]. However, wrinkling can also reduce the intrinsic properties of graphene, such as thermal and electrical behavior [248] as a result of lowering then effective aspect ratio.

It is a not a surprise that GO and rGO are popular choices as filler materials in nanocomposites as opposed to pristine graphene. Due to the functional groups, GO and rGO can easily be dispersed in polar solvents and strongly interact with the polymer matrix allowing for a good dispersion and internal load transfer. However, pristine graphene has not been investigated to the same extent as GO or rGO as polymer reinforcement. The presence of dispersants and the unreactive nature of the pristine graphene surface makes it unlikely to interact with the polymer matrix, and thus leads to poor dispersion and agglomeration [249]. Besides, most of the graphene dispersions produced by LPE methods are dominated by few-layer graphene sheets [76,79,87,89,94,95,83,250–253]. Covalent methods have been use to functionalize GO [254,255], while non covalent methods are used for pristine graphene, because of the low surface chemistry reactivity [256,257]. A comparison of different properties of LPE and GO produced polymer-based nanocomposites is shown in Table 4.

Control over the conditions during the fabrication of the composites, to achieve good dispersion, alignment and polymer interaction, is still a major challenge. Functionalization of the graphene surface can be made to improve the interaction of graphene and the polymer matrix, but controlling other conditions such graphene orientation, graphene contact, i.e. plane-to-plane, edge-to-plane, edge-to-edge remains a big challenge.

6. Economic aspects and outlook of graphene

Graphene, the so-called super material, is a two-dimensional single layer of sp^2 bonded carbon atoms in a honeycomb lattice, and is transparent, more than 200 times stronger than steel and yet flexible as rubber, excellent conductor of energy and has the ability to heal itself when damaged. Graphene can be synthesized from different carbon sources, such as graphite. Methods, such as, LPE, *via* graphite oxide, microcleavage *etc.* rely on natural graphite as a raw material.

Using graphite as a raw material for synthesis of graphene is beneficial in many ways. Firstly, graphite is a natural raw material that is inexpensive, environmentally friendly and readily available. At the time of writing, natural graphite flakes cost about $1000 tonne^{-1}. This means that graphite can easily be used for the production of large quantities of graphene. Therefore, it is essential to optimize the existing graphite based methods for graphene production as well as find newer and better methods that can take advantage of the low cost and availability of graphite for fabrication of high quality graphene.

Other methods that have been extensively used, like CVD, rely on having specialized equipment. CVD technology has been around for a long time and has actively been used for the production of

Table 4
Comparison of thermal, mechanical and electrical properties of LPE and GO produced graphene in polymer composites.

Method	Graphene type	Matrix	Synthesis method	Filler loading	Percolation threshold,wt%	Electrical conductivity, S cm^{-1}	Increase in strength,%	Increase in modulus,%	Thermal properties	Ref.
via LPE method	Graphene	Epoxy	Solution	0.46 vol%	0.088	1E−05	38	37	–	[199]
	Graphene	Poly(vinyl chloride)	Solution	2 wt%	0.6 vol%	0.058 (6.47 vol%)	130	58	T_g ↑ by 3.5 °C	[258]
	Graphene	Epoxy	Solution	0.244 vol%	0.24 vol%	1E−06	−19.6	17.3	T_g ↑ by 7.4 °C	[259]
	Graphene	Nanofibrillated cellulose	Sonication	1.25 wt%	–	–	25	51	–	[260]
	Ionic-Liquid-Functionalized Graphene	Polystyrene	Solution blending	4.19 vol%	0.1 vol%	0.1384	–	–	–	[219]
	Graphene	Poly(vinyl alcohol)	Solution	1.2 vol%	0.265 vol%	1.84E−04 (3 vol%)	129	116	–	[261]
	Graphene nanosheets	Polystyrene	In-situ	2 wt%	–	2.9E−02	–	–	T_g ↑ by 8 °C	[262]
	Functionalized GO	Polystyrene	–	2.5 vol%	0.1 vol%	0.01	–	–	–	[22]
via GO route	GO	Polyurethane	In-situ	2.0 wt%	–	2.15E−08	239	202	Thermal stability by 40 °C at 5% loss	[263]
	GO	Poly(vinyl alcohol)	Solution	0.7 wt%	–	–	76	62	T_g ↑ by 3.3 °C	[214]
	GO	Epoxy	Solution	0.54 vol%	–	–	10	25	–	[264]
	GO	Polyimide	In-situ	3 wt%	–	–	7	27	–	[265]
	TRGO	Polyamide 6	Melt extrusion	12 wt%	7.5 wt%	0.71E−02		47 (10 wt%)	–	[126]
	TRGO	Polyethylene terephthalate	Melt compounding	3 vol%	0.47 vol%	0.0211	–	–	–	[190]
	TRGO	Polycarbonate	Solution blending	2.2 vol%	0.38 vol%	0.226	–	–	T_g ↓ by 3.3 °C	[266]
	TRGO	Polycarbonate	Emulsion mixing	2.2 vol%	0.14 vol%	0.512	–	–	T_g ↓ by 9.7 °C	[266]
	Microwave-Exfoliated GO	Polycarbonate	Melt mixing	3 wt%	1.3 wt%	2.5E−03	–	30	T_g ↑ by 0.6 °C	[267]
	CRGO	Epoxy	Solution	9 wt%	0.52 vol%	0.1	–	–	–	[182]
	TRGO	Polystyrene	Solution	1.1 vol%	0.33 vol%	0.0349	–	–	–	[268]
	GO	Poly (ε-caprolactone)	Electrospin	0.3 wt%	–	–	95	66	T_c ↑ by 7.2 °C	[269]
	TRGO	Polyethylene terephthalate	Melt	3 wt%	0.47 vol%	0.0211	–	–	–	[190]
	TRGO	Poly(vinylidene fluoride)	Solution	4 wt%	2 wt%	1E−04	–	93	–	[217]
	TRGO	Poly(methyl methacrylate)	Solution	1 wt%	–	–	20	80	T_g ↑ by 40 °C	[270]
	GO	Poly(vinyl alcohol)	Solution	0.8 wt%	–	1E−09 (1.6 wt%)	52	54	T_g ↓ by 5.8 °C	[271]
	CRGO	Poly(butylene succinate)	Solution, melt	2 wt%	–	–	22	–	lower stability	[272]
	TRGO	Polyurethane	Solution	7 wt%	2 wt%	4.92E−04 (7 wt%)	−22.5 (7 wt%)	43 (3 wt%)	T_g ↓ by 2.4 °C	[273]
	TRGO	High density polyethylene	Solution	3 vol%	1 vol%	0.015	–	–	–	[274]
	RGO	Polystyrene	Solution blending	2.45 vol%	0.19 vol%	0.7218	–	281.94 vol%	T_g ↓ by 5.5 °C	[275]
	RGO	Poly(vinyl alcohol)	–	3 wt%	–	–	53	52.6	Thermal stability ↑ by 12.1 °C	[276]
	Iodo phenyl functionalized GO	Polyimide	In-situ	0.5 wt%	0.5 wt%	9.2E−04 (2 wt%)	64	172	–	[277]
	TRGO	Epoxy	Solution blending	0.2 wt%	–	1.47E−10	0	5	T_g ↑ by 11 °C	[278]
	CRGO	Nanofibrillated cellulose	Solution mixing	10 wt%	–	0.154	12	70	–	[279]
	CRGO	Poly(vinyl alcohol)	Solution mixing	1.8%	–	–	150 (1.8 vol%)	940	–	[213]
	TRGO	Polylactide	Melt blending	3 wt%	3–5 wt%	1E−10 (7 wt%)	12.9	33	Degradation temp ↑ by 14 °C	[280]
	GO	Poly(vinyl alcohol)	Solution	2 wt%	–	–	167	92,2	T_g↑ by 8 °C (3.5wt%)	[281]
	TRGO	Isotactic poly(propylene)	Melt	10 wt%	<5 wt%	1,89E−4	–	53	–	[126]

Notes: TRGO – Thermally reduced Graphene Oxide; CRGR – Chemically Reduced Graphene Oxide; T_g – glass-transition temperature; T_c –crystallization temperature.
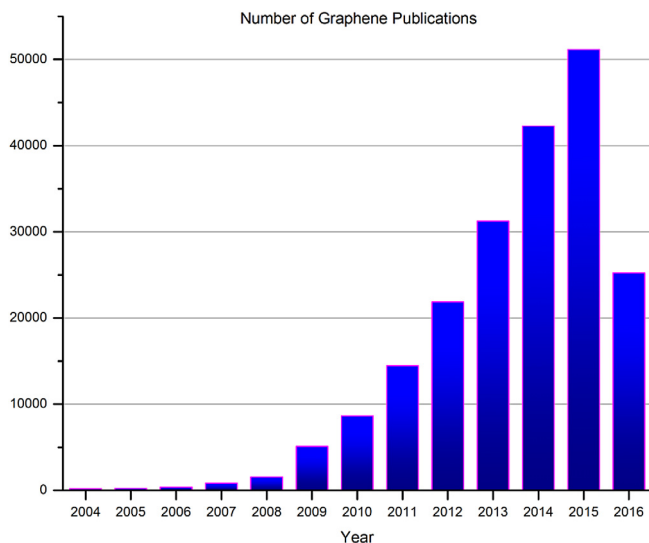
Fig. 11. The approximate number of graphene publications from 2004 to June 2016 using Thomson Reuters Web of Science (searching for graphene in topics).

carbon nanotubes, diamond-like carbon *etc.* Therefore, it is also possible to use the same equipment to fabricate graphene with only minor adjustments. The prices of the CVD equipment vary depending on the size of substrate. They start as low as £59,000 ($77,300) for small substrates, typically for research purposes and a hundred of thousands for large substrates.

LPE is one of the cheapest methods. All the equipment that is required is commonly available in laboratories. Therefore, there is no need to buy new equipment in most cases. Sonication assisted LPE methods use the common bath or tip sonicators, that are typical laboratory equipment, while shear assisted LPE can utilize equipment such as microfluidizers, high shear mixers *etc.*, which are also commonly available. However, low yield, low concentration of single graphene layers, lack of control over the lateral flake size are still the main bottlenecks for this method. Graphene production *via* graphite oxide on the other hand requires use of strong and hazardous oxidizers such as sulfuric acid and potassium permanganate. Moreover, chemical reduction of GO uses toxic and unstable chemicals such as hydrazine. The harsh conditions are detrimental not only to the produced graphene but also to the environment, and this also adds extra costs to the production process not least in waste disposal. Therefore, in order to implement this method for large scale graphene production, there is a need for development of sustainable "green" approaches for oxidation and reduction processes. Both of these methods have, nonetheless, huge potential for scalability, one of the main reasons being that the raw material, graphite, is readily available and low-cost.

Although there has been a few graphene based products on the market, graphene commercialization is still far from reality. However, there is no indication that graphene interest will fade any time soon. The publications on graphene from 2004, when it was first isolated, have increased significantly as shown in Fig. 11. Unless cheaper methods can be found for large scale graphene production, the full potential of graphene will not be reached. Several measures have been taken to ensure commercialization of graphene. For example, an EU program called Graphene Flagship is a ten-year 1 billion Euro (1.11 billion $) funded flagship that was developed in 2013. The idea is to create the right conditions for European innovation in graphene to flourish by bringing together different research groups and help them commercialize their products. The interest from the EU is not surprising looking at the potential of using graphene in a sustainable green economy.

Graphene can be used as a sieve, for example, to reduce emissions into the environment, like in power plants or manufacturing industries, to prevent greenhouse gases escaping. There is also a possibility of replacing lithium-ion (Li-ion) batteries with more efficient and ecological materials. Another potential area of application is in cars and airplanes. By replacing the heavier materials with graphene it can lead to huge fuel savings. For example, it has been estimated that reducing the Boeing 777 by only 5000 kg can lead to savings of $1 m per year, and, of course, that means a reduction in emissions as well. The Graphene Flagship developed by the EU shows that the willingness to take an active role in the graphene revolution is there, because graphene is really a material of the future.

Although commercialization of graphene products has been very slow, the efforts that have been put into graphene research make it easy to look to the future with optimism that graphene will someday become a fundamental part of not only new scientific innovations but also of economic development while maintaining an ecological balance.

7. Conclusions and outlook

It is impossible, in this short review, to discuss all the aspects of graphene. However, it is evident that graphene is an interesting material that exhibits excellent unique properties that make it a compelling candidate for various applications. But despite all these excellent properties, there are still a lot of challenges to be overcome before the true potential of graphene becomes realizable. In this review, three aspects of graphene have been discussed: properties, fabrication methods and application in polymer composites. From the properties aspect of graphene, it is clear that it has a high potential for various applications including nanofiller for functional composites, energy storage devices, flexible electronics, sensors, *etc.* due to its superlative properties. The top-down approaches for graphene exfoliation have been reviewed such as MC, LPE, and *via* GO routes. These methods utilize graphite as a starting material that is low-cost and readily available. However, it is clear from the discussion that the most challenging problem that hinders the wider scale application of graphene is still the lack of an economically viable large scale production method for high quality graphene fabrication that is environmental friendly. At the moment, LPE and GO are still the promising methods with high scalability potential. Despite the progress that has been made in these methods, there are still challenges that require to be addressed. For the LPE system, these include increasing the yield and degree of exfoliation, since the yield for single layer graphene is still very low, and for the GO route the need is to develop greener and more efficient methods for oxidation and reduction processes that could significantly reduce the induced defects. Therefore, it is important in the near future to optimize and increase the efficiency of these mechanical exfoliation methods. It is also vital to control the amount of defects induced, lateral size of the sheets and the number of graphene layers.

The application of graphene in polymer nanocomposite was reviewed. It is evident that GO is the most widely used graphene based nanofiller in polymer composites, largely because of the chemical interaction between the filler and the polymer matrix that enhances homogeneous dispersion of graphene in the matrix, thus improving the overall composite performance. Application of pristine graphene in polymer composites is still limited. More work is needed in this area because only by implementation of defect-free graphene can the maximum properties of the composites be achieved. Several challenges must be overcome to benefit fully from the properties of pristine graphene in polymer composites, including achieving homogeneous dispersion and spatial dis-

tribution in the matrix, and strong interfacial interaction of graphene and the polymer matrix, alignment and overlapping *etc*.

Looking at the big picture, the progress that has been made to date is quite impressive, keeping in mind that graphene is just over a decade old in science terms, and so it is still a very "young" technological material. The prototypes of graphene-based products that have been commercialized, such as batteries, sensors, graphene inks *etc*. give good reason to be optimistic about the future for graphene. We can all be confident that graphene is here to stay and it will someday prove to be the 'miracle material' when it finally becomes a fundamental part of our essential applications.

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