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1 **General Overview of Graphene: Production, Properties**  
2 **and Application in Polymer Composites**

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7  
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1 **Abstract**

2

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

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24 *Keywords:* graphene, graphite, electrical properties, thermal properties, composites,  
25 polymers, liquid phase exfoliation, graphene oxide, graphene/polymer composites

# Table of Contents

1		
2		
3	1.	Introduction ..... 5
4	2.	Scope of review ..... 6
5	3.	Fabrication of graphene ..... 7
6	3.1.	Micromechanical cleavage ..... 9
7	3.2.	Liquid-phase exfoliation ..... 11
8	3.3.	Graphene <i>via</i> graphite oxide ..... 15
9	3.4.	Graphene from mechanical milling of graphite ..... 19
10	3.5.	Electrochemical exfoliation of graphite ..... 21
11	4.	Properties of graphene ..... 24
12	4.1.	Electronic properties ..... 24
13	4.2.	Mechanical properties ..... 25
14	4.3.	Optical properties ..... 26
15	4.4.	Thermal properties ..... 27
16	4.5.	Chemical properties..... 28
17	5.	Graphene/polymer nanocomposites ..... 29
18	5.1.	Fabrication methods of graphene/polymer nanocomposites ..... 29
19	5.1.1.	<i>In-situ</i> polymerization ..... 30
20	5.1.2.	Melt intercalation technique ..... 30
21	5.1.3.	Solution mixing ..... 31
22	5.2.	Examples of graphene/polymer composites..... 32

1	5.2.1.	Graphene/epoxy composites.....	32
2	5.2.2.	Graphene/cellulose composites .....	33
3	5.2.3.	Graphene/ Polyaniline (PANI) composites .....	34
4	5.2.4.	PVA/graphene nanocomposites.....	35
5	5.2.5.	Polyurethane (PU)/graphene composites .....	35
6	5.2.6.	Poly (vinylidene fluoride) (PVDF)/graphene composites .....	36
7	5.2.7.	Graphene/Polyethylene terephthalate (PET) nanocomposites .....	36
8	5.2.8.	Polycarbonate (PC)/graphene nanocomposites .....	37
9	5.2.9.	Poly(amido amine) (PAMAM)/graphene composites.....	37
10	5.2.10.	Polystyrene (PS)/graphene nanocomposites .....	38
11	5.2.11.	Graphene/alginate composites .....	39
12	5.2.12.	Graphene nanocomposites for thermal interface materials.....	40
13	5.3.	Outlook of graphene/polymer nanocomposites.....	41
14	6.	Economic aspects and outlook of graphene .....	47
15	7.	Conclusions and outlook .....	50
16		References .....	52
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18			
19			
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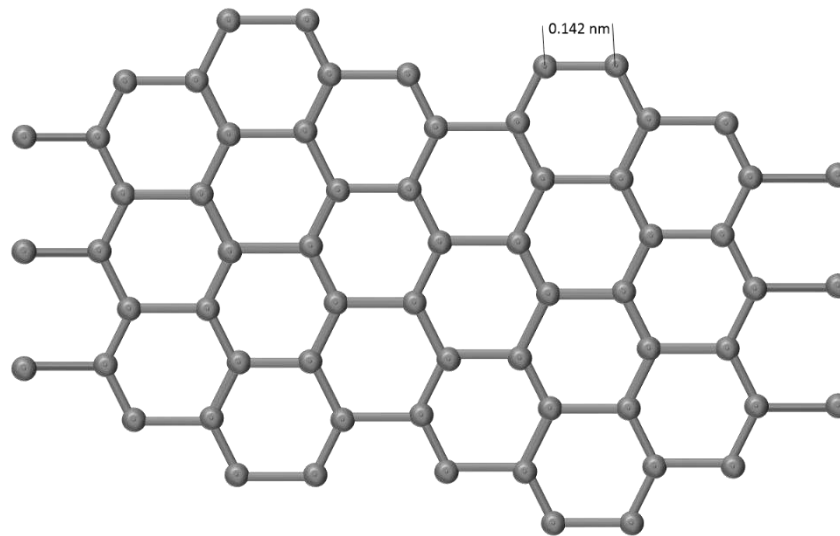
## 1        **1. Introduction**

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

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

14            The exceptional interest in graphene is not surprising given the various excellent  
15 mechanical and chemical properties exhibited by graphene, such as high surface area  
16 ( $2\,630\text{ m}^2\text{g}^{-1}$ ) [8], excellent thermal conductivity ( $5000\text{ W m}^{-1}\text{K}^{-1}$ ) [9], high electron  
17 mobility at room temperature around  $250\,000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  at electron densities of  $2 \times 10^{11}\text{ cm}^{-2}$   
18 [10], very high Young’s modulus 1 TPa [11], very high light transmittance  $\sim 98\%$  [12],  
19 excellent gas impermeability despite only being single atom thick, chemical stability,  
20 anomalous quantum Hall effect (QHE) *etc.* [1,13-18]. Due to these properties, graphene has  
21 found a wide range of potential applications, from medical to paper to electronics to  
22 composite materials *etc.* [19-23]. Graphene can also be modified to generate a band gap that  
23 can lead to application in the semiconductor industry for developing devices such as  
24 transistors [21,24-26]. Due to all these unique properties, graphene has been often called a  
25 “supermaterial” or “miracle material” in the world of materials science.

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



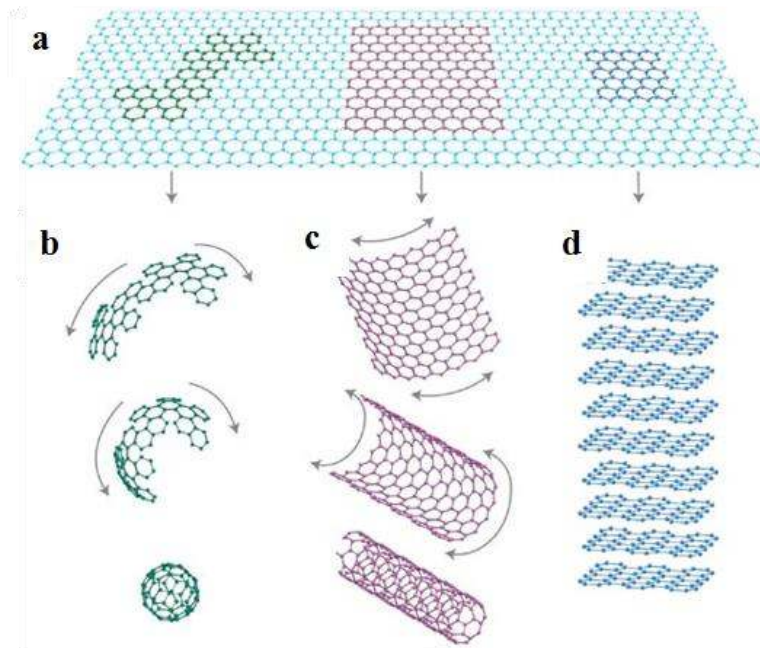
8  
9 *Figure 1 Carbon atoms bonded in a honeycomb lattice, showing C-C bond length of 0.142*  
10 *nm in graphene structure.*

## 11 12 13 **2. Scope of review**

14  
15 The interest in graphene research from 2004 has increased exponentially. Several  
16 reviews about graphene have been published all with a different focus [15,27,30-35]. In this  
17 review, rather, we shall consider a panoramic approach of the synthesis methods of graphene  
18 (particularly from graphite), and some properties and application in polymer composites.  
19 When needed, the reader will be directed to a more detailed reference.



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

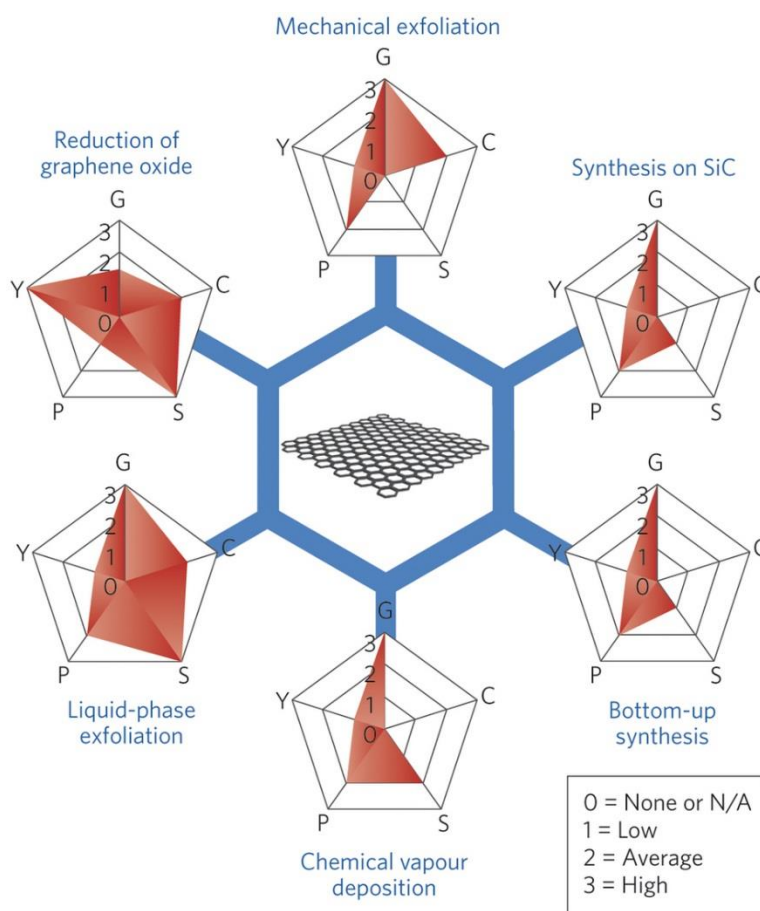


6  
7 *Figure 2 Allotropes of carbon: a) 2-D graphene b) 0-D fullerene, c) 1-D carbon nanotube*  
8 *d) 3-D graphite. Reproduced with permission from reference [27]. Copyright: 2007 Nature*  
9 *Publishing Group.*

### 10 11 12 **3. Fabrication of graphene**

13  
14 One of the major challenges of graphene since it was discovered has been finding a  
15 fabrication method that can not only produce high quality graphene but also at large scale.  
16 Utilization of graphene by various industries depends mostly on finding fabrication methods  
17 for large scale production. The current lack of viable large scale production method has  
18 hindered large scale industrial application of graphene despite its excellent properties. Some

1 of the methods that have been reported so far range from mechanical and chemical  
 2 exfoliation of graphite include [1,20], epitaxial growth of graphene on silicon carbide (SiC)  
 3 [36,37], titanium carbide (TiC) [38], tantalum carbide (TaC) [39], and different metal  
 4 substrates, such as Ni, Cu, Pt, Ru, Ir, Co *etc.* [40-43], and graphene formed from un-zipping  
 5 of carbon nanotubes[44-46], solvothermal synthesis [47], organic synthesis [48], chemical  
 6 vapor deposition methods (CVD) [49-51], and synthesis of graphene from graphite oxide via  
 7 oxidation of graphite [52-56]. Some of these methods are depicted in Figure 3, and each  
 8 method can be utilized depending on the application and desired quality of graphene.



9

10 *Figure 3 Some common production methods of graphene in relation to quality and*  
 11 *scalability potential. Each method has been evaluated in terms of graphene quality (G), cost*  
 12 *aspect (C; a low value corresponds to high cost of production), scalability (S), purity (P)*  
 13 *and yield (Y) of the overall production process. Reproduced with permission from reference*  
 14 *[57]. Copyright: 2015 Nature Publishing Group.*

15 Graphite is a highly anisotropic natural mineral [58] that has been known for  
 16 hundreds of years and is used as a lubricant, for electrodes and pencil lead. The thermal and

1 electrical conductivities of in-plane graphite are about a thousand times higher than out-of-  
2 plane, which is also a similar scenario with strength and modulus [59]. Graphite is made up  
3 of single sheets of stacked graphene held together by the weak van der Waals forces. These  
4 sheets can be peeled off by application of a force that exceeds these forces. Since graphite is  
5 cheap and readily available, production of graphene based on exfoliation of graphite may be  
6 considered to have huge potential for large scale application [60].

7 One other method that has been reported for production of graphene is from biomass  
8 [61-64]. This is also an interesting method given the nature of biomass, i.e. its cheapness,  
9 sustainability and non-toxic nature. Therefore, it is probably safe to say that it already has  
10 potential for scalability [64]. Given that the biorefinery industry is already well established,  
11 graphene production could in principle easily be integrated into a biorefinery facility.  
12 However, prior to this eventuality, a lot of effort is needed from the research community to  
13 develop and optimize the methodology for high quality graphene production from biomass.

14 Graphene derivatives such as graphene oxide, graphane, graphene fluoride *etc.* have  
15 shown interesting functional properties that could be utilized in various applications [65-67].  
16 In this review however, only graphene oxide is considered. Detailed discussion regarding  
17 graphene derivatives can be found in the following publications [67-71].

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

### 21 **3.1. Micromechanical cleavage**

22  
23 Micromechanical cleavage (MC), also known as micromechanical exfoliation or the  
24 Scotch tape method is an old method that has been around for decades and extensively used  
25 in fields such as crystallography [72]. Amongst the graphene research community,

1 micromechanical cleavage is one of the most popular methods for graphene production - not  
2 surprising given that it led to the ‘birth of graphene’ [1]. The MC method is a simple method  
3 that does not require any special equipment. The only ‘equipment’ required basically is an  
4 adhesive tape. Graphite flakes are placed between the adhesive tape and the surface is peeled  
5 off continuously. This continuous peeling of graphite causes the cleaved thin flakes to adhere  
6 to the surface with almost an atomically clean flat surface [73]. To get few-layer and even  
7 single-layer graphene sheets, a clean tape is used to peel off the first flakes that stack to the  
8 surface and this continuous repeating process, i.e. peeling and replacing with a new tape  
9 breaks the flakes into thinner and thinner flakes until even single layers are achieved [74].

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

19 Graphene is not the only material that can be produced with the Scotch tape  
20 technique, in fact other 2-dimensional materials can also be produced using this technique  
21 [75,76]. For example, Geim *et al.* [16] used the MC technique to exfoliate other 2-  
22 dimensional materials such as molybdenum disilicide, boron nitride, and the compound  
23 oxide of bismuth-strontium-calcium-copper ( $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ).

24 Although the mechanical cleavage technique is a versatile and simple method for  
25 fabrication of defect free graphene, scalability is still the main challenge. Despite the

1 drawbacks, micromechanical exfoliation still remains the popular choice for fundamental  
2 research because of the high quality of the produced graphene flakes. The majority of the  
3 new graphene properties discovered and the potential application in new device prototypes  
4 have been achieved using mechanically cleaved graphene flakes. It is clear that the MC  
5 method did not only start the graphene revolution but still remains the main tool for further  
6 exploration of graphene properties and potential applications.

7

### 8 **3.2. Liquid-phase exfoliation**

9

10 Liquid phase exfoliation (LPE) can be used to exfoliate graphite in different liquid  
11 media via ultrasound or shear forces to extract single to few-layer graphene sheets (Figure  
12 4). Graphite is held together by the weak van der Waals, therefore the first step to successful  
13 exfoliation of graphene is to overcome these forces. Wang *et al.* [77] estimated the surface  
14 energy of graphene to be  $46.7 \text{ mN}\cdot\text{m}^{-1}$ . Therefore, the suitable liquid medium should have  
15 similar surface energy in order to minimize the interfacial tension between the solvent and  
16 the graphene layers [78]. Some of the solvents that have been successfully used to exfoliate  
17 and stabilize graphene include, but not limited to, N-methylpyrrolidone (NMP) and N,N-  
18 dimethylformamide (DMF) [78-84].

19 LPE is a simple method that has huge potential for scalability [85,86]. The main  
20 principle of LPE is that graphite is dispersed into a suitable solvent and then exfoliated with  
21 the aid of ultra-sonication or shear forces. During these processes, the growth and collapse  
22 of the micrometer-sized bubbles or voids in liquids due to pressure fluctuations, act on  
23 graphite and induce exfoliation into single and few-layer graphene sheets.

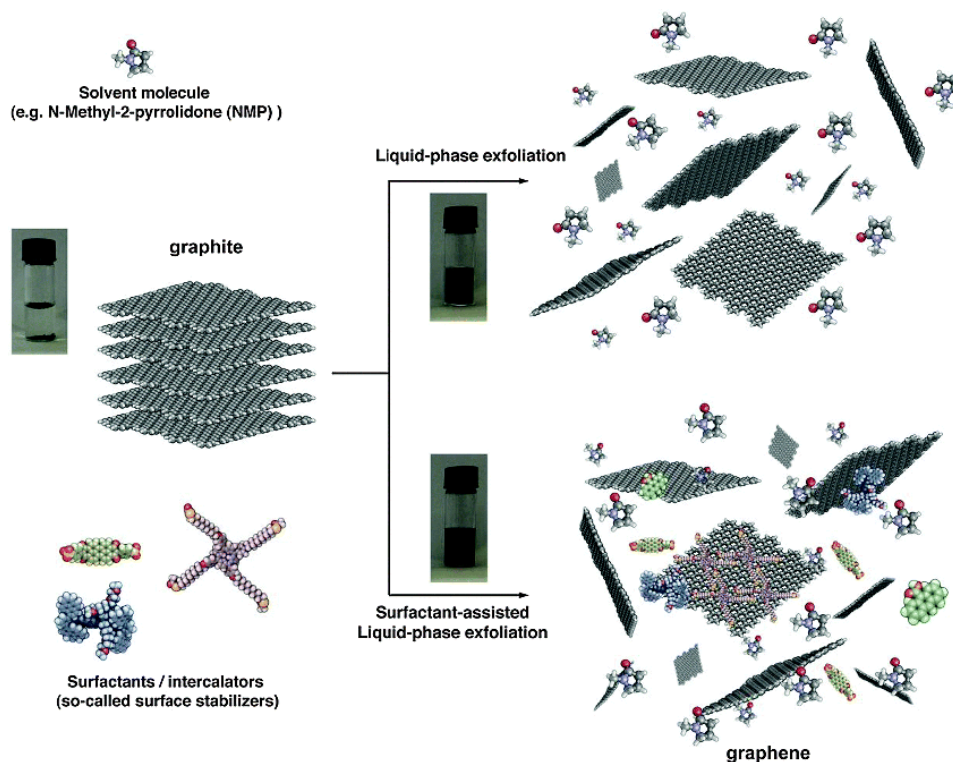


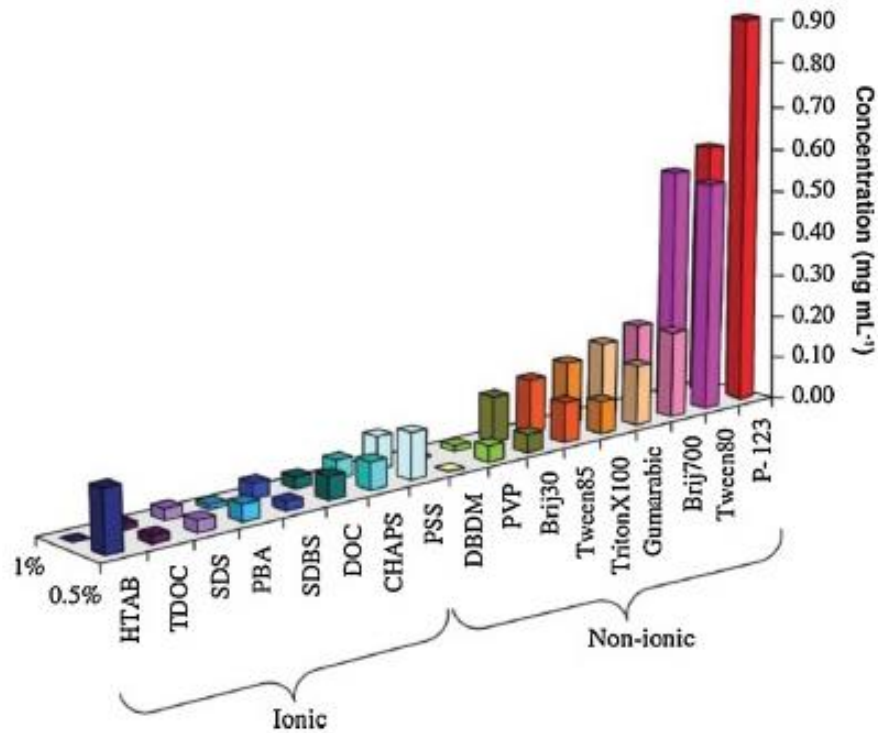
Figure 4 Schematic representation of the liquid-phase exfoliation process of graphite in the absence (top-right) and presence (bottom-right) of surfactant molecules. Reproduced with permission from reference [85]. Copyright: 2014 The Royal Society of Chemistry.

1           The main challenges in exfoliation of graphite in solvents, i.e. suitable solvents with  
 2 a surface energy around  $40 \text{ mN.m}^{-1}$  is that most of these solvents are not only expensive and  
 3 corrosive but have also high boiling point and normally toxic. Therefore, there have been  
 4 attempts to exfoliate graphite in low boiling point solvents such as acetone, ethanol,  
 5 methanol, acetonitrile *etc.* [87-89]. For example, Zhang *et al.* [83] reported exfoliation of  
 6 graphite in ethanol by solvent exchange from NMP. Graphene was first exfoliated in NMP  
 7 then filtered and subsequently re-dispersed into ethanol. After several centrifugation and  
 8 washing steps, a dispersion in ethanol of stable graphene with a low concentration of  
 9  $0.04 \text{ mg.cm}^{-3}$  was achieved. However, the dispersion was not only low in concentration but  
 10 also very unstable, observed by 20 % sedimentation after just a week.

11           Another solvent that can be used for graphene exfoliation is water. Unfortunately,  
 12 water cannot be used without modification because of its high surface tension of around

1 72 mN.m<sup>-1</sup> and also because of its hydrophilic nature that makes it incompatible with  
2 hydrophobic graphene/graphite. These challenges are normally overcome by using  
3 surfactants or polymers [54,80]. Various polymers, nonionic and ionic surfactants such as  
4 sodium cholate, 4-dodecylbenzenesulfonic acid, sodium deoxycholate, sodium  
5 dodecylbenzenesulfonate, polymer poly(vinyl pyrrolidone) have been successfully utilized  
6 to exfoliate graphite under high concentrations [78,90-95].

7 A thorough investigation of surfactant-assisted graphite exfoliation using ionic and  
8 nonionic surfactants was explored by Guardia *et al.* [96]. It was found that nonionic  
9 surfactants performed better than ionic to stabilize graphene (Figure 5). Nonionic surfactants  
10 have a hydrophobic tail and a long hydrophilic part that creates a steric repulsion between  
11 the hydrophilic moieties in water, and this plays a significant role in stabilizing graphene  
12 [82]. As clearly seen in Figure 5, triblock copolymer Pluronic P-123 achieved the best  
13 results. After two and four hours of sonication, a high concentration yield of 1 mg.cm<sup>-3</sup> and  
14 1.5 mg.cm<sup>-3</sup>, respectively, was achieved. It is also important to note that most of the  
15 surfactant systems act as insulators, therefore, utilizing them results in compromising, or  
16 decreasing, the conductive properties of graphene [92].



1

2 *Figure 5 Concentration of graphene in aqueous dispersions achieved by the use of different*  
 3 *surfactants, as estimated from UV-Vis absorption measurements. Two surfactant*  
 4 *concentrations are shown: 0.5 % and 1.0 % wt/vol. Reproduced with permission from*  
 5 *reference [96]. Copyright: 2011 Elsevier.*

6

7 Ionic liquids have also been shown to be promising candidates for high concentration  
 8 graphene dispersions in LPE systems. Wang *et al.* [97] exfoliated graphite in 1-butyl-3-  
 9 methylimidazolium bis(trifluoromethanesulfonyl)imide achieving a concentration of 0.95  
 10 mg.cm<sup>-3</sup> of 1-5 layers of graphene sheets after one hour of sonication. This was also reported  
 11 by Nuvoli *et al.* [98], and showed that 24 h sonication of graphite in 1-hexyl-3-  
 12 methylimidazolium hexafluorophosphate (HMIM) yielded a high concentration of 5.33  
 13 mg.cm<sup>-3</sup> of thin sheets of graphene of about 2 nm despite having a really low yield of just 1-  
 14 2 wt%. Bari *et al.* [99] reported a high concentration of graphene 5.8 mg.cm<sup>-3</sup> after just one  
 15 hour of bath sonication dispersed in 1,3-Bis(phenylmethyl)imidazolium  
 16 bis(trifluoromethylsulfonyl)amide.

17

The general challenge for all LPE systems, be it in surfactants, polymers, solvents or  
 18 ionic liquid stabilized systems, is that it is very difficult to control the sizes of produced



1 graphene flakes [100]. It has been shown that graphene concentration can be increased with  
2 an increase in processing time but this is at the cost of lateral graphene sheet sizes as well as  
3 purity of graphene [81,101,102]. The longer it is exposed to shear or cavitation forces the  
4 greater the defects and smaller the average sheet size becomes [101,103]. Therefore, it is  
5 critical to find the right balance between the processing parameters that can lead to not only  
6 high concentration of graphene dispersions but also reduce the amount of defects induced in  
7 graphene. It is also important to develop ways to control the size of the flakes during  
8 exfoliation other than having random sizes in dispersions. Despite the challenges presented  
9 by LPE, its simplicity, cost-effective and potential for scale-up, makes it a versatile method  
10 for exfoliation of graphite to graphene.

11

### 12 **3.3. Graphene *via* graphite oxide**

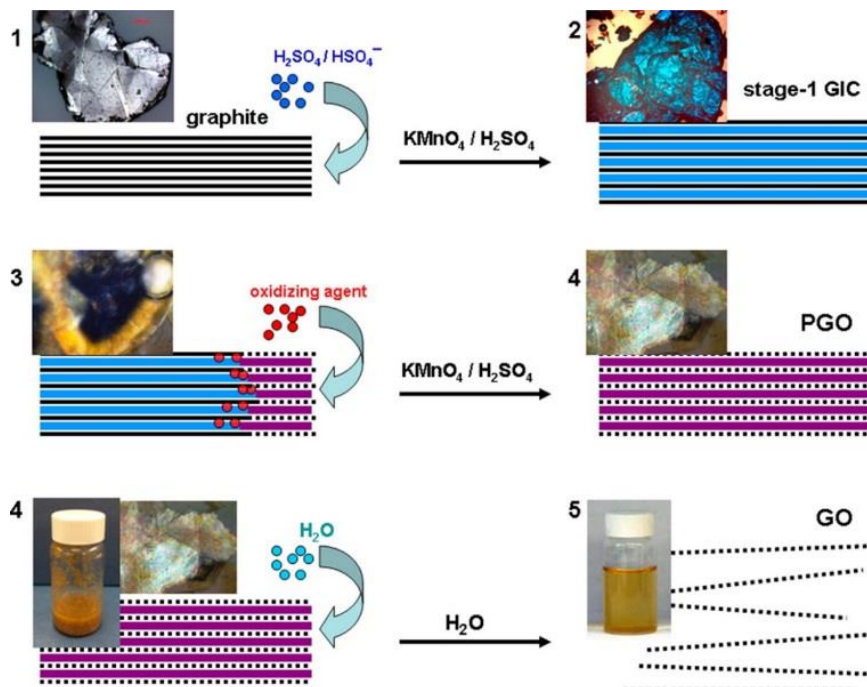
13

14 The popular method for production of graphene is *via* the reduction of graphite oxide  
15 or graphene oxide (GO) to reduced graphene oxide (RGO) [101,104,105]. The popularity of  
16 this method is due to low-cost, high scalability potential, excellent yield and ability to  
17 disperse functionalized graphene in various solvents.

18 This method involves intercalation of graphite with an oxidant, which introduces  
19 functional oxygen groups on the surface of graphene sheets. These functional groups help to  
20 disperse and stabilize graphene oxide in water [106,107]. Fabrication of graphite oxide is  
21 normally achieved by the so-called Hummers method [108], which is the most widely used  
22 protocol for oxidation of graphite. After oxidation, graphite oxide is dispersed in water and  
23 subjected to sonication resulting in individual dispersed graphene oxide sheets in water. A  
24 comprehensive study of graphite oxidation was conducted by Tour *et al.* [109]. They  
25 identified three main steps involved in converting graphite to GO (Figure 6). Graphite is first

1 intercalated with sulfuric acid, then oxidized to form graphite oxide and finally dispersed in  
 2 water. Potassium permanganate reacts with sulfuric acid to form an active oxidizing agent,  
 3 dimanganese heptoxide ( $Mn_2O_7$ ) [110]. This aggressive chemical treatment of graphite  
 4 destroys the  $sp^2$  structure of graphene and introduces functional groups such as hydroxyl (-  
 5 OH) or epoxide (C-O-C) in the basal plane and carbonyl (C=O) and carboxylic (-COOH) on  
 6 the edges [111-115] (see Figure 7). These functional groups help to disperse graphene in  
 7 water homogeneously. We note that the Hummers' method utilizes chemicals such as sodium  
 8 nitrate, concentrated sulfuric acid and potassium permanganate [108], which are in turn not  
 9 environmentally friendly. Since these materials are processed at high temperatures, there is  
 10 a high risk of an explosion during processing. Besides, sodium nitrate produces toxic nitrous  
 11 gas, thus making this method unsuitable for large scale application. Several efforts have been  
 12 made to improve the Hummers' method, for example, by eliminating the use of sodium  
 13 nitrate [116].

14



15

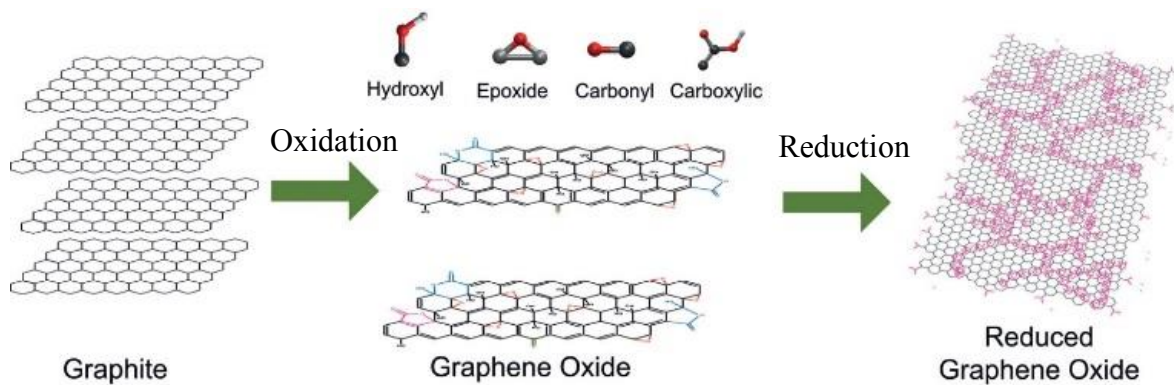
16 *Figure 6 Schematics of conversion of graphite into graphene oxide with corresponding*  
 17 *sample appearance at each stage. The three steps signify formation of the two intermediate*  
 18 *products (stage-1 GIC and PGO) and the final GO product. The solid black and dotted black*  
 19 *lines represent graphene layers and single layers of GO, respectively; while the wide blue*

1 lines represent  $H_2SO_4/HSO_4^-$  intercalant; wide purple lines represent a layer of the mixture  
2 of  $H_2SO_4/HSO_4^-$  intercalant with the reduced form of oxidizing agent. Reproduced from  
3 reference [109].

4

5 Graphene or reduced graphene oxide is obtained from graphene oxide by a reduction  
6 process. Different methods exist for the reduction of GO and there is a lot of research going  
7 on in this area [117-122]. This step is very important, because the chosen method affects the  
8 quality and properties of the produced graphene and the potential areas of application.

9



10

11 *Figure 7 RGO synthesis steps from oxidation to reduction. Graphite can be oxidized using*  
12 *different approaches. This introduces various functional groups on the surface and edges of*  
13 *the sheets, which act as defects. These defects can be partially removed by suitable reduction*  
14 *processes. Reproduced with permission from reference [123]. Copyright: 2012 Elsevier.*

15

16 Oxidation of graphite *via* Hummers' method introduces defects to the graphene  
17 sheets. Some of these defects can be partially removed by the reduction processes. However,  
18 none of the current known methods is able to restore and remove fully all graphene defects  
19 introduced by oxidation [124]. The three main methods that are utilized for the reduction of  
20 graphene oxide are chemical, thermal and microwave. In chemical methods, GO is  
21 chemically treated with reducing agents such as hydrazine hydrate, hydroiodic acid, sodium  
22 borohydride, amino acid, dopamine, ascorbic acid *etc.* [56,118,120-122,125-130]. GO can  
23 also be thermally treated at high temperature to thermally reduced graphene (TRG) [131-  
24 134]. The oxygen containing functional groups are decomposed to  $CO_2$  and  $H_2O$ . Microwave  
25 irradiation has also been efficiently used to reduce graphene oxide to few-layer graphene

1 [135-138]. Most of the materials used in chemical reduction methods that are effective, such  
 2 as hydrazine, are very toxic and dangerous, especially in large volumes. Thermal and  
 3 microwave treatment eliminate the need for chemical treatment but high local temperatures  
 4 on the surface in excess of 1 000 °C can be detrimental, for example, on flexible substrates.  
 5 A detailed analysis of reduction methods was conducted by Pei *et.al.* [124], Pumera *et al.*  
 6 [117] and also briefly by Khaled *et al.* [82]. A summary of some of these methods is provided  
 7 in Table 1, together with corresponding C/O ratio and electrical conductivity. The reader is  
 8 referred to references [117,124] for more comprehensive reviews on the various reduction  
 9 methods of graphene oxide.

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

20

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

<b>Reduction methods/conditions</b>	<b>C/O ratio</b>	<b>Conductivity, <math>\sigma</math> (S.m<sup>-1</sup>)</b>	<b>Cited reference</b>
Hydrazine hydrate, 100 °C, 24 h	10.3	2 420	[56]

Thermal, H <sub>2</sub> gas, 700 °C, 30 min	28.6	8 100	[131]
L-Ascorbic acid/NH <sub>3</sub> , 95 °C, 15 min	12.5	7 700	[122]
plasma assisted, CH <sub>4</sub> gas, 700 °C, 20 s	9.2	34 500	[139]
150 mM NaBH <sub>4</sub> solution, RT, 2 h	8.6	45	[120]
NaBH <sub>4</sub> , 80 °C, 1 h	4.8	82	[111]
NH <sub>3</sub> BH <sub>3</sub> , 80 °C, 12 h	14.2	19 300	[130]
Thermal, 1 000 °C, C <sub>2</sub> H <sub>2</sub> , 30 min	50.2	142 500	[132]
DMF + 0.6 M H <sub>2</sub> SO <sub>4</sub> , 1 h	8.4	1 223	[140]
Zn/HCl, RT, 1 min	33.5	15 000	[141]
HI/AcOH, 40 °C, 40 h	11.5	30 400	[125]

### 3.4. Graphene from mechanical milling of graphite

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The first known study of graphene production by graphite milling was made by Antisari *et al.* [142]. 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.* [143] 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

1 were able to estimate that the graphene sheets exfoliated in DMF via ball milling were  
2 around three layers. The quantity and quality of produced graphene flakes depended on  
3 parameters such as speed of rotation, diameter of milling ball, milling time, type of graphite  
4 used, concentration of graphite in the solvent and centrifugation speed. In another study  
5 [144], the same authors were able to show that the same method can be used to exfoliate  
6 graphite in various organic solvents to form stable colloidal dispersions of graphene sheets  
7 such as N-methylpyrrolidone (NMP), ethanol, tetramethylurea (TMU), acetone, formamide  
8 and tetrahydrofuran (THF).

9 It was also demonstrated by Peipei *et al.* [145] that by co-processing graphite with  
10 cellulose in a ball mill, graphene-like sheets can be produced. Subsequently, the production  
11 of graphene from graphite via ball milling in the presence of melamine was also investigated  
12 [146,147]. The maximum concentration of graphene managed to be produced by using DMF  
13 as a stabilizing agent was  $0.13 \text{ mg cm}^{-3}$  in less than 1 h.

14 Cao *et al.* [148] also utilized the ball milling method to exfoliate graphite with dry  
15 ice for 48 h in the presence of carbon dioxide to produce graphene oxide nanoplatelets  
16 (GONPs) that were later combined with poly(p-phenylenediamine) to produce the  
17 composites. The resulting GONPs showed a high specific surface area of  $589.7 \text{ m}^2\text{g}^{-1}$ . This  
18 reported value was much higher than was achieved by Jeon *et al.* [149] for edge-selectively  
19 carboxylated graphite ( $389.4 \text{ m}^2\text{g}^{-1}$ ), also produced by milling graphite in dry ice.

20 It is evident from the above that mechanical milling of graphite is a simple, low-cost  
21 and effective method providing control over a wide range of parameters during processing  
22 and shows potential for large scale production [150,151]. However, long processing times,  
23 high energy consumption, low graphene yield, as well as induced defects in the final  
24 products, still hinders this method for wider applicability [151-153].

25

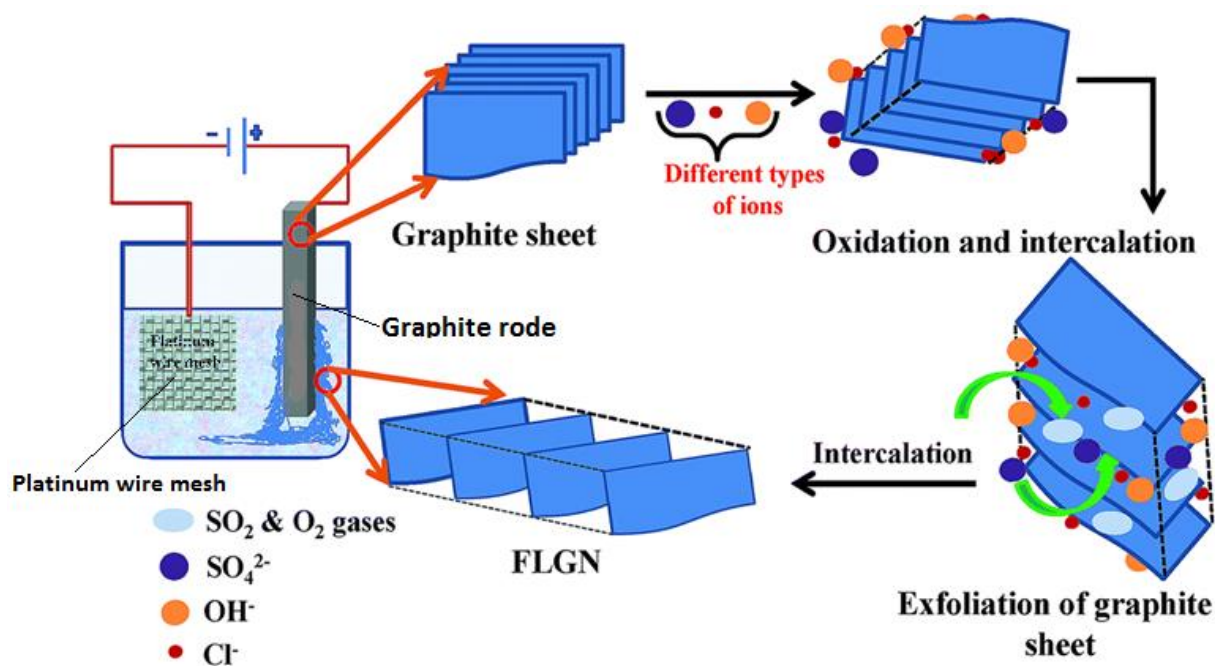
### 1        **3.5. Electrochemical exfoliation of graphite**

2  
3        Electrochemical exfoliation is a well-known technique that has been around for many  
4 decades. The most popular application of electrochemical methods is found in the metal  
5 industry, in particular for the production of aluminum. It has also found wide application in  
6 industrial chemicals for the production of peroxyacids, chlorates *etc.* [154]. Coincidentally,  
7 carbon materials have been extensively used as electrodes in electrochemistry [155,156].  
8 Due to their excellent electrical properties, in particular, graphite and graphene have been  
9 utilized as electrodes in devices such as supercapacitors, batteries, solar cells *etc.* [156]. As  
10 already mentioned earlier, graphite can be intercalated to form graphite intercalate  
11 compounds (GIC). One of the methods utilized for this process is electrochemistry. Ever  
12 since the graphene revolution started in 2004, a lot of interest has been generated to find  
13 methods other than mechanical exfoliation for synthesis of graphene. In recent years, some  
14 researchers have successfully used the well-known electrochemical method to exfoliate  
15 natural graphite [157-161].

16        The mechanism of electromechanical exfoliation is well illustrated in Figure 8. This  
17 process involves reduction and oxidation processes at the cathode and anode, respectively,  
18 in the presence of an aqueous or organic electrolyte [162]. One of the electrodes is graphite  
19 based and the other auxiliary is usually platinum. The exfoliation process is usually  
20 commenced by application of a positive current to the electrodes. The graphite based  
21 electrode will undergo oxidation and the negatively charged ions from the electrolyte will  
22 be intercalated into the graphite layers. To facilitate the exfoliation process, application of a  
23 negative potential is subsequently applied [163]. The choice of electrolyte is vital for  
24 successful graphite exfoliation and active research is continuing in this field to find the best

1 aqueous and non-aqueous based electrolytes that can be used efficiently to achieve effective  
2 electrochemical exfoliation of graphite.

3



4

5 *Figure 8 Schematic diagram of the mechanism of electrochemical exfoliation of graphite.*  
6 *The electrodes used were graphite rod and platinum wire mesh for the anode and cathode,*  
7 *respectively. Reproduced with permission from reference [164]. Copyright: 2007 The Royal*  
8 *Society of Chemistry.*

9

10 Electrochemical exfoliation is showing itself to be a fast growing method for the  
11 production of graphene sheets, and it is easy to see why [165]. Unlike the Hummers' method  
12 that utilizes aggressive oxidants, the electrochemical method takes advantage of the  
13 electrical conductivity of graphite to intercalate charged ions, and the subsequent  
14 electrochemically initiated reaction with the electrolyte to provide the exfoliation  
15 mechanism. Another advantage of this method over the chemical and mechanical methods  
16 is the possibility of mass production of graphene at a much lower cost [166].

17 One of the drawbacks of the electrochemical exfoliation of graphite is the need for  
18 an unbroken voltage bias to the electrode, which can be problematic in some instances. Since  
19 exfoliation does not only occur on the surface of the graphite electrode, but rather throughout



1 its complete thickness, exfoliation of thick graphite layers is a common result. The higher  
 2 the surface area that is exposed to the electrolyte the higher the possibility of having large  
 3 junks of graphite in the final product. Unless it can be successfully addressed, this limitation  
 4 will continue to be a big hindrance for the electrochemical exfoliation method to become a  
 5 viable option for large scale graphene production.

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

*Table 2 Comparison of graphite based graphene production methods*

Method	Advantages	Drawbacks
Micromechanical cleavage	<ul style="list-style-type: none"> <li>▪ High quality flakes</li> <li>▪ Simple preparation method</li> <li>▪ Low-cost and easy</li> <li>▪ No special equipment needed</li> </ul>	<ul style="list-style-type: none"> <li>▪ Low yield</li> <li>▪ Labor intensive (not scalable)</li> <li>▪ Uneven films</li> <li>▪ Dimensions dependent on initial crystal size</li> </ul>
Graphene via graphite oxide	<ul style="list-style-type: none"> <li>▪ High dispersability</li> <li>▪ Scalable method</li> <li>▪ High processability</li> <li>▪ High yield</li> <li>▪ Relatively inexpensive</li> </ul>	<ul style="list-style-type: none"> <li>▪ Poor electrical/electronic properties</li> <li>▪ Fragile stability of the colloidal dispersion</li> <li>▪ Potentially explosive process</li> <li>▪ Time consuming</li> <li>▪ Use of toxic chemicals</li> <li>▪ Small area flakes</li> <li>▪ Reduction to graphene is only partial</li> </ul>
Liquid-phase exfoliation	<ul style="list-style-type: none"> <li>▪ High Quality</li> <li>▪ Good Scalability</li> <li>▪ Low Temperature</li> <li>▪ Relatively inexpensive</li> </ul>	<ul style="list-style-type: none"> <li>▪ Small area graphene flakes (&lt;5 μm)</li> <li>▪ Low yield of thin graphene layers</li> <li>▪ Limited dispersability</li> <li>▪ Limited processability</li> </ul>
Mechanical milling of graphite	<ul style="list-style-type: none"> <li>▪ Simple technique</li> <li>▪ Control over the various process parameters</li> <li>▪ Relatively inexpensive</li> </ul>	<ul style="list-style-type: none"> <li>▪ Long processing times</li> <li>▪ Induces defects</li> <li>▪ Low graphene concentration</li> <li>▪ Low yield</li> </ul>

Electrochemical exfoliation	<ul style="list-style-type: none"> <li>▪ High yield</li> <li>▪ Cost effectiveness</li> <li>▪ High processability</li> <li>▪ Environmentally benign</li> <li>▪ Scalable</li> <li>▪ Fast production</li> <li>▪ Good electronic properties</li> </ul>	<ul style="list-style-type: none"> <li>▪ Slight oxidation</li> <li>▪ Inhomogeneous flake thickness</li> </ul>
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1        **4. Properties of graphene**

2

3            The rapid interest in graphene research arose from the unusual properties exhibited

4 by graphene. These properties have made it a fascinating material with huge potential for

5 application in different industries and devices. It is important to note that most of the

6 excellent properties that have been reported are in regard to single layer defect-free graphene.

7 Most of the methods discussed above are unable to produce pristine graphene that can exhibit

8 all these superlative properties. In this section, some of these exciting properties will be

9 briefly discussed.

10

11        **4.1. Electronic properties**

12

13            The graphene revolution started with the study of electrical and electronic properties

14 of graphene [1]. These properties are much dependent on the number of graphene layers in

15 graphene sheets. The properties shown by single layer, bilayer or trilayer are very different

16 materials. One of the earlier works of Novoselov *et al.* [16] on graphene, showed the

17 potential application in transistors due to the possibility of varying charge carriers from holes

18 to electrons. This electron-hole dependence is only applicable to single layer graphene

1 sheets, but, if the number of layers begin to increase, the dependence becomes weaker due  
2 to the electrical field screening by other layers.

3 The quantum Hall effect of graphene for both electron and hole carriers has been  
4 found to be due to the extremely high electron mobility of graphene at various temperatures  
5 and under exposure to magnetic fields [16,167]. At room temperature this can exceed 2 000  
6  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  for mechanically produced graphene. Typically, the classic integer quantum Hall  
7 effect occurs at  $4e^2/h$ , where  $e$  is the electron charge and  $h$  is Planck's constant, but in  
8 graphene it occurs at only half integers. It is believed that this effect is due to the unique  
9 graphene band structure.

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

14

#### 15 **4.2. Mechanical properties**

16

17 Carbon based materials have naturally exhibited excellent mechanical properties.  
18 Diamond, for example, is the hardest known natural material, whilst carbon nanotubes have  
19 been known to have the highest tensile strength. Graphene is no different in respect to its  
20 extreme mechanical properties. Lee *et al.* [11] showed graphene to be the strongest material  
21 known by nanoindentation using an AFM, with a tensile strength of 130 GPa. They also  
22 showed single layer graphene to have a breaking strength of more than 200 times that of  
23 steel, and Young's modulus of 1 TPa. However, these values are believed to be dependent  
24 on the purity of graphene sheets. Frank *et al.* [168] measured the Young's modulus of single  
25 layer graphene using AFM to be 0.5 TPa.

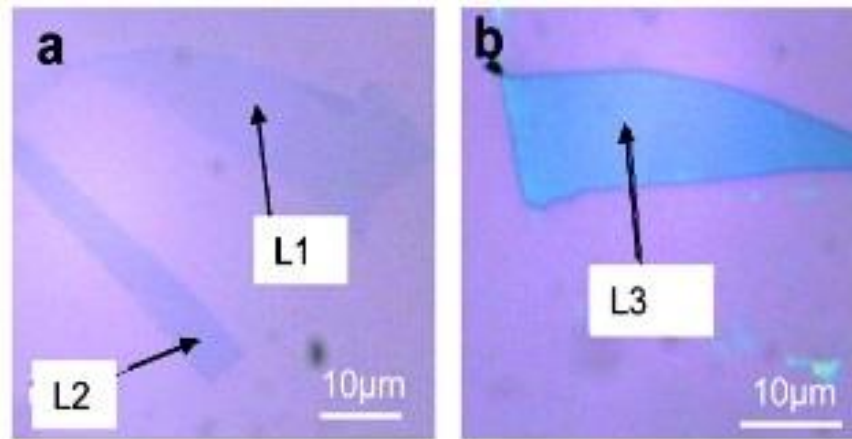
Dikin *et al.* [169] prepared graphene oxide paper that showed the elastic modulus to be around 32 GPa and fracture strength around 120 MPa. To improve the mechanical properties of these graphene papers, divalent ions and polyallylamine [170,171] were introduced between the layers by chemical cross linking. 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.

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

Graphene layers	Mechanical properties		Cited references
	Young's modulus, E (TPa)	Intrinsic strength, $\sigma$ (GPa)	
One	1	130	[11]
One	1	131	[172]
Two	1.04	125	
Three	0.98	101	

### 4.3. Optical properties

Despite being only one atom thick, graphene is able to absorb 2.3 % of white light [51]. 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<sub>2</sub> substrate due to interference. Individual graphene layers can be identified by different contrast as shown in Figure 9(a) and (b) [173]. In the UV region, from 900 down to 300 nm the absorption spectrum of graphene is featureless, and the maximum absorption peak can be seen to be at around 270 nm [51].



1  
2 *Figure 9 (a) Microscopic images of a single layer (right), bilayer (left), and (b) multilayer*  
3 *( $n \sim \infty$ ) of graphene. Reprinted with permission from reference [173]. Copyright 2010*  
4 *American Chemical Society.*

#### 6 **4.4. Thermal properties**

7  
8 The thermal conductivity of graphene is dominated by phonon transport, i.e.  
9 diffusive and ballistic conduction at high and low temperatures respectively [8]. However,  
10 due to the low carrier density of non-doped graphene, the electronic thermal transport in  
11 graphene is negligible [174]. The intrinsic thermal conductivity of graphene is about  
12  $2\,000 - 6\,000 \text{ Wm}^{-1}\text{K}^{-1}$  for suspended graphene sheets at room temperature [175,176] and  
13  $\sim 600 \text{ Wm}^{-1}\text{K}^{-1}$  for suspended graphene on  $\text{SiO}_2$  substrate [177]. These values are very much  
14 dependent on the defects of graphene such as edge scattering [178], isotopic doping [179],  
15 and sample fabrication residues [180] that causes phonon scattering and localization.  
16 Therefore, the higher values of thermal conductivity are achieved by graphene produced by  
17 MC method due to high quality of the sheets.

18 Balandin *et al.* [9] measured the thermal properties of a suspended graphene sheet.  
19 They produced graphene *via* mechanical exfoliation and the measured thermal conductivity  
20 was in the range of  $4\,800 - 5\,300 \text{ Wm}^{-1}\text{K}^{-1}$ , which is higher than that of natural diamond,  
21  $\sim 2\,200 \text{ Wm}^{-1}\text{K}^{-1}$  [181] and  $\sim 3\,000 \text{ Wm}^{-1}\text{K}^{-1}$  [182] for multi-wall, and  $\sim 3\,500 \text{ Wm}^{-1}\text{K}^{-1}$  [183]

1 for single wall carbon nanotubes at room temperature. At these values, the thermal  
2 conductivity of graphene is more than ten times higher than that of copper. It was also  
3 determined by Cai *et al.* [184] that chemical vapor deposited graphene exhibited values of  
4 up to 3 000 Wm<sup>-1</sup>K<sup>-1</sup>, lower than earlier reported for mechanically produced graphene. In  
5 spite of that, these excellent thermal properties of graphene can be exploited to manufacture  
6 devices such as thermal sensors, heat dissipators and composites with excellent thermal  
7 conductivity. The reader is referred to [176,178,185-187] for a more comprehensive  
8 coverage of the thermal properties of graphene.

9

#### 10 **4.5. Chemical properties**

11

12 Pure graphene sheets are mostly unreactive. Functionalization of the surface is  
13 required to make them reactive with other material. Graphene sheet chemistry is dominated  
14 by its surface, while in the form of graphene nanoribbons by its edges. Thickness also plays  
15 a crucial part in graphene reactivity. For instance, it has been determined by Sharma *et al.*  
16 [173], by using the relative disorder (D) peak in the Raman spectroscopy, that single layer  
17 graphene is almost 10 times more reactive than bi- or multi-layer graphene. Using the  
18 spectroscopic test, they compared the reactivity of graphene edges with bulk materials. It  
19 was found that the reactivity of edges is at least two times higher than the reactivity of the  
20 bulk single graphene sheet.

21 One way to functionalize graphene sheets is *via* nitrene chemistry [188], i.e.  
22 introducing reactive species covalently linked to the graphene surface, such as hydroxyl,  
23 bromine, carboxyl, amino *etc.* The resulting functionalized graphene nanosheets can be  
24 controlled to be electrically conductive, and readily dispersible in different solvents. These

1 sheets can be easily processed and utilized in various applications such as nanohybrids and  
2 for fabrication of polymer composites.

## 3 4 **5. Graphene/polymer nanocomposites**

5  
6 Graphene and its derivatives have been extensively used as fillers in composites  
7 because of their excellent resultant properties. The properties of polymer-graphene  
8 composites depend on filler dispersity, filler and matrix bonding, ratio of filler to matrix and  
9 the quality of graphene filler and polymer matrix. These factors can be altered by the  
10 fabrication processes and methods. The advantage of graphene compared with other fillers  
11 is that it allows for large changes in the properties of composites at very low percolation  
12 thresholds due to the ultrahigh aspect ratio of graphene. This section briefly discusses a few  
13 examples where graphene has been used to enhance the properties of polymer composites.  
14 However, before we discuss the examples, we shall take a look into how graphene and  
15 polymer are incorporated together to form composites.

### 16 17 **5.1. Fabrication methods of graphene/polymer nanocomposites**

18  
19 There are three main methods for incorporation of graphene into polymer matrices  
20 that are commonly used, *in situ* polymerization, melt intercalation and solution mixing.  
21 When considering the type of method to pick, it is important to understand the interaction  
22 dependence of graphene and polymers on hydrophobicity, molar mass, polarity, reactivity  
23 *etc.* These three main methods will now be briefly discussed.

### 1           **5.1.1. *In-situ* polymerization**

2

3           In the *in-situ* polymerization method, a monomer and graphene fillers are mixed

4 together, in some cases in the presence of catalyst(s). This step is normally followed by

5 polymerization initiation by heat or radiation [189]. Utilization of epoxy in *in-situ*

6 polymerization is a good example where this method has been extensively applied [190,191].

7 Some examples of polymer/graphene composites that have been fabricated using this method

8 include graphene/polystyrene (PS) [189,192], graphene/polyaniline (PANI) composite

9 [193], and graphene/silicone composites [194]. The main advantages of this method are that

10 there is a strong interaction between the filler and the polymer matrix that leads to a faster

11 stress transfer, and so enables a rapid formation of a homogeneous dispersion, that, in turn,

12 facilitates a homogeneous distribution of the filler in the polymer matrix [195]. *In-situ*

13 polymerization provides excellent miscibility for high filler loading in polymer matrices.

14 However, the polymerization process itself usually increases the viscosity of the mixture and

15 thus further processing becomes difficult, and this eventually restricts the loading fraction

16 [195]. In some cases, this method requires the use of solvents, and this adds the need for

17 further purification steps for solvent removal [196].

### 18

### 19           **5.1.2. Melt intercalation technique**

20

21           In the melt intercalation method, graphene is mixed with the polymer matrix in the

22 molten state, meaning that no solvent is required in this technique. Basically, homogeneous

23 mixing of graphitic materials and polymers is achieved by high shear mixing at elevated

24 temperatures. This method has found extensive application for preparation of thermoplastic

25 composites. Some examples of the application of this method for graphene/polymer



1 composites include exfoliated graphite/polypropylene nanocomposites [197],  
2 polystyrene/graphite nanosheet composites [198], polyethylene terephthalate  
3 (PET)/graphene nanocomposites [199] *etc.* The main drawbacks of this method are that the  
4 dispersity and distribution of the fillers in the matrix are quite poor when compared with  
5 other methods. Besides, the utilization of high shear forces induces defects and breakage of  
6 graphene sheets [200].

7

### 8 **5.1.3. Solution mixing**

9

10 Solution mixing is the most commonly used technique for polymer composite  
11 fabrication amongst all of the methods discussed. This is because of its simplicity, potential  
12 for large scale application, and it does not require specialized equipment. The idea is that the  
13 polymer is solubilized in a suitable solvent and graphene is allowed to swell, i.e. increase  
14 the curvature of its curvilinear surface. Solubility and dispersity of graphene can be a  
15 challenging problem in polymer solution. To alleviate this problems, graphene sheets need  
16 to be functionalized to provide easy dispersability in different solvents, such as organics.  
17 Poly(vinyl alcohol) (PVOH)/graphene oxide (GO) composites were easily fabricated due to  
18 the high solubility of PVOH [201]. In some cases especially involving organic solvents,  
19 homogeneous mixing is achieved via sonication or shear mixing. Other examples where this  
20 method has been used include poly(methyl methacrylate) (PMMA)/graphene [190], graphite  
21 oxide nanoplatelets (GONPs)/polycaprolactone (PCL) [202], graphite oxide  
22 nanoplatelet/polyurethane (PU) composite [203] *etc.* This method should be used with  
23 caution, as re-aggregation of the sheets usually occurs during solvent evaporation. It is  
24 important to find ways to functionalize graphene sheets to prevent against aggregation by  
25 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 [204] and are found in applications ranging from aerospace, electronics, automotive, adhesives *etc.* [191,204-206]. 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.* [207] 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.* [208] 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.*[209] 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.* [210] 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 [211,212]. Therefore, because graphene has a

1 very high aspect ratio, the percolation threshold is achieved at very low graphene loading  
2 [213]. Wajid *et al.* [208] used sonication and shear mixing methods to disperse graphene  
3 into the epoxy matrix and achieved the percolation threshold at 0.088 vol%. In another study,  
4 the composites were fabricated by incorporation of functionalized graphene into the epoxy  
5 matrix by an *in-situ* process [191]. The percolation threshold was reached only after 0.52  
6 wt% loading of graphene, and electrical conductivity increased from  $1^{-10}$  to  $1^{-2}$  S.cm<sup>-1</sup> by ~9  
7 vol.% loading of reduced graphene oxide. Zhao *et al.* [214] conducted a thorough  
8 investigation into the properties of epoxy composite filled with epoxide-functionalized  
9 graphene (G-EP). The tensile strength and Young's modulus increased by 116 % and 96 %,   
10 respectively, compared to the polymer at only 1 wt% loading of G-EP. The percolation  
11 threshold was reached at only 0.33 wt% loading, and electrical conductivity increased from  
12 about  $1^{-17}$  to  $1^{-2}$  S.cm<sup>-1</sup> at ~2 vol.% loading. Thermal conductivity also improved by 189 %  
13 at 10 wt% G-EP loading.

14 For a more comprehensive review on graphene/epoxy nanocomposites, the reader is  
15 referred to a review by Rasheed *et al.* [215].

16

### 17 **5.2.2. Graphene/cellulose composites**

18

19 Graphene has been incorporated in cellulose composites to enhance mechanical and  
20 electrical properties. GO and cellulose were dissolved in N-methylmorpholine-N-oxide  
21 (NMMO) monohydrate to prepare the composite films [216]. Despite being brittle, the  
22 produced graphene/cellulose composites showed improved thermal and electrical properties.  
23 Nguyen *et al.* [217] used reduced graphene oxide sheets (RGO) and amine-modified  
24 nanofibrillated cellulose (A-NFC) to produce composites with enhanced properties. These  
25 composites showed good electrical conductivity of up to 71.8 S.m<sup>-1</sup> and tensile strength of

1 up to 273 MPa. Graphene-cellulose paper (GCP) membranes are used to fabricate flexible  
2 supercapacitors [218]. These composites displayed high electrical conductivity stability with  
3 a decrease of only 6 % after being bent 1 000 times. The capacitance of these supercapacitors  
4 per geometric area is  $81 \text{ mF.cm}^{-2}$ , which is equivalent to a gravimetric capacitance of  
5  $120 \text{ F.g}^{-1}$  of graphene, and these supercapacitors did not lose any capacitance after 5 000  
6 cycles. Manman *et al.* [219] reported cellulose/graphene composite hydrogels prepared from  
7 ionic liquids (IL). They used Vitamin C to prepare RGO directly in IL. These hydrogels  
8 showed enhanced mechanical and thermal properties. At only 0.5 wt% doping of RGO in  
9 cellulose composite, the Young's modulus was improved more than four times.

### 11 **5.2.3. Graphene/ Polyaniline (PANI) composites**

13 Wang *et al.*[193] prepared a PANI/graphene composite paper (GPCP) via *in-situ*  
14 anodic electropolymerization (AEP). This graphene/polyaniline composite was shown to  
15 have a tensile strength of 12.6 MPa and a stable large electrochemical gravimetric and  
16 volumetric capacitance of  $233 \text{ F.g}^{-1}$  and of  $135 \text{ F.cm}^{-3}$  respectively. The mechanical strength  
17 was also shown to have improved by 43 %.

18 In another example, flexible graphene/polyaniline hybrid material, for use as a  
19 supercapacitor electrode, was synthesized by an *in-situ* polymerization-reduction/dedoping-  
20 redoping process [220]. This composite showed a high specific capacitance, as high as 1  
21  $126 \text{ F.g}^{-1}$  compared to  $115 \text{ F.g}^{-1}$  for pure PANI. Wang *et al.* [221] reported a composite of  
22 fibrillar polyaniline (PANI) doped with graphene oxide sheets. For a mass ratio of  
23 aniline/graphite oxide of 100:1, the composite displayed a high electrical conductivity of  
24  $10 \text{ S.cm}^{-1}$  and specific capacitance of  $531 \text{ F.g}^{-1}$ .

#### 1           **5.2.4. PVA/graphene nanocomposites**

2  
3           Zhao *et al.* [222] reported the preparation of graphene nanosheets and poly(vinyl  
4 alcohol) (PVOH) *via* a facial aqueous solution. In their study, they showed that it is possible  
5 to increase the tensile strength by as much 150 % by only 1.8 vol % loading of graphene,  
6 and at the same time elongation breakage decreased by more than 100 %.

7           Liang *et al.* [223] also studied poly(vinyl alcohol) (PVOH)/graphene  
8 nanocomposites. In this study, they used water as a solvent to fuse GO into the PVOH matrix.  
9 At only 0.7 wt% GO loading, tensile strength increased by 76 % and Young's modulus by  
10 62 %.

#### 11 12           **5.2.5. Polyurethane (PU)/graphene composites**

13  
14           Lee *et al.* [224] reported the study of waterborne polyurethane (WPU)/graphene  
15 sheets (FGS) nanocomposites prepared using an *in-situ* method. The electrical conductivity  
16 of the nanocomposites was increased 10<sup>5</sup>-fold compared with that of pure WPU. This was  
17 attributed to high dispersity and homogeneity of graphene sheets in the WPU matrix. They  
18 obtained a percolation threshold of graphene sheets at only 2 wt%.

19           Liang *et al.* [225] used thermoplastic polyurethane (TPU) to fabricate  
20 nanocomposites with three differently processed graphene samples. They were able to show  
21 that the rate of thermal degradation for thermoplastic polyurethane/isocyanate modified  
22 graphene composites are much higher than that of the sulfonated graphene and reduced  
23 graphene based TPU nanocomposites. The TPU/graphene nanocomposites doped with only  
24 1 wt% sulfonated graphene showed enhanced infrared-triggered actuation performance. The  
25 tests showed that the composite could contract and lift a 21.6 g weight up to 3.1 cm with

1 0.21 N of force when exposed to IR. The mechanical properties of this composite were also  
2 increased. The tensile strength of TPU/sulfonated graphene nanocomposites with 1 wt%  
3 graphene was increased by 75 % at a strain of 100 %, and the Young's modulus was enhanced  
4 by 120 % [225]. However, IR-triggered actuation performance of isocyanate modified  
5 graphene/TPU nanocomposites showed inferior results.

#### 7 **5.2.6. Poly (vinylidene fluoride) (PVDF)/graphene composites**

8  
9 PVDF/graphene nanocomposites were prepared by a simple solution mixing  
10 followed by compression molding from graphite oxide and exfoliated graphite (EG) [226].  
11 GO based composites displayed higher thermal stability than EG based composites.  
12 However, the mechanical properties of both composites outperformed those based on only  
13 PVDF. A lower percolation threshold of 2 wt% was obtained for GO/PVDF composites  
14 compared to EG/PVDF composites, having above 5 wt%. The difference is attributed to the  
15 higher aspect ratio of GO compared with EG. With the addition of 2 wt% of GO, the storage  
16 modulus of neat PVDF increased from 1 275 MPa to 1 859 MPa, whilst with EG it increased  
17 to 1 739 MPa. At a 4 wt% filler loading, the storage modulus for GO/PVDF and EG/PVDF  
18 was increased to 2 460 and 2 695 MPa, respectively.

#### 20 **5.2.7. Graphene/Polyethylene terephthalate (PET) nanocomposites**

21  
22 The melt intercalation technique was used to prepare PET/graphene composites by  
23 Zhang *et al.* [199] Transmission electron microscopy analysis showed that graphene  
24 nanosheets were evenly distributed in the PET matrix. This criterion was confirmed by the  
25 high electrical conductivity values they got from the PET/graphene composites. The

1 threshold percolation was only 0.47 vol.% loading, and with graphite 2.4 vol%. A high  
2 electrical conductivity of 2.11 S.m<sup>-1</sup> was achieved with the addition of only 3.0 vol%  
3 graphene.

#### 5 **5.2.8. Polycarbonate (PC)/graphene nanocomposites**

6  
7 Kim *et al.* [227] studied PC composites doped with graphite and functionalized  
8 graphene sheets (FGS) by the melt intercalation technique. In this study, they used melt  
9 rheology to study the viscoelastic properties of the composites. They annealed the  
10 composites for 10 000 s and observed that the composites manifest a solid-like state above  
11 the percolation threshold, which was around 1 wt% for the FGS, while around 3 wt% for  
12 graphite loading. In terms of electrical properties, FGS/PC showed lower percolation  
13 threshold as compared to graphite/PC composites. Both graphite and FGS fillers lead to  
14 improved PC composites stiffness and dimensional stability. The composites also exhibited  
15 good barrier properties. The permeability of nitrogen and helium of the PC composites is  
16 significantly reduced by incorporation of both FGS and graphite. Moreover, FGS showed  
17 potential for application in gas separation processes as it was more effective against  
18 molecules with large kinetic diameter.

#### 20 **5.2.9. Poly(amido amine) (PAMAM)/graphene composites**

21  
22 Ramanathan *et al.* [190] studied the mechanical, thermal and electrical properties of  
23 graphite/PMMA composites. PAMAM and graphitic nanoplatelets (FNPs) were mixed  
24 together in THF *via* sonication and shearing. The glass transition temperature ( $T_g$ ) of the  
25 fabricated composites increased by 30 °C with 1-5 wt% filler loading. When FNPs were

1 replaced with functionalized graphene sheets (FNPs) as nanofillers, the composites exhibited  
2 enhanced properties, because the FNPs contain a higher percentage of wrinkled single-layer  
3 sheets, and thus have a high aspect ratio which, in turn, increases the filler-matrix bonding.  
4 With only 0.05 wt% loading,  $T_g$  increased by 30 % for the PAMAM/FGS composite, while  
5 a loading of 1 wt% led to a  $T_g$  of 40 °C. The modulus at room temperature increased by 66  
6 % at only 1 wt% loading of graphite nanoplatelets, and as high as 133 % at 5 wt% GNP  
7 loading.

8

#### 9 **5.2.10. Polystyrene (PS)/graphene nanocomposites**

10

11 Polystyrene/graphene composites have been extensively studied for various  
12 application. Stankovich *et al.* [52] reported PS/isocyanate modified graphene composites  
13 prepared using a solution blending method in DMF. They obtained a percolation threshold  
14 for the electrical conductivity at 0.1 vol% GO in PS. The low percolation value is due to the  
15 homogeneous dispersion and extremely large aspect ratio of graphene sheets. The  
16 PS/graphene composite showed an electrical conductivity of  $\sim 0.1$  to  $\sim 1 \text{ S.m}^{-1}$  at 2.5 vol%  
17 loading.

18 Liu *et al.* [228] prepared a PS/GNP composite in ionic liquids. The electrical  
19 conductivity increased from  $10^{-14} \text{ S.m}^{-1}$  for pure PU to  $5.77 \text{ S.m}^{-1}$  with the addition  
20 0.38 vol% GNP, which is 3-15 times higher than that of polystyrene composites filled with  
21 single-walled carbon nanotubes. They also studied the thermal stability of PS/GNP  
22 composite and pure polystyrene. The degradation temperature of the PS/GNP composite was  
23 about 50 °C higher than that of pure PS. This enhancement is due to the strong interaction  
24 of GNP and the polymer matrix at the interface, which leads to a decrease of polymer chain  
25 mobility near the interface and, hence, the increase in thermal stability.



### 1           **5.2.11. Graphene/alginate composites**

2  
3           Alginate is a natural polysaccharide that can be extracted from seaweed and other  
4 moisture loving plant and cellular life forms, such as algae, and is composed of (1–4)-linked  
5  $\beta$ -D-mannuronic acid (M) and  $\alpha$ -L-guluronic acid (G) units [229]. The material is nontoxic,  
6 biocompatible, and formable [230], and therefore alginates have been used in food, paper  
7 and textiles as stabilizers and emulsifiers and also for biomedical applications [231,232].

8           To enhance the functional properties, alginates have been incorporated with fillers,  
9 including graphene, to fabricate composites. Wu *et al.* [233] investigated the adsorption  
10 properties of graphene oxide/calcium alginate (GO/CA) nanocomposite of ciprofloxacin  
11 (CPX) from wastewater. It was found to remove CPX to levels as high as 78.9 % compared  
12 with only 30 % using calcium alginate. In another study, GO was encapsulated in calcium  
13 alginate and formed into macroporous alginic beads for the adsorption of acridine orange  
14 dye [234]. The incorporation of GO into the CA matrix improved the overall adsorption  
15 kinetics and increased the effective pH range compared to CA beads alone.

16           Zheng *et al.* [RW.ERROR - Unable to find reference:2016] synthesized graphene  
17 oxide/sodium alginate (GO/Na-alg) composites with multivalent cations that resulted in  
18 enhanced thermal and mechanical properties. The tensile of Na-alg increased from 33.6 MPa  
19 to ~80.2 MPa. However, this was lower than that for Ca-alg/GO, Ba-alg/GO and Fe-alg/GO  
20 with the tensile strengths 122.3, 137.6 and 161.8 MPa respectively. The lower value with  
21  $\text{Na}^+$  cations was attributed to lack of crosslinking with the alginate chains. In another study  
22 [236], sodium alginate/graphene oxide fibers were prepared by wet spinning. At 4 wt% GO  
23 loading, the tensile strength and Young's modulus increased from 0.32 and 1.9 to 0.62 and  
24 4.3 GPa, respectively. Li *et al.* [237] investigated the adsorption properties of GO/CA  
25 composites prepared by the sol-gel method for methylene blue removal. The ecofriendly

1 composite showed a high adsorption capacity of 181.81 mg/g in a wide pH range and it is  
2 easily separated from the water solutions. The adsorption process was exothermic with  
3 increasing temperature.

#### 5 **5.2.12. Graphene nanocomposites for thermal interface materials**

6  
7 High power densities of modern devices in the electronics industry, for example, has  
8 created a need for more efficient ways to dissipate generated heat [238]. Poor dissipation of  
9 heat flux generated in these devices can deteriorate not only the performance but also shorten  
10 the lifetime of devices. Thermal interface materials (TMI) have been developed to minimize  
11 the thermal resistance between the heat sources and heat sinks by filling the interface surface  
12 irregularities such as air gaps and grooves [238-240]. Due to high intrinsic thermal  
13 conductivity and strong thermal coupling abilities, graphene has been used as a filler in TMIs  
14 [176,241-244].

15 Shahil *et al.* [241] prepared a graphene/epoxy composite for TMI application. Using  
16 a “laser flash” method, thermal conductivity of the composite was determined to have  
17 increased by 2 300 % at a graphene loading of 10 % and this was attributed to the presence  
18 of high concentration of single and bilayer graphene sheets (~10-15 %) as well as the  
19 presence of flakes with large lateral size ~1  $\mu\text{m}$ . Renteria *et al.* [245] also studied the  
20 efficiency of  $\text{Fe}_3\text{O}_4$  functionalized graphene nanocomposite in thermal applications. By  
21 using the external magnetic field, the fillers were able to be aligned on the interfaces during  
22 dispersion of thermal paste which led to an enhanced thermal conductivity by a factor of two  
23 than with the random oriented fillers at ~1 % graphene loading. Real-life computer testing  
24 with these materials incorporated as thermal dissipators showed that at 1 % loading with  
25 oriented filler, the temperature was reduced by 10  $^\circ\text{C}$  [245].

1           In another study [246], Goli *at al.* demonstrated that the efficiency of thermal  
2 management in Li-ion batteries could be improved by incorporation of graphene fillers in  
3 phase change materials such as paraffin wax. It was shown that the thermal conductivity of  
4 material was increased by more than two orders of magnitude whilst keeping the latent heat  
5 storage constant, successfully decreasing the temperature increase in Li-ion batteries [246].

### 7           **5.3. Outlook of graphene/polymer nanocomposites**

8  
9           It is clear that graphene has a lot of potential as a filler to enhance the mechanical,  
10 electrical and thermal properties of polymer materials. However, a number of barriers must  
11 be overcome in order to reach the full potential of the resulting composites with acceptable  
12 properties for wider applications. The composites properties depend on the interaction  
13 between graphene and the polymer as well as graphene dispersion in the polymer matrix  
14 [196,247].

15           In order to achieve significant improvement of the polymer properties, nanoscale  
16 homogenous dispersion of graphene in the polymer matrix is essential [248]. Homogeneous  
17 dispersion minimizes the formation of concentrated local stresses and promotes uniform load  
18 transfer throughout the matrix [249-251]. However, achieving good dispersion is still a  
19 critical challenge, because graphene has a strong interaction between the layers due to the  
20 van der Waals force, and thus tend to agglomerate irreversibly or even to restack into  
21 graphite-like structures in the polymer matrix [196,252,253]. Therefore, the excellent  
22 potential in the composite cannot be fully realized. Functionalization of the graphene surface  
23 is normally implemented to enhance the dispersion capability of graphene. Unlike LPE  
24 produced graphene, reduced graphene oxide (rGO) or GO are often used as fillers in polymer  
25 composites. This is because GO contains oxygen functional groups such as hydroxyl, epoxy

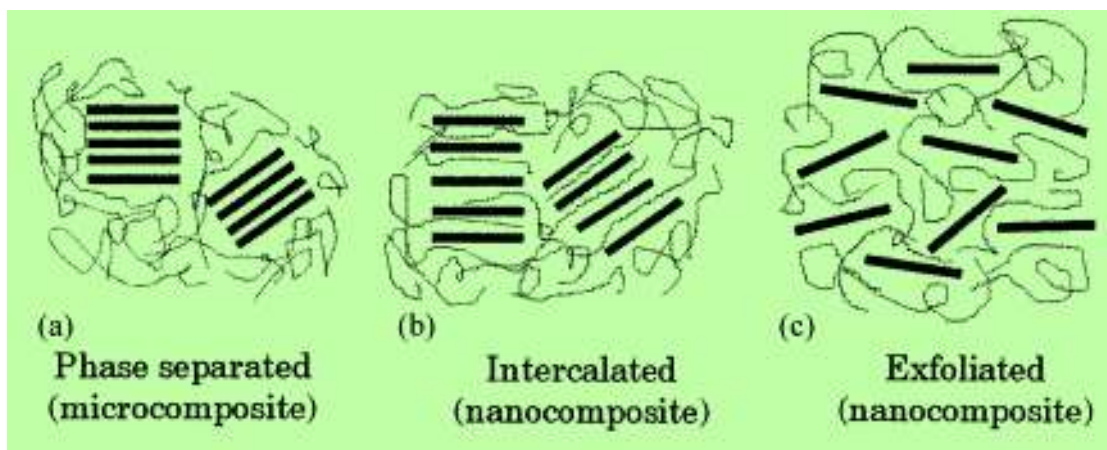
1 and carboxylic, which can easily interact with the polymer matrix [110,254]. rGO produced  
2 from the reduction of GO oxide also still contains a lot of these residual functional groups  
3 [117], which act to increase the interlayer spacing and reduce the interaction effects of the  
4 van der Waals force between the graphene layers [196].

5         Studies have shown that when layered materials such as graphene are used as  
6 nanofillers in polymer-based composites, three types of phases are possible: stacked,  
7 intercalated or exfoliated, as shown in Figure 10 [254,255]. When the polymer is unable to  
8 intercalate between the graphene sheets, because of insufficient exfoliation of graphite in the  
9 case of LPE systems, or restacking of layers during reduction of GO, a phase separated  
10 composite is formed that consists of large stacked agglomerates of graphene sheets [256].  
11 Superior properties can be achieved if there is a strong interfacial bonding interaction  
12 between graphene and the host polymer matrix. In the exfoliated structure (Figure 10(c)),  
13 exfoliated graphene flakes have the largest possible interfacial contact with the polymer  
14 matrix. This significantly enhances the mechanical properties of the composites since,  
15 graphene develops a curved wrinkled surface that increases mechanical interlocking with the  
16 polymer chains [215]. However, wrinkling can also reduce the intrinsic properties of  
17 graphene, such as thermal and electrical behavior [257] as a result of lowering then effective  
18 aspect ratio.

19         It is a not a surprise that GO and rGO are popular choices as filler materials in  
20 nanocomposites as opposed to pristine graphene. Due to the functional groups, GO and rGO  
21 can easily be dispersed in polar solvents and strongly interact with the polymer matrix  
22 allowing for a good dispersion and internal load transfer. However, pristine graphene has  
23 not been investigated to the same extent as GO or rGO as polymer reinforcement. The  
24 presence of dispersants and the unreactive nature of the pristine graphene surface makes it  
25 unlikely to interact with the polymer matrix, and thus leads to poor dispersion and

1 agglomeration [258]. Besides, most of the graphene dispersions produced by LPE methods  
2 are dominated by few-layer graphene sheets [78,81,90,92,97,98,259-263]. Covalent  
3 methods have been use to functionalize GO [264,265], while non covalent methods are used  
4 for pristine graphene, because of the low surface chemistry reactivity [266,267]. A  
5 comparison of different properties of LPE and GO produced polymer-based nanocomposites  
6 is shown in Table 4.

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



12  
13 Figure 10 schematic representation of three morphological states of graphene based  
14 nanocomposites: (a) phase separated (b) intercalated (c) exfoliated. Adapted from reference  
15 [255] with permission from Elsevier.

1 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 <sup>-1</sup>	Increase in strength, %	Increase in modulus, %	Thermal properties	Ref.
via LPE method	Graphene	Epoxy	solution	0.46 vol%	0.088	1E-05	38	37	-	[208]
	Graphene	Poly(vinyl chloride)	solution	2 wt%	0.6 vol%	0.058 (6.47 vol%)	130	58	$T_g \uparrow$ by 3.5 °C	[268]
	Graphene	Epoxy	solution	0.244 vol%	0.24 vol%	1E-06	-19.6	17.3	$T_g \uparrow$ by 7.4 °C	[269]
	Graphene	Nanofibrillated cellulose	sonication	1.25 wt%	-	-	25	51	-	[270]
	Ionic-Liquid-Functionalized Graphene	Polystyrene	Solution blending	4.19 vol%	0.1 vol%	0.1384	-	-	-	[228]
	Graphene	Poly(vinyl alcohol)	solution	1.2 vol%	0.265 vol%	1.84E-04 (3 vol%)	129	116	-	[271]
	Graphene nanosheets	Polystyrene	in-situ	2 wt%	-	2.9E-02	-	-	$T_g \uparrow$ by 8 °C	[272]
via GO route	Functionalized GO	Polystyrene	-	2.5 vol%	0.1 vol%	0.01	-	-	-	[126]
	GO	Polyurethane	in-situ	2.0 wt%	-	2.15E-08	239	202	thermal stability by 40 °C at 5 % loss	[273]
	GO	Poly(vinyl alcohol)	solution	0.7 wt%	-	-	76	62	$T_g \uparrow$ by 3.3 °C	[223]
	GO	Epoxy	solution	0.54 vol%	-	-	10	25	-	[274]

GO	Polyimide	in-situ	3 wt%	-	-	7	27	-	[275]
TRGO	Polyamide 6	melt extrusion	12 wt%	7.5 wt%	0.71E-02		47 (10 wt%)	-	[134]
TRGO	Polyethylene terephthalate	melt compounding	3 vol%	0.47 vol%	0.0211	-	-	-	[199]
TRGO	Polycarbonate	Solution blending	2.2 vol%	0.38 vol%	0.226	-	-	$T_g \downarrow$ by 3.3 °C	[276]
TRGO	Polycarbonate	emulsion mixing	2.2 vol%	0.14 vol%	0.512	-	-	$T_g \downarrow$ by 9.7 °C	[276]
Microwave-Exfoliated GO	Polycarbonate	melt mixing	3 wt%	1.3 wt%	2.5E-03	-	30	$T_g \uparrow$ by 0.6 °C	[277]
CRGO	Epoxy	solution	9 wt%	0.52 vol%	0.1	-	-	-	[278]
TRGO	Polystyrene	solution	1.1 vol%	0.33 vol%	0.0349	-	-	-	[279]
GO	Poly ( $\epsilon$ -caprolactone)	electrospin	0.3 wt%	-	-	95	66	$T_c \uparrow$ by 7.2 °C	[280]
TRGO	Polyethylene terephthalate	melt	3 wt%	0.47 vol%	0.0211	-	-	-	[199]
TRGO	Poly(vinylidene fluoride)	solution	4 wt%	2 wt%	1E-04	-	93	-	[226]
TRGO	Poly(methyl methacrylate)	solution	1 wt%	-	-	20	80	$T_g \uparrow$ by 40 °C	[281]
GO	Poly(vinyl alcohol)	solution	0.8 wt%	-	1E-09 (1.6 wt%)	52	54	$T_g \downarrow$ by 5.8 °C	[282]
CRGO	Poly(butylene succinate)	solution, melt	2 wt%	-	-	22	-	lower stability	[283]
TRGO	Polyurethane	solution	7 wt%	2 wt%	4.92E-04 (7 wt%)	-22.5 (3 wt%)	43 (3 wt%)	$T_g \downarrow$ by 2.4 °C	[284]

TRGO	High density polyethylene	solution	3 vol%	1 vol%	0.015	-	-	-	[285]
RGO	Polystyrene	solution blending	2.45 vol%	0.19 vol%	0.7218	-	28 1.94 vol%	T <sub>g</sub> ↓ by 5.5 °C	[286]
RGO	poly(vinyl alcohol)		3 wt%	-	-	53	52.6	Thermal stability ↑ by 12.1 °C	[287]
iodo phenyl functionalized GO	polyimide	in-situ	0.5 wt%	0.5 wt%	9.2E-04 (2 wt%)	64	172	-	[288]
TRGO	Epoxy	Solution blending	0.2 wt%	-	1.47E-10	0	5	T <sub>g</sub> ↑ by 11 °C	[289]
CRGO	Nanofibrillated cellulose	Solution mixing	10 wt%	-	0.154	12	70	-	[290]
CRGO	Poly(vinyl alcohol)	Solution mixing	1.8%	-	-	150 (1.8 vol.%)	940	-	[222]
TRGO	Polylactide	Melt blending	3 wt%	3–5 wt %	1E-10 (7 wt%)	12.9	33	Degradation temp ↑ by 14 °C	[291]
GO	poly(vinyl alcohol)	Solution	2 wt%	-	-	167	92,2	T <sub>g</sub> ↑ by 8 °C (3.5wt%)	[292]
TRGO	isotactic poly(propylene)	Melt	10 wt%	<5 wt%	1,89E-4	-	53	-	[134]

Notes: TRGO – Thermally reduced Graphene Oxide; CRGR – Chemically Reduced Graphene Oxide; T<sub>g</sub> - glass-transition temperature; T<sub>c</sub> – crystallization temperature

1  
2  
3  
4  
5



## 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 \$1 000 tonne<sup>-1</sup>. 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.

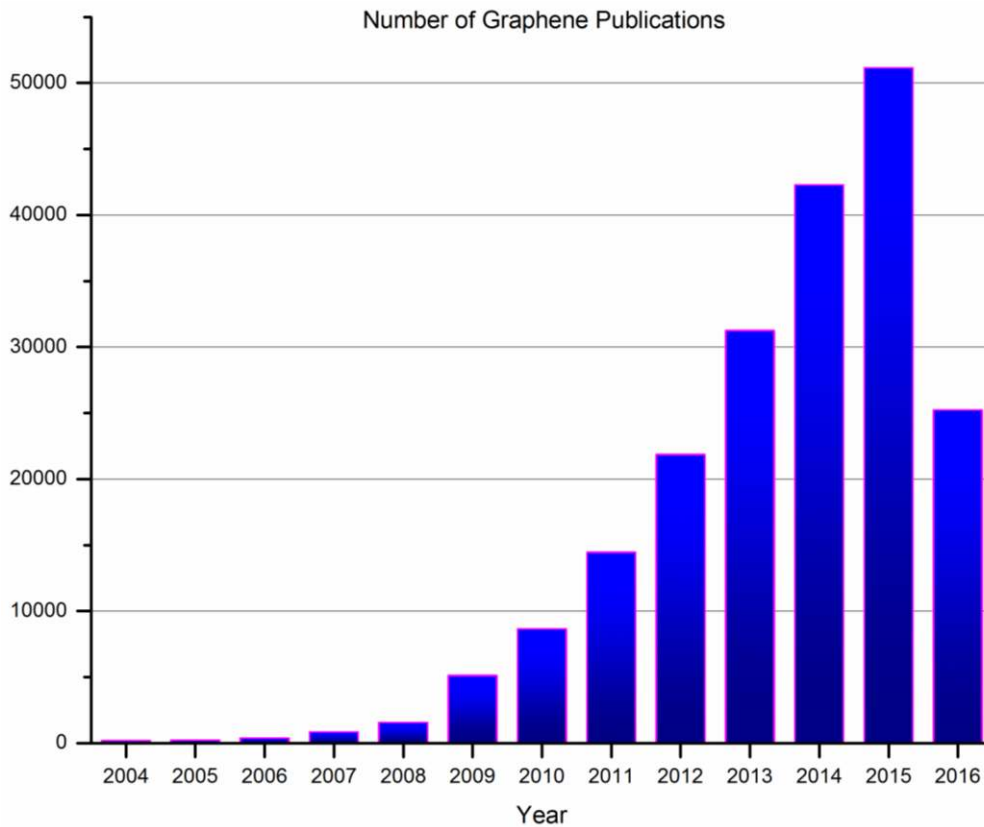
Other methods that have been extensively used, like CVD, rely on having specialized equipment. CVD technology has been around for a long time and has actively been used for the production of carbon nanotubes, diamond-like carbon *etc.* Therefore, it is also possible to use the same equipment to fabricate 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

1 laboratory equipment, while shear assisted LPE can utilize equipment such as  
2 microfluidizers, high shear mixers *etc.*, which are also commonly available. However, low  
3 yield, low concentration of single graphene layers, lack of control over the lateral flake size  
4 are still the main bottlenecks for this method. Graphene production *via* graphite oxide on the  
5 other hand requires use of strong and hazardous oxidizers such as sulfuric acid and potassium  
6 permanganate. Moreover, chemical reduction of GO uses toxic and unstable chemicals such  
7 as hydrazine. The harsh conditions are detrimental not only to the produced graphene but  
8 also to the environment, and this also adds extra costs to the production process not least in  
9 waste disposal. Therefore, in order to implement this method for large scale graphene  
10 production, there is a need for development of sustainable “green” approaches for oxidation  
11 and reduction processes. Both of these methods have, nonetheless, huge potential for  
12 scalability, one of the main reasons being that the raw material, graphite, is readily available  
13 and low-cost.

14

15



1  
2 *Figure 11 The approximate number of graphene publications from 2004 to June 2016*  
3 *using Thomson Reuters Web of Science (searching for graphene in topics).*  
4

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

1 Graphene can be used as a sieve, for example, to reduce emissions into the  
2 environment, like in power plants or manufacturing industries, to prevent greenhouse gases  
3 escaping. There is also a possibility of replacing lithium-ion (Li-ion) batteries with more  
4 efficient and ecological materials. Another potential area of application is in cars and  
5 airplanes. By replacing the heavier materials with graphene it can lead to huge fuel savings.  
6 For example, it has been estimated that reducing the Boeing 777 by only 5 000 kg can lead  
7 to savings of \$1 m per year, and, of course, that means a reduction in emissions as well. The  
8 Graphene Flagship developed by the EU shows that the willingness to take an active role in  
9 the graphene revolution is there, because graphene is really a material of the future.

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

## 15 **7. Conclusions and outlook**

16  
17 It is impossible, in this short review, to discuss all the aspects of graphene. However,  
18 it is evident that graphene is an interesting material that exhibits excellent unique properties  
19 that make it a compelling candidate for various applications. But despite all these excellent  
20 properties, there are still a lot of challenges to be overcome before the true potential of  
21 graphene becomes realizable. In this review, three aspects of graphene have been discussed:  
22 properties, fabrication methods and application in polymer composites. From the properties  
23 aspect of graphene, it is clear that it has a high potential for various applications including  
24 nanofiller for functional composites, energy storage devices, flexible electronics, sensors,  
25 *etc.* due to its superlative properties. The top-down approaches for graphene exfoliation have

1 been reviewed such as MC, LPE, and via GO routes. These methods utilize graphite as a  
2 starting material that is low-cost and readily available. However, it is clear from the  
3 discussion that the most challenging problem that hinders the wider scale application of  
4 graphene is still the lack of an economically viable large scale production method for high  
5 quality graphene fabrication that is environmental friendly. At the moment, LPE and GO are  
6 still the promising methods with high scalability potential. Despite the progress that has been  
7 made in these methods, there are still challenges that require to be addressed. For the LPE  
8 system, these include increasing the yield and degree of exfoliation, since the yield for single  
9 layer graphene is still very low, and for the GO route the need is to develop greener and more  
10 efficient methods for oxidation and reduction processes that could significantly reduce the  
11 induced defects. Therefore, it is important in the near future to optimize and the increase the  
12 efficiency of these mechanical exfoliation methods. It is also vital to control the amount of  
13 defects induced, lateral size of the sheets and the number of graphene layers.

14         The application of graphene in polymer nanocomposite was reviewed. It is evident  
15 that GO is the most widely used graphene based nanofiller in polymer composites, largely  
16 because of the chemical interaction between the filler and the polymer matrix that enhances  
17 homogeneous dispersion of graphene in the matrix, thus improving the overall composite  
18 performance. Application of pristine graphene in polymer composites is still limited. More  
19 work is needed in this area because only by implementation of defect-free graphene can the  
20 maximum properties of the composites be achieved. Several challenges must be overcome  
21 to benefit fully from the properties of pristine graphene in polymer composites, including  
22 achieving homogeneous dispersion and spatial distribution in the matrix, and strong  
23 interfacial interaction of graphene and the polymer matrix, alignment and overlapping *etc.*

24         Looking at the big picture, the progress that has been made to date is quite  
25 impressive, keeping in mind that graphene is just over a decade old in science terms, and so

1 it is still a very “young” technological material. The prototypes of graphene-based products  
2 that have been commercialized, such as batteries, sensors, graphene inks *etc.* give good  
3 reason to be optimistic about the future for graphene. We can all be confident that graphene  
4 is here to stay and it will someday prove to be the ‘miracle material’ when it finally becomes  
5 a fundamental part of our essential applications.

6

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11

## 12 **References**

13 [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos,  
14 I.V. Grigorieva, A.A. Firsov, Electric Field Effect in Atomically Thin Carbon Films,  
15 *Science*. 306 (2004) 666-669.

16 [2] K.S. Novoselov, Nobel Lecture: Graphene: Materials in the Flatland,  
17 *Rev.Mod.Phys.* 83 (2011) 837-849.

18 [3] A.K. Geim, Nobel Lecture: Random walk to graphene, *Rev. Mod. Phys.* 83  
19 (2011) 851-862.

20 [4] J. Wei, R. Atif, T. Vo, F. Inam, Graphene Nanoplatelets in Epoxy System:  
21 Dispersion, Reaggregation, and Mechanical Properties of Nanocomposites, *Journal of*  
22 *Nanomaterials*. 2015 (2015) 12.

23 [5] N. Koratkar, *Graphene in Composite Materials: Synthesis, Characterization and*  
24 *Applications*, DEStech Publications, Inc, USA, 2013.

25 [6] A.C. Ferrari, F. Bonaccorso, V. Fal'ko, K.S. Novoselov, S. Roche, P. Boggild,  
26 S. Borini, F.H. Koppens, V. Palermo, N. Pugno, J.A. Garrido, R. Sordan, A. Bianco, L.  
27 Ballerini, M. Prato, E. Lidorikis, J. Kivioja, C. Marinelli, T. Ryhanen, A. Morpurgo, J.N.  
28 Coleman, V. Nicolosi, L. Colombo, A. Fert, M. Garcia-Hernandez, A. Bachtold, G.F.  
29 Schneider, F. Guinea, C. Dekker, M. Barbone, Z. Sun, C. Galiotis, A.N. Grigorenko, G.  
30 Konstantatos, A. Kis, M. Katsnelson, L. Vandersypen, A. Loiseau, V. Morandi, D.  
31 Neumaier, E. Treossi, V. Pellegrini, M. Polini, A. Tredicucci, G.M. Williams, B.H. Hong,

- 1 J.H. Ahn, J.M. Kim, H. Zirath, B.J. van Wees, H. van der Zant, L. Occhipinti, A. Di  
2 Matteo, I.A. Kinloch, T. Seyller, E. Quesnel, X. Feng, K. Teo, N. Rupesinghe, P. Hakonen,  
3 S.R. Neil, Q. Tannock, T. Lofwander, J. Kinaret, Science and technology roadmap for  
4 graphene, related two-dimensional crystals, and hybrid systems, *Nanoscale*. 7 (2015) 4598-  
5 4810.
- 6 [7] J.C. Slonczewski, P.R. Weiss, Band Structure of Graphite, *Phys.Rev.* 109  
7 (1958) 272-279.
- 8 [8] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, Graphene  
9 and Graphene Oxide: Synthesis, Properties, and Applications, *Adv Mater.* 22 (2010) 3906-  
10 3924.
- 11 [9] A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C.N.  
12 Lau, Superior Thermal Conductivity of Single-Layer Graphene, *Nano Lett.* 8 (2008) 902-  
13 907.
- 14 [10] K.I. Bolotin, K.J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim,  
15 H.L. Stormer, Ultrahigh electron mobility in suspended graphene, *Solid State Commun.*  
16 146 (2008) 351-355.
- 17 [11] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the Elastic Properties  
18 and Intrinsic Strength of Monolayer Graphene, *Science*. 321 (2008) 385-388.
- 19 [12] R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber,  
20 N.M.R. Peres, A.K. Geim, Fine Structure Constant Defines Visual Transparency of  
21 Graphene, *Science*. 320 (2008) 1308-1308.
- 22 [13] A.K. Geim, Graphene: Status and Prospects, *Science*. 324 (2009) 1530-1534.
- 23 [14] K.S. Novoselov, P. Blake, M.I. Katsnelson, Graphene: Electronic Properties,  
24 in: Veysseyre, K.H. Jürgen Buschow Robert W. Cahn Merton C. Flemings Bernhard  
25 Ilschner Edward J. Kramer Subhash Mahajan Patrick (Ed.), *Encyclopedia of Materials:*  
26 *Science and Technology* (Second Edition), Elsevier, Oxford, 2008, pp. 1-6.
- 27 [15] M.J. Allen, V.C. Tung, R.B. Kaner, Honeycomb carbon: A review of  
28 graphene, *Chem. Rev.* 110 (2010) 132-145.
- 29 [16] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V.  
30 Morozov, A.K. Geim, Two-dimensional atomic crystals, *Proceedings of the National*  
31 *Academy of Sciences of the United States of America*. 102 (2005) 10451-10453.
- 32 [17] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I.V.  
33 Grigorieva, S.V. Dubonos, A.A. Firsov, Two-dimensional gas of massless Dirac fermions  
34 in graphene, *Nature*. 438 (2005) 197-200.
- 35 [18] J.S. Bunch, S.S. Verbridge, J.S. Alden, A.M. van der Zande, J.M. Parpia, H.G.  
36 Craighead, P.L. McEuen, Impermeable atomic membranes from graphene sheets, *Nano*  
37 *Lett.* 8 (2008) 2458-2462.

- 1 [19] E. Yoo, J. Kim, E. Hosono, H.S. Zhou, T. Kudo, I. Honma, Large reversible Li  
2 storage of graphene nanosheet families for use in rechargeable lithium ion batteries, *Nano*  
3 *Lett.* 8 (2008) 2277-2282.
- 4 [20] V.C. Tung, M.J. Allen, Y. Yang, R.B. Kaner, High-throughput solution  
5 processing of large-scale graphene, *Nat. Nanotechnol.* 4 (2009) 25-29.
- 6 [21] X. Li, X. Wang, L. Zhang, S. Lee, H. Dai, Chemically derived, ultrasmooth  
7 graphene nanoribbon semiconductors, *Science.* 319 (2008) 1229-1232.
- 8 [22] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney,  
9 E.A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, Graphene-based composite materials,  
10 *Nature.* 442 (2006) 282-286.
- 11 [23] F. Schedin, A.K. Geim, S.V. Morozov, E.W. Hill, P. Blake, M.I. Katsnelson,  
12 K.S. Novoselov, Detection of individual gas molecules adsorbed on graphene, *Nature*  
13 *Materials.* 6 (2007) 652-655.
- 14 [24] K.S. Novoselov, V.I. Fal'ko, L. Colombo, P.R. Gellert, M.G. Schwab, K. Kim,  
15 A roadmap for graphene, *Nature.* 490 (2012) 192-200.
- 16 [25] J. Wu, H.A. Becerril, Z. Bao, Z. Liu, Y. Chen, P. Peumans, Organic solar cells  
17 with solution-processed graphene transparent electrodes, *Appl. Phys. Lett.* 92 (2008)  
18 263302.
- 19 [26] K.A. Ritter, J.W. Lyding, The influence of edge structure on the electronic  
20 properties of graphene quantum dots and nanoribbons, *Nat. Mater.* 8 (2009) 235-242.
- 21 [27] A.K. Geim, K.S. Novoselov, The rise of graphene, *Nat. Mater.* 6 (2007) 183-  
22 191.
- 23 [28] V. Singh, D. Joung, L. Zhai, S. Das, S.I. Khondaker, S. Seal, Graphene based  
24 materials: Past, present and future, *Progress in Materials Science.* 56 (2011) 1178-1271.
- 25 [29] A. Fasolino, J.H. Los, M.I. Katsnelson, Intrinsic ripples in graphene, *Nature*  
26 *Materials.* 6 (2007) 858-861.
- 27 [30] V. Singh, D. Joung, L. Zhai, S. Das, S.I. Khondaker, S. Seal, Graphene based  
28 materials: Past, present and future, *Progress in Materials Science.* 56 (2011) 1178-1271.
- 29 [31] C. Soldano, A. Mahmood, E. Dujardin, Production, properties and potential of  
30 graphene, *Carbon.* 48 (2010) 2127-2150.
- 31 [32] U.K. Sur, Graphene: A Rising Star on the Horizon of Materials Science,  
32 *International Journal of Electrochemistry.* 2012 (2012) 12.
- 33 [33] P. Avouris, C. Dimitrakopoulos, Graphene: synthesis and applications,  
34 *Materials Today.* 15 (2012) 86-97.



- 1 [34] E.P. Randviir, D.A.C. Brownson, C.E. Banks, A decade of graphene research:  
2 production, applications and outlook, *Materials Today*. 17 (2014) 426-432.
- 3 [35] A. Vijayaraghavan, Graphene - Properties and Characterization, in: R. Vajtai  
4 (Ed.), Springer Berlin Heidelberg, 2013, pp. 39-82.
- 5 [36] K.V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G.L. Kellogg, L. Ley, J.L.  
6 McChesney, T. Ohta, S.A. Reshanov, J. Rohrl, E. Rotenberg, A.K. Schmid, D. Waldmann,  
7 H.B. Weber, T. Seyller, Towards wafer-size graphene layers by atmospheric pressure  
8 graphitization of silicon carbide, *Nat. Mater.* 8 (2009) 203-207.
- 9 [37] A. Charrier, A. Coati, T. Argunova, F. Thibaudau, Y. Garreau, R. Pinchaux, I.  
10 Forbeaux, J.-. Debever, M. Sauvage-Simkin, J.-. Themlin, Solid-state decomposition of  
11 silicon carbide for growing ultra-thin heteroepitaxial graphite films, *J. Appl. Phys.* 92  
12 (2002) 2479.
- 13 [38] M. Terai, N. Hasegawa, M. Okusawa, S. Otani, C. Oshima, Electronic states of  
14 monolayer micrographite on TiC(111)-faceted and TiC(410) surfaces, *Appl. Surf. Sci.* 130-  
15 132 (1998) 876-882.
- 16 [39] A. Nagashima, H. Itoh, T. Ichinokawa, C. Oshima, S. Otani, Change in the  
17 electronic states of graphite overlayers depending on thickness, *Physical Review B.* 50  
18 (1994) 4756-4763.
- 19 [40] J. Coraux, A.T. N'Diaye, C. Busse, T. Michely, Structural coherency of  
20 graphene on Ir(111), *Nano Lett.* 8 (2008) 565-570.
- 21 [41] T. Tanaka, A. Itoh, K. Yamashita, E. Rokuta, C. Oshima, Heteroepitaxial  
22 System of h-BN/Monolayer Graphene on Ni(111), *Surface Review and Letters.* 10 (2003)  
23 697-703.
- 24 [42] P.W. Sutter, J.I. Flege, E.A. Sutter, Epitaxial graphene on ruthenium, *Nat.*  
25 *Mater.* 7 (2008) 406-411.
- 26 [43] T. Fujita, W. Kobayashi, C. Oshima, Novel structures of carbon layers on a  
27 Pt(111) surface, *Surf. Interface Anal.* 37 (2005) 120-123.
- 28 [44] L. Jiao, L. Zhang, X. Wang, G. Diankov, H. Dai, Narrow graphene  
29 nanoribbons from carbon nanotubes, *Nature.* 458 (2009) 877-880.
- 30 [45] D.V. Kosynkin, A.L. Higginbotham, A. Sinitskii, J.R. Lomeda, A. Dimiev,  
31 B.K. Price, J.M. Tour, Longitudinal unzipping of carbon nanotubes to form graphene  
32 nanoribbons, *Nature.* 458 (2009) 872-876.
- 33 [46] D.B. Shinde, J. Debgupta, A. Kushwaha, M. Aslam, V.K. Pillai,  
34 Electrochemical unzipping of multi-walled carbon nanotubes for facile synthesis of high-  
35 quality graphene nanoribbons, *J. Am. Chem. Soc.* 133 (2011) 4168-4171.
- 36 [47] M. Choucair, P. Thordarson, J.A. Stride, Gram-scale production of graphene  
37 based on solvothermal synthesis and sonication, *Nat. Nanotechnol.* 4 (2009) 30-33.

- 1 [48] X. Yang, X. Dou, A. Rouhanipour, L. Zhi, H.J. Rader, K. Mullen, Two-  
2 dimensional graphene nanoribbons, *J. Am. Chem. Soc.* 130 (2008) 4216-4217.
- 3 [49] K.S. Kim, Y. Zhao, H. Jang, S.Y. Lee, J.M. Kim, K.S. Kim, J.H. Ahn, P. Kim,  
4 J.Y. Choi, B.H. Hong, Large-scale pattern growth of graphene films for stretchable  
5 transparent electrodes, *Nature*. 457 (2009) 706-710.
- 6 [50] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I.  
7 Jung, E. Tutuc, S.K. Banerjee, L. Colombo, R.S. Ruoff, Large-area synthesis of high-  
8 quality and uniform graphene films on copper foils, *Science*. 324 (2009) 1312-1314.
- 9 [51] S. Bae, H. Kim, Y. Lee, X. Xu, J.S. Park, Y. Zheng, J. Balakrishnan, T. Lei,  
10 H.R. Kim, Y.I. Song, Y.J. Kim, K.S. Kim, B. Ozyilmaz, J.H. Ahn, B.H. Hong, S. Iijima,  
11 Roll-to-roll production of 30-inch graphene films for transparent electrodes, *Nat.*  
12 *Nanotechnol.* 5 (2010) 574-578.
- 13 [52] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney,  
14 E.A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, Graphene-based composite materials,  
15 *Nature*. 442 (2006) 282-286.
- 16 [53] S. Park, R.S. Ruoff, Chemical methods for the production of graphenes, *Nat.*  
17 *Nanotechnol.* 4 (2009) 217-224.
- 18 [54] D. Li, M.B. Muller, S. Gilje, R.B. Kaner, G.G. Wallace, Processable aqueous  
19 dispersions of graphene nanosheets, *Nat. Nanotechnol.* 3 (2008) 101-105.
- 20 [55] S. Gilje, S. Han, M. Wang, K.L. Wang, R.B. Kaner, A chemical route to  
21 graphene for device applications, *Nano Lett.* 7 (2007) 3394-3398.
- 22 [56] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y.  
23 Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, Synthesis of graphene-based nanosheets via chemical  
24 reduction of exfoliated graphite oxide, *Carbon*. 45 (2007) 1558-1565.
- 25 [57] R. Raccichini, A. Varzi, S. Passerini, B. Scrosati, The role of graphene for  
26 electrochemical energy storage, *Nat. Mater.* 14 (2015) 271-279.
- 27 [58] L.L. Zhang, R. Zhou, X.S. Zhao, Graphene-based materials as supercapacitor  
28 electrodes, *Journal of Materials Chemistry*. 20 (2010) 5983.
- 29 [59] X. Tian, M.E. Itkis, E.B. Bekyarova, R.C. Haddon, Anisotropic Thermal and  
30 Electrical Properties of Thin Thermal Interface Layers of Graphite Nanoplatelet-Based  
31 Composites, *Scientific Reports*. 3 (2013).
- 32 [60] A. Ciesielski, P. Samori, Graphene via sonication assisted liquid-phase  
33 exfoliation, *Chem. Soc. Rev.* 43 (2014) 381-398.
- 34 [61] F. Chen, J. Yang, T. Bai, B. Long, X. Zhou, Facile synthesis of few-layer  
35 graphene from biomass waste and its application in lithium ion batteries, *J Electroanal*  
36 *Chem.* 768 (2016) 18-26.

- 1 [62] A. Primo, P. Atienzar, E. Sanchez, J.M. Delgado, H. Garcia, From biomass  
2 wastes to large-area, high-quality, N-doped graphene: catalyst-free carbonization of  
3 chitosan coatings on arbitrary substrates, *Chem. Commun. (Camb)*. 48 (2012) 9254-9256.
- 4 [63] G.B. Barin, Y.H. Santos, J.A. Rocha, L. Pereira da Costa, A.G. Souza Filho, I.  
5 de Fátima Gimenez, L.S. Barreto, Graphene-like nanostructures obtained from Biomass,  
6 *MRS Proceedings*. 1505 (2013).
- 7 [64] Z. Wang, J. Yu, X. Zhang, N. Li, B. Liu, Y. Li, Y. Wang, W. Wang, Y. Li, L.  
8 Zhang, S. Dissanayake, S.L. Suib, L. Sun, Large-Scale and Controllable Synthesis of  
9 Graphene Quantum Dots from Rice Husk Biomass: A Comprehensive Utilization Strategy,  
10 *ACS Applied Materials & Interfaces*. 8 (2016) 1434-1439.
- 11 [65] L.M. Pastrana-Martínez, S. Morales-Torres, J.L. Figueiredo, J.L. Faria,  
12 A.M.T. Silva, Graphene-based Energy Devices; Graphene Derivatives in Photocatalysis,  
13 (2015) 249-276.
- 14 [66] J. Sun, Y. Deng, J. Li, G. Wang, P. He, S. Tian, X. Bu, Z. Di, S. Yang, G.  
15 Ding, X. Xie, A New Graphene Derivative: Hydroxylated Graphene with Excellent  
16 Biocompatibility, *ACS Appl. Mater. Interfaces*. 8 (2016) 10226-10233.
- 17 [67] Wan Wubo, Zhao Zongbin, Fan Yanru, Hu Han, Zhou Quan, Qiu Jieshan,  
18 Graphene Derivatives: Synthesis and Applications, *Progress in Chemistry*. 23 (2011) 1883-  
19 1891.
- 20 [68] M. Inagaki, F. Kang, Graphene derivatives: graphane, fluorographene,  
21 graphene oxide, graphyne and graphdiyne, *Journal of Materials Chemistry A*. 2 (2014)  
22 13193.
- 23 [69] Q. Tang, Z. Zhou, Z. Chen, Graphene-related nanomaterials: tuning properties  
24 by functionalization, *Nanoscale*. 5 (2013) 4541-4583.
- 25 [70] H. Bares, Jean-Baptiste Verlhac, D. Bassani, *Chemistry and Applications of*  
26 *Supramolecular Graphene Derivatives*, CRC Press, 2016, pp. 337-352.
- 27 [71] F. Karlicky, K. Kumara Ramanatha Datta, M. Otyepka, R. Zboril, Halogenated  
28 graphenes: rapidly growing family of graphene derivatives, *ACS Nano*. 7 (2013) 6434-  
29 6464.
- 30 [72] R.A. Schultz, M.C. Jensen, R.C. Bradt, Single crystal cleavage of brittle  
31 materials, *Int. J. Fract.* 65 (1994) 291-312.
- 32 [73] M.S. Dresselhaus, G. Dresselhaus, Intercalation compounds of graphite, *Adv.*  
33 *Phys.* 51 (2002) 1-186.
- 34 [74] R. Van Noorden, Production: Beyond sticky tape, *Nature*. 483 (2012) S32-3.
- 35 [75] G.R. Bhimanapati, Z. Lin, V. Meunier, Y. Jung, J. Cha, S. Das, D. Xiao, Y.  
36 Son, M.S. Strano, V.R. Cooper, L. Liang, S.G. Louie, E. Ringe, W. Zhou, S.S. Kim, R.R.  
37 Naik, B.G. Sumpter, H. Terrones, F. Xia, Y. Wang, J. Zhu, D. Akinwande, N. Alem, J.A.

- 1 Schuller, R.E. Schaak, M. Terrones, J.A. Robinson, Recent Advances in Two-Dimensional  
2 Materials beyond Graphene, ACS Nano. 9 (2015) 11509-11539.
- 3 [76] V. Nicolosi, M. Chhowalla, M.G. Kanatzidis, M.S. Strano, J.N. Coleman,  
4 Liquid Exfoliation of Layered Materials, Science. 340 (2013) 1226419-1226419.
- 5 [77] S. Wang, Y. Zhang, N. Abidi, L. Cabrales, Wettability and surface free energy  
6 of graphene films, Langmuir. 25 (2009) 11078-11081.
- 7 [78] Y. Hernandez, V. Nicolosi, M. Lotya, F.M. Blighe, Z. Sun, S. De, I.T.  
8 McGovern, B. Holland, M. Byrne, Y.K. Gun'Ko, J.J. Boland, P. Niraj, G. Duesberg, S.  
9 Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A.C. Ferrari, J.N. Coleman, High-  
10 yield production of graphene by liquid-phase exfoliation of graphite, Nat. Nanotechnol. 3  
11 (2008) 563-568.
- 12 [79] L. Zhu, X. Zhao, Y. Li, X. Yu, C. Li, Q. Zhang, High-quality production of  
13 graphene by liquid-phase exfoliation of expanded graphite, Mater. Chem. Phys. 137 (2013)  
14 984-990.
- 15 [80] J. Texter, Graphene dispersions, Current Opinion in Colloid & Interface  
16 Science. 19 (2014) 163-174.
- 17 [81] U. Khan, A. O'Neill, M. Lotya, S. De, J.N. Coleman, High-Concentration  
18 Solvent Exfoliation of Graphene, Small. 6 (2010) 864-871.
- 19 [82] K. Parvez, S. Yang, X. Feng, K. Müllen, Exfoliation of graphene via wet  
20 chemical routes, Synth. Met. 210, Part A (2015) 123-132.
- 21 [83] X. Zhang, A.C. Coleman, N. Katsonis, W.R. Browne, B.J. van Wees, B.L.  
22 Feringa, Dispersion of graphene in ethanol using a simple solvent exchange method,  
23 Chem. Commun. (Camb). 46 (2010) 7539-7541.
- 24 [84] J. Xu, D.K. Dang, V.T. Tran, X. Liu, J.S. Chung, S.H. Hur, W.M. Choi, E.J.  
25 Kim, P.A. Kohl, Liquid-phase exfoliation of graphene in organic solvents with addition of  
26 naphthalene, J. Colloid Interface Sci. 418 (2014) 37-42.
- 27 [85] A. Ciesielski, P. Samori, Graphene via sonication assisted liquid-phase  
28 exfoliation, Chem. Soc. Rev. 43 (2014) 381-398.
- 29 [86] W. Du, X. Jiang, L. Zhu, From graphite to graphene: direct liquid-phase  
30 exfoliation of graphite to produce single- and few-layered pristine graphene, Journal of  
31 Materials Chemistry A. 1 (2013) 10592.
- 32 [87] A. O'Neill, U. Khan, P.N. Nirmalraj, J. Boland, J.N. Coleman, Graphene  
33 Dispersion and Exfoliation in Low Boiling Point Solvents, The Journal of Physical  
34 Chemistry C. 115 (2011) 5422-5428.
- 35 [88] L. Xu, J. McGraw, F. Gao, M. Grundy, Z. Ye, Z. Gu, J.L. Shepherd,  
36 Production of High-Concentration Graphene Dispersions in Low-Boiling-Point Organic  
37 Solvents by Liquid-Phase Noncovalent Exfoliation of Graphite with a Hyperbranched

- 1 Polyethylene and Formation of Graphene/Ethylene Copolymer Composites, *The Journal of*  
2 *Physical Chemistry C*. 117 (2013) 10730-10742.
- 3 [89] F. Fedi, F. Ricciardella, T. Polichetti, M.L. Miglietta, E. Massera, G. Di  
4 Francia, Exfoliation of Graphite and Dispersion of Graphene in Solutions of Low-Boiling-  
5 Point Solvents for Use in Gas Sensors, in: C. Di Natale, V. Ferrari, A. Ponzoni, G.  
6 Sberveglieri, M. Ferrari (Eds.), *Sensors and Microsystems: Proceedings of the 17th*  
7 *National Conference, Brescia, Italy, 5-7 February 2013*, Springer International Publishing,  
8 Cham, 2014, pp. 143-147.
- 9 [90] K.R. Paton, E. Varrla, C. Backes, R.J. Smith, U. Khan, A. O'Neill, C. Boland,  
10 M. Lotya, O.M. Istrate, P. King, T. Higgins, S. Barwich, P. May, P. Puczkarski, I. Ahmed,  
11 M. Moebius, H. Pettersson, E. Long, J. Coelho, S.E. O'Brien, E.K. McGuire, B.M.  
12 Sanchez, G.S. Duesberg, N. McEvoy, T.J. Pennycook, C. Downing, A. Crossley, V.  
13 Nicolosi, J.N. Coleman, Scalable production of large quantities of defect-free few-layer  
14 graphene by shear exfoliation in liquids, *Nat. Mater.* 13 (2014) 624-630.
- 15 [91] O.M. Marago, F. Bonaccorso, R. Saija, G. Privitera, P.G. Gucciardi, M.A. Iati,  
16 G. Calogero, P.H. Jones, F. Borghese, P. Denti, V. Nicolosi, A.C. Ferrari, Brownian  
17 motion of graphene, *ACS Nano*. 4 (2010) 7515-7523.
- 18 [92] S. De, P.J. King, M. Lotya, A. O'Neill, E.M. Doherty, Y. Hernandez, G.S.  
19 Duesberg, J.N. Coleman, Flexible, transparent, conducting films of randomly stacked  
20 graphene from surfactant-stabilized, oxide-free graphene dispersions, *Small*. 6 (2010) 458-  
21 464.
- 22 [93] A.A. Green, M.C. Hersam, Solution phase production of graphene with  
23 controlled thickness via density differentiation, *Nano Lett.* 9 (2009) 4031-4036.
- 24 [94] A.B. Bourlinos, V. Georgakilas, R. Zboril, T.A. Steriotis, A.K. Stubos, C.  
25 Trapalis, Aqueous-phase exfoliation of graphite in the presence of polyvinylpyrrolidone  
26 for the production of water-soluble graphenes, *Solid State Commun.* 149 (2009) 2172-  
27 2176.
- 28 [95] A.S. Wajid, S. Das, F. Irin, H.S.T. Ahmed, J.L. Shelburne, D. Parviz, R.J.  
29 Fullerton, A.F. Jankowski, R.C. Hedden, M.J. Green, Polymer-stabilized graphene  
30 dispersions at high concentrations in organic solvents for composite production, *Carbon*.  
31 50 (2012) 526-534.
- 32 [96] L. Guardia, M.J. Fernández-Merino, J.I. Paredes, P. Solís-Fernández, S. Villar-  
33 Rodil, A. Martínez-Alonso, J.M.D. Tascón, High-throughput production of pristine  
34 graphene in an aqueous dispersion assisted by non-ionic surfactants, *Carbon*. 49 (2011)  
35 1653-1662.
- 36 [97] X. Wang, P.F. Fulvio, G.A. Baker, G.M. Veith, R.R. Unocic, S.M. Mahurin,  
37 M. Chi, S. Dai, Direct exfoliation of natural graphite into micrometre size few layers  
38 graphene sheets using ionic liquids, *Chem. Commun. (Camb)*. 46 (2010) 4487-4489.

- 1 [98] D. Nuvoli, L. Valentini, V. Alzari, S. Scognamillo, S.B. Bon, M. Piccinini, J.  
2 Illescas, A. Mariani, High concentration few-layer graphene sheets obtained by liquid  
3 phase exfoliation of graphite in ionic liquid, *J.Mater.Chem.* 21 (2011) 3428-3431.
- 4 [99] R. Bari, G. Tamas, F. Irin, A.J.A. Aquino, M.J. Green, E.L. Quitevis, Direct  
5 exfoliation of graphene in ionic liquids with aromatic groups, *Colloids Surf. Physicochem.*  
6 *Eng. Aspects.* 463 (2014) 63-69.
- 7 [100] C. Backes, K.R. Paton, D. Hanlon, S. Yuan, M.I. Katsnelson, J. Houston, R.J.  
8 Smith, D. McCloskey, J.F. Donegan, J.N. Coleman, Spectroscopic metrics allow in situ  
9 measurement of mean size and thickness of liquid-exfoliated few-layer graphene  
10 nanosheets, *Nanoscale.* 8 (2016) 4311-4323.
- 11 [101] Y.L. Zhong, Z. Tian, G.P. Simon, D. Li, Scalable production of graphene via  
12 wet chemistry: progress and challenges, *Materials Today.* 18 (2015) 73-78.
- 13 [102] T.J. Nacken, C. Damm, J. Walter, A. Rüger, W. Peukert, Delamination of  
14 graphite in a high pressure homogenizer, *RSC Adv.* 5 (2015) 57328-57338.
- 15 [103] U. Khan, A. O'Neill, H. Porwal, P. May, K. Nawaz, J.N. Coleman, Size  
16 selection of dispersed, exfoliated graphene flakes by controlled centrifugation, *Carbon.* 50  
17 (2012) 470-475.
- 18 [104] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney,  
19 E.A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, Graphene-based composite materials,  
20 *Nature.* 442 (2006) 282-286.
- 21 [105] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y.  
22 Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, Synthesis of graphene-based nanosheets via chemical  
23 reduction of exfoliated graphite oxide, *Carbon.* 45 (2007) 1558-1565.
- 24 [106] V. Singh, D. Joung, L. Zhai, S. Das, S.I. Khondaker, S. Seal, Graphene based  
25 materials: Past, present and future, *Progress in Materials Science.* 56 (2011) 1178-1271.
- 26 [107] D. Li, M.B. Muller, S. Gilje, R.B. Kaner, G.G. Wallace, Processable aqueous  
27 dispersions of graphene nanosheets, *Nat. Nanotechnol.* 3 (2008) 101-105.
- 28 [108] W.S. Hummers, R.E. Offeman, Preparation of Graphitic Oxide, *J. Am.*  
29 *Chem. Soc.* 80 (1958) 1339.
- 30 [109] A.M. Dimiev, J.M. Tour, Mechanism of graphene oxide formation, *ACS*  
31 *Nano.* 8 (2014) 3060-3068.
- 32 [110] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, The chemistry of  
33 graphene oxide, *Chem. Soc. Rev.* 39 (2010) 228-240.
- 34 [111] W. Gao, L.B. Alemany, L. Ci, P.M. Ajayan, New insights into the structure  
35 and reduction of graphite oxide, *Nat. Chem.* 1 (2009) 403-408.

- 1 [112] W. Cai, R.D. Piner, F.J. Stadermann, S. Park, M.A. Shaibat, Y. Ishii, D.  
2 Yang, A. Velamakanni, S.J. An, M. Stoller, J. An, D. Chen, R.S. Ruoff, Synthesis and  
3 Solid-State NMR Structural Characterization of <sup>13</sup>C-Labeled Graphite Oxide, *Science*.  
4 321 (2008) 1815-1817.
- 5 [113] H. He, J. Klinowski, M. Forster, A. Lerf, A new structural model for graphite  
6 oxide, *Chemical Physics Letters*. 287 (1998) 53-56.
- 7 [114] A. Lerf, H. He, M. Forster, J. Klinowski, Structure of Graphite Oxide  
8 Revisited, *The Journal of Physical Chemistry B*. 102 (1998) 4477-4482.
- 9 [115] T. Szabó, O. Berkesi, P. Forgó, K. Josepovits, Y. Sanakis, D. Petridis, I.  
10 Dékány, Evolution of Surface Functional Groups in a Series of Progressively Oxidized  
11 Graphite Oxides, *Chem. Mater.* 18 (2006) 2740-2749.
- 12 [116] D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev,  
13 L.B. Alemany, W. Lu, J.M. Tour, Improved Synthesis of Graphene Oxide, *ACS Nano*. 4  
14 (2010) 4806- 4814.
- 15 [117] C.K. Chua, M. Pumera, Chemical reduction of graphene oxide: a synthetic  
16 chemistry viewpoint, *Chem. Soc. Rev.* 43 (2014) 291-312.
- 17 [118] T. Zhou, F. Chen, K. Liu, H. Deng, Q. Zhang, J. Feng, Q. Fu, A simple and  
18 efficient method to prepare graphene by reduction of graphite oxide with sodium  
19 hydrosulfite, *Nanotechnology*. 22 (2011) 045704.
- 20 [119] T. Kuila, S. Bose, A.K. Mishra, P. Khanra, N.H. Kim, J.H. Lee, Chemical  
21 functionalization of graphene and its applications, *Progress in Materials Science*. 57 (2012)  
22 1061-1105.
- 23 [120] H. Shin, K.K. Kim, A. Benayad, S. Yoon, H.K. Park, I. Jung, M.H. Jin, H.  
24 Jeong, J.M. Kim, J. Choi, Y.H. Lee, Efficient Reduction of Graphite Oxide by Sodium  
25 Borohydride and Its Effect on Electrical Conductance, *Advanced Functional Materials*. 19  
26 (2009) 1987-1992.
- 27 [121] Z.J. Fan, W. Kai, J. Yan, T. Wei, L.J. Zhi, J. Feng, Y.M. Ren, L.P. Song, F.  
28 Wei, Facile synthesis of graphene nanosheets via Fe reduction of exfoliated graphite oxide,  
29 *ACS Nano*. 5 (2011) 191-198.
- 30 [122] M.J. Fernández-Merino, L. Guardia, J.I. Paredes, S. Villar-Rodil, P. Solís-  
31 Fernández, A. Martínez-Alonso, J.M.D. Tascón, Vitamin C Is an Ideal Substitute for  
32 Hydrazine in the Reduction of Graphene Oxide Suspensions, *The Journal of Physical*  
33 *Chemistry C*. 114 (2010) 6426-6432.
- 34 [123] F. Bonaccorso, A. Lombardo, T. Hasan, Z. Sun, L. Colombo, A.C. Ferrari,  
35 Production and processing of graphene and 2d crystals, *Materials Today*. 15 (2012) 564-  
36 589.
- 37 [124] S. Pei, H. Cheng, The reduction of graphene oxide, *Carbon*. 50 (2012) 3210-  
38 3228.

- 1 [125] I.K. Moon, J. Lee, R.S. Ruoff, H. Lee, Reduced graphene oxide by chemical  
2 graphitization, *Nat. Commun.* 1 (2010) 73.
- 3 [126] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney,  
4 E.A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, Graphene-based composite materials,  
5 *Nature.* 442 (2006) 282-286.
- 6 [127] G. Wang, J. Yang, J. Park, X. Gou, B. Wang, H. Liu, J. Yao, Facile Synthesis  
7 and Characterization of Graphene Nanosheets, *The Journal of Physical Chemistry C.* 112  
8 (2008) 8192-8195.
- 9 [128] Z. Fan, K. Wang, T. Wei, J. Yan, L. Song, B. Shao, An environmentally  
10 friendly and efficient route for the reduction of graphene oxide by aluminum powder,  
11 *Carbon.* 48 (2010) 1686-1689.
- 12 [129] D.R. Dreyer, S. Murali, Y. Zhu, R.S. Ruoff, C.W. Bielawski, Reduction of  
13 graphite oxide using alcohols, *J.Mater.Chem.* 21 (2011) 3443-3447.
- 14 [130] V.H. Pham, S.H. Hur, E.J. Kim, B.S. Kim, J.S. Chung, Highly efficient  
15 reduction of graphene oxide using ammonia borane, *Chem. Commun. (Camb).* 49 (2013)  
16 6665-6667.
- 17 [131] C. Vallés, J. David Núñez, A.M. Benito, W.K. Maser, Flexible conductive  
18 graphene paper obtained by direct and gentle annealing of graphene oxide paper, *Carbon.*  
19 50 (2012) 835-844.
- 20 [132] Y. Liang, J. Frisch, L. Zhi, H. Norouzi-Arasi, X. Feng, J.P. Rabe, N. Koch,  
21 K. Mullen, Transparent, highly conductive graphene electrodes from acetylene-assisted  
22 thermolysis of graphite oxide sheets and nanographene molecules, *Nanotechnology.* 20  
23 (2009) 434007-4484/20/43/434007. Epub 2009 Oct 2.
- 24 [133] M.J. McAllister, J. Li, D.H. Adamson, H.C. Schniepp, A.A. Abdala, J. Liu,  
25 M. Herrera-Alonso, D.L. Milius, R. Car, R.K. Prud'homme, I.A. Aksay, Single Sheet  
26 Functionalized Graphene by Oxidation and Thermal Expansion of Graphite, *Chemistry of*  
27 *Materials.* 19 (2007) 4396-4404.
- 28 [134] P. Steurer, R. Wissert, R. Thomann, R. Mülhaupt, Functionalized Graphenes  
29 and Thermoplastic Nanocomposites Based upon Expanded Graphite Oxide,  
30 *Macromolecular Rapid Communications.* 30 (2009) 316-327.
- 31 [135] Y.M. Shulga, S.A. Baskakov, E.I. Knerelman, G.I. Davidova, E.R.  
32 Badamshina, N.Y. Shulga, E.A. Skryleva, A.L. Agapov, D.N. Voylov, A.P. Sokolov, V.M.  
33 Martynenko, Carbon nanomaterial produced by microwave exfoliation of graphite oxide:  
34 new insights, *RSC Adv.* 4 (2014) 587-592.
- 35 [136] K. Saranya, N. Sivasankar, A. Subramania, Microwave-assisted exfoliation  
36 method to develop platinum-decorated graphene nanosheets as a low cost counter electrode  
37 for dye-sensitized solar cells, *RSC Advances.* 4 (2014) 36226.



- 1 [137] X. Liu, J. Liu, D. Zhan, J. Yan, J. Wang, D. Chao, L. Lai, M. Chen, J. Yin, Z.  
2 Shen, Repeated microwave-assisted exfoliation of expandable graphite for the preparation  
3 of large scale and high quality multi-layer graphene, RSC Advances. 3 (2013) 11601.
- 4 [138] H.J. Han, Y.N. Chen, Z.J. Wang, Effect of microwave irradiation on  
5 reduction of graphene oxide films, RSC Adv. 5 (2015) 92940-92946.
- 6 [139] Z.S. Wu, K. Parvez, X. Feng, K. Mullen, Graphene-based in-plane micro-  
7 supercapacitors with high power and energy densities, Nat. Commun. 4 (2013) 2487.
- 8 [140] H.N. Tien, V.H. Luan, T.K. Lee, B.-. Kong, J.S. Chung, E.J. Kim, S.H. Hur,  
9 Enhanced solvothermal reduction of graphene oxide in a mixed solution of sulfuric acid  
10 and organic solvent, Chem. Eng. J. 211-212 (2012) 97-103.
- 11 [141] X. Mei, J. Ouyang, Ultrasonication-assisted ultrafast reduction of graphene  
12 oxide by zinc powder at room temperature, Carbon. 49 (2011) 5389-5397.
- 13 [142] M.V. Antisari, A. Montone, N. Jovic, E. Piscopiello, C. Alvani, L. Pilloni,  
14 Low energy pure shear milling: A method for the preparation of graphite nano-sheets, Scr.  
15 Mater. 55 (2006) 1047-1050.
- 16 [143] W. Zhao, M. Fang, F. Wu, H. Wu, L. Wang, G. Chen, Preparation of  
17 graphene by exfoliation of graphite using wet ball milling, Journal of Materials Chemistry.  
18 20 (2010) 5817.
- 19 [144] W. Zhao, F. Wu, H. Wu, G. Chen, Preparation of Colloidal Dispersions of  
20 Graphene Sheets in Organic Solvents by Using Ball Milling, Journal of Nanomaterials.  
21 2010 (2010) 1-5.
- 22 [145] P. Sun, S. Kuga, M. Wu, Y. Huang, Exfoliation of graphite by dry ball  
23 milling with cellulose, Cellulose. 21 (2014) 2469-2478.
- 24 [146] V. Leon, A.M. Rodriguez, P. Prieto, M. Prato, E. Vazquez, Exfoliation of  
25 graphite with triazine derivatives under ball-milling conditions: preparation of few-layer  
26 graphene via selective noncovalent interactions, ACS Nano. 8 (2014) 563-571.
- 27 [147] V. Leon, M. Quintana, M.A. Herrero, J.L. Fierro, A. de la Hoz, M. Prato, E.  
28 Vazquez, Few-layer graphenes from ball-milling of graphite with melamine, Chem.  
29 Commun. (Camb). 47 (2011) 10936-10938.
- 30 [148] Y. Cao, H.J. Choi, W.L. Zhang, B. Wang, C. Hao, J. Liu, Eco-friendly mass  
31 production of poly(p-phenylenediamine)/graphene oxide nanoplatelet composites and their  
32 electrorheological characteristics, Composites Sci. Technol. 122 (2016) 36-41.
- 33 [149] I.Y. Jeon, Y.R. Shin, G.J. Sohn, H.J. Choi, S.Y. Bae, J. Mahmood, S.M.  
34 Jung, J.M. Seo, M.J. Kim, D. Wook Chang, L. Dai, J.B. Baek, Edge-carboxylated  
35 graphene nanosheets via ball milling, Proc. Natl. Acad. Sci. U. S. A. 109 (2012) 5588-  
36 5593.

- 1 [150] X. Fan, D.W. Chang, X. Chen, J. Baek, L. Dai, Functionalized graphene  
2 nanoplatelets from ball milling for energy applications, *Current Opinion in Chemical*  
3 *Engineering*. 11 (2016) 52-58.
- 4 [151] M. Ullah, M.E. Ali, S.B. Abd Hamid, Surfactant-Assisted Ball Milling: a  
5 Novel Route to Novel Materials with Controlled Nanostructure - a Review, *Reviews on*  
6 *Advanced Materials Science*. 37 (2014) 1-14.
- 7 [152] S. Rosenkranz, S. Breitung-Faes, A. Kwade, Experimental investigations and  
8 modelling of the ball motion in planetary ball mills, *Powder Technol.* 212 (2011) 224-230.
- 9 [153] P. Balaz, High-Energy Milling, in: P. Balaz (Ed.), *Mechanochemistry in*  
10 *Nanoscience and Minerals Engineering*, Springer Berlin Heidelberg, Berlin, Heidelberg,  
11 2008, pp. 103-132.
- 12 [154] H. Wendt, G. Kreysa, *Electrochemical Engineering: Science and Technology*  
13 *in Chemical and Other Industries*, Springer-Verlag Berlin Heidelberg, 1999.
- 14 [155] C.E. Banks, T.J. Davies, G.G. Wildgoose, R.G. Compton, Electrocatalysis at  
15 graphite and carbon nanotube modified electrodes: edge-plane sites and tube ends are the  
16 reactive sites, *Chem. Commun. (Camb)*. 7 (2005) 829-841.
- 17 [156] L.L. Zhang, X.S. Zhao, Carbon-based materials as supercapacitor electrodes,  
18 *Chem. Soc. Rev.* 38 (2009) 2520-2531.
- 19 [157] A.M. Abdelkader, A.J. Cooper, R.A. Dryfe, I.A. Kinloch, How to get  
20 between the sheets: a review of recent works on the electrochemical exfoliation of  
21 graphene materials from bulk graphite, *Nanoscale*. 7 (2015) 6944-6956.
- 22 [158] A. Ambrosi, C.K. Chua, A. Bonanni, M. Pumera, Electrochemistry of  
23 graphene and related materials, *Chem. Rev.* 114 (2014) 7150-7188.
- 24 [159] Z. Qiu, J. Yu, P. Yan, Z. Wang, Q. Wan, N. Yang, Electrochemical Grafting  
25 of Graphene Nano Platelets with Aryl Diazonium Salts, *ACS Appl. Mater. Interfaces*.  
26 (2016).
- 27 [160] J. Liu, M. Notarianni, G. Will, V.T. Tiong, H. Wang, N. Motta,  
28 Electrochemically exfoliated graphene for electrode films: effect of graphene flake  
29 thickness on the sheet resistance and capacitive properties, *Langmuir*. 29 (2013) 13307-  
30 13314.
- 31 [161] K. Parvez, Z.S. Wu, R. Li, X. Liu, R. Graf, X. Feng, K. Mullen, Exfoliation  
32 of graphite into graphene in aqueous solutions of inorganic salts, *J. Am. Chem. Soc.* 136  
33 (2014) 6083-6091.
- 34 [162] P. Yu, S.E. Lowe, G.P. Simon, Y.L. Zhong, Electrochemical exfoliation of  
35 graphite and production of functional graphene, *Current Opinion in Colloid & Interface*  
36 *Science*. 20 (2015) 329-338.

- 1 [163] C.T.J. Low, F.C. Walsh, M.H. Chakrabarti, M.A. Hashim, M.A. Hussain,  
2 Electrochemical approaches to the production of graphene flakes and their potential  
3 applications, *Carbon*. 54 (2013) 1-21.
- 4 [164] N. Parveen, M.O. Ansari, M.H. Cho, Simple route for gram synthesis of less  
5 defective few layered graphene and its electrochemical performance, *RSC Adv.* 5 (2015)  
6 44920-44927.
- 7 [165] Y.L. Zhong, Z. Tian, G.P. Simon, D. Li, Scalable production of graphene via  
8 wet chemistry: Progress and challenges, *Mater. Today*. 18 (2015) 73-78.
- 9 [166] C.Y. Su, A.Y. Lu, Y. Xu, F.R. Chen, A.N. Khlobystov, L.J. Li, High-quality  
10 thin graphene films from fast electrochemical exfoliation, *ACS Nano*. 5 (2011) 2332-2339.
- 11 [167] Y. Zhang, Y. Tan, H.L. Stormer, P. Kim, Experimental observation of the  
12 quantum Hall effect and Berry's phase in graphene, *Nature*. 438 (2005) 201-204.
- 13 [168] I.W. Frank, D.M. Tanenbaum, A.M. van der Zande, P.L. McEuen,  
14 Mechanical properties of suspended graphene sheets, *Journal of Vacuum Science &  
15 Technology B: Microelectronics and Nanometer Structures*. 25 (2007) 2558.
- 16 [169] D.A. Dikin, S. Stankovich, E.J. Zimney, R.D. Piner, G.H.B. Dommett, G.  
17 Evmenenko, S.T. Nguyen, R.S. Ruoff, Preparation and characterization of graphene oxide  
18 paper, *Nature*. 448 (2007) 457-460.
- 19 [170] S. Park, K.S. Lee, G. Bozoklu, W. Cai, S.T. Nguyen, R.S. Ruoff, Graphene  
20 oxide papers modified by divalent ions-enhancing mechanical properties via chemical  
21 cross-linking, *ACS Nano*. 2 (2008) 572-578.
- 22 [171] S. Park, D.A. Dikin, S.T. Nguyen, R.S. Ruoff, Graphene Oxide Sheets  
23 Chemically Cross-Linked by Polyallylamine, *The Journal of Physical Chemistry C*. 113  
24 (2009) 15801-15804.
- 25 [172] C. Lee, X. Wei, Q. Li, R. Carpick, J.W. Kysar, J. Hone, Elastic and frictional  
26 properties of graphene, *physica status solidi (b)*. 246 (2009) 2562-2567.
- 27 [173] R. Sharma, J.H. Baik, C.J. Perera, M.S. Strano, Anomalously large reactivity  
28 of single graphene layers and edges toward electron transfer chemistries, *Nano Lett.* 10  
29 (2010) 398-405.
- 30 [174] C. Yu, L. Shi, Z. Yao, D. Li, A. Majumdar, Thermal conductance and  
31 thermopower of an individual single-wall carbon nanotube, *Nano Lett.* 5 (2005) 1842-  
32 1846.
- 33 [175] S. Chen, A.L. Moore, W. Cai, J.W. Suk, J. An, C. Mishra, C. Amos, C.W.  
34 Magnuson, J. Kang, L. Shi, R.S. Ruoff, Raman measurements of thermal transport in  
35 suspended monolayer graphene of variable sizes in vacuum and gaseous environments,  
36 *ACS Nano*. 5 (2011) 321-328.

- 1 [176] A.A. Balandin, Thermal properties of graphene and nanostructured carbon  
2 materials, *Nature Materials*. 10 (2011) 569-581.
- 3 [177] J.H. Seol, I. Jo, A.L. Moore, L. Lindsay, Z.H. Aitken, M.T. Pettes, X. Li, Z.  
4 Yao, R. Huang, D. Broido, N. Mingo, R.S. Ruoff, L. Shi, Two-dimensional phonon  
5 transport in supported graphene, *Science*. 328 (2010) 213-216.
- 6 [178] D.L. Nika, E.P. Pokatilov, A.S. Askerov, A.A. Balandin, Phonon thermal  
7 conduction in graphene: Role of Umklapp and edge roughness scattering, *Physical Review*  
8 *B*. 79 (2009).
- 9 [179] J. Jiang, J. Lan, J. Wang, B. Li, Isotopic effects on the thermal conductivity  
10 of graphene nanoribbons: Localization mechanism, *J. Appl. Phys.* 107 (2010) 054314.
- 11 [180] M.T. Pettes, I. Jo, Z. Yao, L. Shi, Influence of polymeric residue on the  
12 thermal conductivity of suspended bilayer graphene, *Nano Lett.* 11 (2011) 1195-1200.
- 13 [181] T.R. Anthony, W.F. Banholzer, J.F. Fleischer, L. Wei, P.K. Kuo, R.L.  
14 Thomas, R.W. Pryor, Thermal diffusivity of isotopically enriched <sup>12</sup>C diamond, *Physical*  
15 *Review B*. 42 (1990) 1104-1111.
- 16 [182] P. Kim, L. Shi, A. Majumdar, P. McEuen, Thermal Transport Measurements  
17 of Individual Multiwalled Nanotubes, *Phys. Rev. Lett.* 87 (2001).
- 18 [183] E. Pop, D. Mann, Q. Wang, K. Goodson, H. Dai, Thermal conductance of an  
19 individual single-wall carbon nanotube above room temperature, *Nano Lett.* 6 (2006) 96-  
20 100.
- 21 [184] W. Cai, Thermal transport in suspended and supported monolayer graphene  
22 grown by chemical vapor deposition, *Nano letters*. 10 (2010) 1645.
- 23 [185] E. Pop, V. Varshney, A.K. Roy, Thermal properties of graphene:  
24 Fundamentals and applications, *MRS Bull.* 37 (2012) 1273-1281.
- 25 [186] D.L. Nika, A.A. Balandin, Two-dimensional phonon transport in graphene, *J.*  
26 *Phys. Condens Matter*. 24 (2012) 233203.
- 27 [187] D.L. Nika, A.A. Balandin, Thermal Transport in Graphene, Few-Layer  
28 Graphene and Graphene Nanoribbons, in: S. Lepri (Ed.), *Thermal Transport in Low*  
29 *Dimensions: From Statistical Physics to Nanoscale Heat Transfer*, Springer International  
30 Publishing, Cham, 2016, pp. 339-363.
- 31 [188] H. He, C. Gao, General Approach to Individually Dispersed, Highly Soluble,  
32 and Conductive Graphene Nanosheets Functionalized by Nitrene Chemistry, *Chemistry of*  
33 *Materials*. 22 (2010) 5054-5064.
- 34 [189] W. Zheng, X. Lu, S. Wong, Electrical and mechanical properties of expanded  
35 graphite-reinforced high-density polyethylene, *J Appl Polym Sci.* 91 (2004) 2781-2788.

- 1 [190] T. Ramanathan, S. Stankovich, D.A. Dikin, H. Liu, H. Shen, S.T. Nguyen,  
2 L.C. Brinson, Graphitic nanofillers in PMMA nanocomposites—An investigation of  
3 particle size and dispersion and their influence on nanocomposite properties, *Journal of*  
4 *Polymer Science Part B: Polymer Physics*. 45 (2007) 2097-2112.
- 5 [191] J. Liang, Y. Wang, Y. Huang, Y. Ma, Z. Liu, J. Cai, C. Zhang, H. Gao, Y.  
6 Chen, Electromagnetic interference shielding of graphene/epoxy composites, *Carbon*. 47  
7 (2009) 922-925.
- 8 [192] L. Ye, X.-. Meng, X. Ji, Z.-. Li, J.-. Tang, Synthesis and characterization of  
9 expandable graphite-poly(methyl methacrylate) composite particles and their application to  
10 flame retardation of rigid polyurethane foams, *Polym Degradation Stab*. 94 (2009) 971-  
11 979.
- 12 [193] D.W. Wang, F. Li, J. Zhao, W. Ren, Z.G. Chen, J. Tan, Z.S. Wu, I. Gentle,  
13 G.Q. Lu, H.M. Cheng, Fabrication of Graphene/Polyaniline Composite Paper via In Situ  
14 Anodic Electropolymerization for High-Performance Flexible Electrode, *ACS Nano*. 3  
15 (2009) 1745-1752.
- 16 [194] R. Verdejo, F. Barroso-Bujans, M.A. Rodriguez-Perez, J. Antonio de Saja,  
17 M.A. Lopez-Manchado, Functionalized graphene sheet filled silicone foam  
18 nanocomposites, *Journal of Materials Chemistry*. 18 (2008) 2221.
- 19 [195] R. Verdejo, M.M. Bernal, L.J. Romasanta, M.A. Lopez-Manchado, Graphene  
20 filled polymer nanocomposites, *J.Mater.Chem*. 21 (2011) 3301-3310.
- 21 [196] J. Du, H. Cheng, The Fabrication, Properties, and Uses of Graphene/Polymer  
22 Composites, *Macromolecular Chemistry and Physics*. 213 (2012) 1060-1077.
- 23 [197] K. Kalaitzidou, H. Fukushima, L.T. Drzal, A new compounding method for  
24 exfoliated graphite-polypropylene nanocomposites with enhanced flexural properties and  
25 lower percolation threshold, *Compos. Sci. Technol*. 67 (2007) 2045-2051.
- 26 [198] G. Chen, C. Wu, W. Weng, D. Wu, W. Yan, Preparation of  
27 polystyrene/graphite nanosheet composite, *Polymer*. 44 (2003) 1781-1784.
- 28 [199] H. Zhang, W. Zheng, Q. Yan, Y. Yang, J. Wang, Z. Lu, G. Ji, Z. Yu,  
29 Electrically conductive polyethylene terephthalate/graphene nanocomposites prepared by  
30 melt compounding, *Polymer*. 51 (2010) 1191-1196.
- 31 [200] A. Dasari, Z. Yu, Y. Mai, Electrically conductive and super-tough  
32 polyamide-based nanocomposites, *Polymer*. 50 (2009) 4112-4121.
- 33 [201] Y. Xu, W. Hong, H. Bai, C. Li, G. Shi, Strong and ductile poly(vinyl  
34 alcohol)/graphene oxide composite films with a layered structure, *Carbon*. 47 (2009) 3538-  
35 3543.
- 36 [202] D. Cai, M. Song, A simple route to enhance the interface between graphite  
37 oxide nanoplatelets and a semi-crystalline polymer for stress transfer, *Nanotechnology*. 20  
38 (2009) 315708-4484/20/31/315708. Epub 2009 Jul 14.

- 1 [203] D. Cai, K. Yusoh, M. Song, The mechanical properties and morphology of a  
2 graphite oxide nanoplatelet/polyurethane composite, *Nanotechnology*. 20 (2009) 085712-  
3 4484/20/8/085712. Epub 2009 Feb 3.
- 4 [204] L. Guadagno, M. Raimondo, V. Vittoria, L. Vertuccio, C. Naddeo, S. Russo,  
5 B. De Vivo, P. Lamberti, G. Spinelli, V. Tucci, Development of epoxy mixtures for  
6 application in aeronautics and aerospace, *RSC Advances*. 4 (2014) 15474.
- 7 [205] P. Mohan, A Critical Review: The Modification, Properties, and Applications  
8 of Epoxy Resins, *Polym. Plast. Technol. Eng.* 52 (2013) 107-125.
- 9 [206] F.A.K. A Rasheed and, Fabrication and properties of CNTs reinforced  
10 polymeric matrix nanocomposites for sports applications, *IOP Conference Series:  
11 Materials Science and Engineering*. 60 (2014) 012009.
- 12 [207] D.R. Bortz, E.G. Heras, I. Martin-Gullon, Impressive Fatigue Life and  
13 Fracture Toughness Improvements in Graphene Oxide/Epoxy Composites,  
14 *Macromolecules*. 45 (2012) 238-245.
- 15 [208] A.S. Wajid, H.S.T. Ahmed, S. Das, F. Irin, A.F. Jankowski, M.J. Green,  
16 High-Performance Pristine Graphene/Epoxy Composites With Enhanced Mechanical and  
17 Electrical Properties, *Macromolecular Materials and Engineering*. 298 (2012) 339-347.
- 18 [209] D. Galpaya, M. Wang, G. George, N. Motta, E. Waclawik, C. Yan,  
19 Preparation of graphene oxide/epoxy nanocomposites with significantly improved  
20 mechanical properties, *J. Appl. Phys.* 116 (2014) 053518.
- 21 [210] X. Shen, X. Pei, S. Fu, K. Friedrich, Significantly modified tribological  
22 performance of epoxy nanocomposites at very low graphene oxide content, *Polymer*. 54  
23 (2013) 1234-1242.
- 24 [211] D.R. Cooper, B. D'Anjou, N. Ghattamaneni, B. Harack, M. Hilke, A. Horth,  
25 N. Majlis, M. Massicotte, L. Vandsburger, E. Whiteway, V. Yu, Experimental Review of  
26 Graphene, *ISRN Condensed Matter Physics*. 2012 (2012) 56.
- 27 [212] J. Wei, T. Vo, F. Inam, Epoxy/graphene nanocomposites – processing and  
28 properties: a review, *RSC Adv.* 5 (2015) 73510-73524.
- 29 [213] J.K.W. Sandler, J.E. Kirk, I.A. Kinloch, M.S.P. Shaffer, A.H. Windle, Ultra-  
30 low electrical percolation threshold in carbon-nanotube-epoxy composites, *Polymer*. 44  
31 (2003) 5893-5899.
- 32 [214] S. Zhao, H. Chang, S. Chen, J. Cui, Y. Yan, High-performance and  
33 multifunctional epoxy composites filled with epoxide-functionalized graphene, *European  
34 Polymer Journal*. 84 (2016) 300-312.
- 35 [215] R. Atif, I. Shyha, F. Inam, Mechanical, Thermal, and Electrical Properties of  
36 Graphene-Epoxy Nanocomposites—A Review, *Polymers*. 8 (2016) 281.

- 1 [216] C. Kim, W. Khan, D. Kim, K. Cho, S. Park, Graphene oxide/cellulose  
2 composite using NMMO monohydrate, *Carbohydr. Polym.* 86 (2011) 903-909.
- 3 [217] N.D. Luong, N. Pahimanolis, U. Hippi, J.T. Korhonen, J. Ruokolainen, L.  
4 Johansson, J. Nam, J. Seppälä, Graphene/cellulose nanocomposite paper with high  
5 electrical and mechanical performances, *Journal of Materials Chemistry*. 21 (2011) 13991-  
6 13998.
- 7 [218] Z. Weng, Y. Su, D. Wang, F. Li, J. Du, H. Cheng, Graphene-Cellulose Paper  
8 Flexible Supercapacitors, *Advanced Energy Materials*. 1 (2011) 917-922.
- 9 [219] M. Xu, Q. Huang, X. Wang, R. Sun, Highly tough cellulose/graphene  
10 composite hydrogels prepared from ionic liquids, *Industrial Crops and Products*. 70 (2015)  
11 56-63.
- 12 [220] H. Wang, Q. Hao, X. Yang, L. Lu, X. Wang, A nanostructured  
13 graphene/polyaniline hybrid material for supercapacitors, *Nanoscale*. 2 (2010) 2164-2170.
- 14 [221] H. Wang, Q. Hao, X. Yang, L. Lu, X. Wang, Graphene oxide doped  
15 polyaniline for supercapacitors, *Electrochemistry Communications*. 11 (2009) 1158-1161.
- 16 [222] X. Zhao, Q. Zhang, D. Chen, P. Lu, Enhanced Mechanical Properties of  
17 Graphene-Based Poly(vinyl alcohol) Composites, *Macromolecules*. 43 (2010) 2357-2363.
- 18 [223] J. Liang, Y. Huang, L. Zhang, Y. Wang, Y. Ma, T. Guo, Y. Chen, Molecular-  
19 Level Dispersion of Graphene into Poly(vinyl alcohol) and Effective Reinforcement of  
20 their Nanocomposites, *Advanced Functional Materials*. 19 (2009) 2297-2302.
- 21 [224] Y.R. Lee, A.V. Raghu, H.M. Jeong, B.K. Kim, Properties of Waterborne  
22 Polyurethane/Functionalized Graphene Sheet Nanocomposites Prepared by an in situ  
23 Method, *Macromolecular Chemistry and Physics*. 210 (2009) 1247-1254.
- 24 [225] J. Liang, Y. Xu, Y. Huang, L. Zhang, Y. Wang, Y. Ma, F. Li, T. Guo, Y.  
25 Chen, Infrared-Triggered Actuators from Graphene-Based Nanocomposites, *The Journal of*  
26 *Physical Chemistry C*. 113 (2009) 9921-9927.
- 27 [226] S. Ansari, E.P. Giannelis, Functionalized graphene sheet-Poly(vinylidene  
28 fluoride) conductive nanocomposites, *Journal of Polymer Science Part B: Polymer Physics*.  
29 47 (2009) 888-897.
- 30 [227] H. Kim, C.W. Macosko, Processing-property relationships of  
31 polycarbonate/graphene composites, *Polymer*. 50 (2009) 3797-3809.
- 32 [228] N. Liu, F. Luo, H. Wu, Y. Liu, C. Zhang, J. Chen, One-Step Ionic-Liquid-  
33 Assisted Electrochemical Synthesis of Ionic-Liquid-Functionalized Graphene Sheets  
34 Directly from Graphite, *Advanced Functional Materials*. 18 (2008) 1518-1525.
- 35 [229] P.B. Malafaya, G.A. Silva, R.L. Reis, Natural–origin polymers as carriers and  
36 scaffolds for biomolecules and cell delivery in tissue engineering applications, *Adv. Drug*  
37 *Deliv. Rev.* 59 (2007) 207-233.

- 1 [230] Y. Li, F. Liu, B. Xia, Q. Du, P. Zhang, D. Wang, Z. Wang, Y. Xia, Removal  
2 of copper from aqueous solution by carbon nanotube/calcium alginate composites, J.  
3 Hazard. Mater. 177 (2010) 876-880.
- 4 [231] K.Y. Lee, D.J. Mooney, Alginate: properties and biomedical applications,  
5 Prog. Polym. Sci. 37 (2012) 106-126.
- 6 [232] A.D. Augst, H.J. Kong, D.J. Mooney, Alginate hydrogels as biomaterials,  
7 Macromol. Biosci. 6 (2006) 623-633.
- 8 [233] S. Wu, X. Zhao, Y. Li, C. Zhao, Q. Du, J. Sun, Y. Wang, X. Peng, Y. Xia, Z.  
9 Wang, L. Xia, Adsorption of ciprofloxacin onto biocomposite fibers of graphene  
10 oxide/calcium alginate, Chem. Eng. J. 230 (2013) 389-395.
- 11 [234] L. Sun, B. Fugetsu, Graphene oxide captured for green use: Influence on the  
12 structures of calcium alginate and macroporous alginic beads and their application to  
13 aqueous removal of acridine orange, Chem. Eng. J. 240 (2014) 565-573.
- 14 [235] H. Zheng, J. Yang, S. Han, The synthesis and characteristics of sodium  
15 alginate/graphene oxide composite films crosslinked with multivalent cations, J Appl  
16 Polym Sci. 133 (2016).
- 17 [236] Y. He, N. Zhang, Q. Gong, H. Qiu, W. Wang, Y. Liu, J. Gao,  
18 Alginate/graphene oxide fibers with enhanced mechanical strength prepared by wet  
19 spinning, Carbohydr. Polym. 88 (2012) 1100-1108.
- 20 [237] Y. Li, Q. Du, T. Liu, J. Sun, Y. Wang, S. Wu, Z. Wang, Y. Xia, L. Xia,  
21 Methylene blue adsorption on graphene oxide/calcium alginate composites, Carbohydr.  
22 Polym. 95 (2013) 501-507.
- 23 [238] S.V. Garimella, A.S. Fleischer, J.Y. Murthy, A. Keshavarzi, R. Prasher, C.  
24 Patel, S.H. Bhavnani, R. Venkatasubramanian, R. Mahajan, Y. Joshi, B. Sammakia, B.A.  
25 Myers, L. Chorosinski, M. Baelmans, P. Sathyamurthy, P.E. Raad, Thermal Challenges in  
26 Next-Generation Electronic Systems, IEEE Transactions on Components and Packaging  
27 Technologies. 31 (2008) 801-815.
- 28 [239] R.S. Prasher, Je-Young Chang, I. Sauciuc, S. Narasimhan, D. Chau, G.  
29 Chrysler, A. Myers, S. Prstic, C. Hu, Nano and Micro Technology-Based Next-Generation  
30 Package-Level Cooling Solutions, Intel Technology Journal. 9 (2005) 285-296.
- 31 [240] J. Wei, Challenges in Cooling Design of CPU Packages for High-  
32 Performance Servers, Heat Transfer Eng. 29 (2008) 178-187.
- 33 [241] K.M. Shahil, A.A. Balandin, Graphene-multilayer graphene nanocomposites  
34 as highly efficient thermal interface materials, Nano Lett. 12 (2012) 861-867.
- 35 [242] V. Goyal, A.A. Balandin, Thermal properties of the hybrid graphene-metal  
36 nano-micro-composites: Applications in thermal interface materials, Appl. Phys. Lett. 100  
37 (2012) 073113.



- 1 [243] N.K. Mahanta, M.R. Loos, I. Manas Zloczower, A.R. Abramson, Graphite-  
2 graphene hybrid filler system for high thermal conductivity of epoxy composites, *J. Mater.*  
3 *Res.* 30 (2015) 959-966.
- 4 [244] K.M.F. Shahil, A.A. Balandin, Thermal properties of graphene and  
5 multilayer graphene: Applications in thermal interface materials, *Solid State Commun.* 152  
6 (2012) 1331-1340.
- 7 [245] J. Renteria, S. Legedza, R. Salgado, M.P. Balandin, S. Ramirez, M. Saadah,  
8 F. Kargar, A.A. Balandin, Magnetically-functionalized self-aligning graphene fillers for  
9 high-efficiency thermal management applications, *Mater Des.* 88 (2015) 214-221.
- 10 [246] P. Goli, S. Legedza, A. Dhar, R. Salgado, J. Renteria, A.A. Balandin,  
11 Graphene-enhanced hybrid phase change materials for thermal management of Li-ion  
12 batteries, *J. Power Sources.* 248 (2014) 37-43.
- 13 [247] R.K. Layek, A.K. Nandi, A review on synthesis and properties of polymer  
14 functionalized graphene, *Polymer.* 54 (2013) 5087-5103.
- 15 [248] V. Mittal, Functional Polymer Nanocomposites with Graphene: A Review,  
16 *Macromolecular Materials and Engineering.* 299 (2014) 906-931.
- 17 [249] Y.-. Wan, L.-. Tang, D. Yan, L. Zhao, Y.-. Li, L.-. Wu, J.-. Jiang, G.-. Lai,  
18 Improved dispersion and interface in the graphene/epoxy composites via a facile  
19 surfactant-assisted process, *Compos. Sci. Technol.* 82 (2013) 60-68.
- 20 [250] X. Liu, L. Wang, L. Zhao, H. He, X. Shao, G. Fang, Z. Wan, R. Zeng,  
21 Research Progress of Graphene-Based Rubber Nanocomposites, *Polymer Composites.*  
22 (2016).
- 23 [251] P.M. Ajayan, J.M. Tour, Materials Science: Nanotube composites, *Nature.*  
24 447 (2007) 1066-1068.
- 25 [252] H. Pathangi, P.M. Vereecken, A. Klekachev, G. Groeseneken, A. Witvrouw,  
26 Quantifying the Aggregation Factor in Carbon Nanotube Dispersions by Absorption  
27 Spectroscopy, *Journal of Nanoscience.* 2014 (2014) 13.
- 28 [253] F. Inam, T. Peijs, Re-aggregation of carbon nanotubes in two-component  
29 epoxy system, *J. Nanostructured Polym. Nanocomposites.* 2 (2006) 86-94.
- 30 [254] J.R. Potts, D.R. Dreyer, C.W. Bielawski, R.S. Ruoff, Graphene-based  
31 polymer nanocomposites, *Polymer.* 52 (2011) 5-25.
- 32 [255] M. Alexandre, P. Dubois, Polymer-layered silicate nanocomposites:  
33 preparation, properties and uses of a new class of materials, *Materials Science and*  
34 *Engineering: R: Reports.* 28 (2000) 1-63.
- 35 [256] C. Teng, C.M. Ma, C. Lu, S. Yang, S. Lee, M. Hsiao, M. Yen, K. Chiou, T.  
36 Lee, Thermal conductivity and structure of non-covalent functionalized graphene/epoxy  
37 composites, *Carbon.* 49 (2011) 5107-5116.

- 1 [257] K. Xu, P. Cao, J.R. Heath, Scanning tunneling microscopy characterization of  
2 the electrical properties of wrinkles in exfoliated graphene monolayers, *Nano Lett.* 9  
3 (2009) 4446-4451.
- 4 [258] F. Irin, M.J. Hansen, R. Bari, D. Parviz, S.D. Metzler, S.K. Bhattacharia, M.J.  
5 Green, Adsorption and removal of graphene dispersants, *J. Colloid Interface Sci.* 446  
6 (2015) 282-289.
- 7 [259] W. Du, X. Jiang, L. Zhu, From graphite to graphene: direct liquid-phase  
8 exfoliation of graphite to produce single- and few-layered pristine graphene, *Journal of*  
9 *Materials Chemistry A.* 1 (2013) 10592.
- 10 [260] M. Yi, Z. Shen, Kitchen blender for producing high-quality few-layer  
11 graphene, *Carbon.* 78 (2014) 622-626.
- 12 [261] Y. Wei, Z. Sun, Liquid-phase exfoliation of graphite for mass production of  
13 pristine few-layer graphene, *Current Opinion in Colloid & Interface Science.* 20 (2015)  
14 311-321.
- 15 [262] M. Lotya, P.J. King, U. Khan, S. De, J.N. Coleman, High-concentration,  
16 surfactant-stabilized graphene dispersions, *ACS Nano.* 4 (2010) 3155-3162.
- 17 [263] M. Lotya, Y. Hernandez, P.J. King, R.J. Smith, V. Nicolosi, L.S. Karlsson,  
18 F.M. Blighe, S. De, Z. Wang, I.T. McGovern, G.S. Duesberg, J.N. Coleman, Liquid phase  
19 production of graphene by exfoliation of graphite in surfactant/water solutions, *J. Am.*  
20 *Chem. Soc.* 131 (2009) 3611-3620.
- 21 [264] M. Cano, U. Khan, T. Sainsbury, A. O'Neill, Z. Wang, I.T. McGovern, W.K.  
22 Maser, A.M. Benito, J.N. Coleman, Improving the mechanical properties of graphene  
23 oxide based materials by covalent attachment of polymer chains, *Carbon.* 52 (2013) 363-  
24 371.
- 25 [265] Y. Zhang, J.E. Mark, Y. Zhu, R.S. Ruoff, D.W. Schaefer, Mechanical  
26 properties of polybutadiene reinforced with octadecylamine modified graphene oxide,  
27 *Polymer.* 55 (2014) 5389-5395.
- 28 [266] V. Georgakilas, M. Otyepka, A.B. Bourlinos, V. Chandra, N. Kim, K.C.  
29 Kemp, P. Hobza, R. Zboril, K.S. Kim, Functionalization of graphene: covalent and non-  
30 covalent approaches, derivatives and applications, *Chem. Rev.* 112 (2012) 6156-6214.
- 31 [267] L. Rodriguez-Perez, M.A. Herranz, N. Martin, The chemistry of pristine  
32 graphene, *Chem. Commun. (Camb).* 49 (2013) 3721-3735.
- 33 [268] S. Vadukumpully, J. Paul, N. Mahanta, S. Valiyaveetil, Flexible conductive  
34 graphene/poly(vinyl chloride) composite thin films with high mechanical strength and  
35 thermal stability, *Carbon.* 49 (2011) 198-205.
- 36 [269] I. Zaman, H. Kuan, Q. Meng, A. Michelmores, N. Kawashima, T. Pitt, L.  
37 Zhang, S. Gouda, L. Luong, J. Ma, A Facile Approach to Chemically Modified Graphene  
38 and its Polymer Nanocomposites, *Advanced Functional Materials.* 22 (2012) 2735-2743.

- 1 [270] J.M. Malho, P. Laaksonen, A. Walther, O. Ikkala, M.B. Linder, Facile  
2 method for stiff, tough, and strong nanocomposites by direct exfoliation of multilayered  
3 graphene into native nanocellulose matrix, *Biomacromolecules*. 13 (2012) 1093-1099.
- 4 [271] S. Das, F. Irin, H.S. Tanvir Ahmed, A.B. Cortinas, A.S. Wajid, D. Parviz,  
5 A.F. Jankowski, M. Kato, M.J. Green, Non-covalent functionalization of pristine few-layer  
6 graphene using triphenylene derivatives for conductive poly (vinyl alcohol) composites,  
7 *Polymer*. 53 (2012) 2485-2494.
- 8 [272] H. Hu, X. Wang, J. Wang, L. Wan, F. Liu, H. Zheng, R. Chen, C. Xu,  
9 Preparation and properties of graphene nanosheets–polystyrene nanocomposites via in situ  
10 emulsion polymerization, *Chemical Physics Letters*. 484 (2010) 247-253.
- 11 [273] X. Wang, Y. Hu, L. Song, H. Yang, W. Xing, H. Lu, In situ polymerization  
12 of graphene nanosheets and polyurethane with enhanced mechanical and thermal  
13 properties, *Journal of Materials Chemistry*. 21 (2011) 4222.
- 14 [274] J. Qiu, S. Wang, Enhancing polymer performance through graphene sheets, *J*  
15 *Appl Polym Sci*. 119 (2010) 3670-3674.
- 16 [275] J. Wang, S. Yang, Y. Huang, H. Tien, W. Chin, C.M. Ma, Preparation and  
17 properties of graphene oxide/polyimide composite films with low dielectric constant and  
18 ultrahigh strength via in situ polymerization, *Journal of Materials Chemistry*. 21 (2011)  
19 13569.
- 20 [276] M. Yoonessi, J.R. Gaier, Highly conductive multifunctional graphene  
21 polycarbonate nanocomposites, *ACS Nano*. 4 (2010) 7211-7220.
- 22 [277] J.R. Potts, S. Murali, Y. Zhu, X. Zhao, R.S. Ruoff, Microwave-Exfoliated  
23 Graphite Oxide/Polycarbonate Composites, *Macromolecules*. 44 (2011) 6488-6495.
- 24 [278] J. Liang, Y. Wang, Y. Huang, Y. Ma, Z. Liu, J. Cai, C. Zhang, H. Gao, Y.  
25 Chen, Electromagnetic interference shielding of graphene/epoxy composites, *Carbon*. 47  
26 (2009) 922-925.
- 27 [279] X.Y. Qi, D. Yan, Z. Jiang, Y.K. Cao, Z.Z. Yu, F. Yavari, N. Koratkar,  
28 Enhanced electrical conductivity in polystyrene nanocomposites at ultra-low graphene  
29 content, *ACS Appl. Mater. Interfaces*. 3 (2011) 3130-3133.
- 30 [280] C. Wan, B. Chen, Poly( $\epsilon$ -caprolactone)/graphene oxide biocomposites:  
31 mechanical properties and bioactivity, *Biomedical Materials*. 6 (2011) 055010.
- 32 [281] T. Ramanathan, A.A. Abdala, S. Stankovich, D.A. Dikin, M. Herrera-Alonso,  
33 R.D. Piner, D.H. Adamson, H.C. Schniepp, X. Chen, R.S. Ruoff, S.T. Nguyen, I.A. Aksay,  
34 R.K. Prud'Homme, L.C. Brinson, Functionalized graphene sheets for polymer  
35 nanocomposites, *Nature Nanotechnology*. 3 (2008) 327-331.
- 36 [282] C. Bao, Y. Guo, L. Song, Y. Hu, Poly(vinyl alcohol) nanocomposites based  
37 on graphene and graphite oxide: a comparative investigation of property and mechanism,  
38 *Journal of Materials Chemistry*. 21 (2011) 13942.

- 1 [283] X. Wang, L. Song, H. Yang, H. Lu, Y. Hu, Synergistic Effect of Graphene on  
2 Antidripping and Fire Resistance of Intumescent Flame Retardant Poly(butylene succinate)  
3 Composites, *Ind Eng Chem Res.* 50 (2011) 5376-5383.
- 4 [284] D.A. Nguyen, Y.R. Lee, A.V. Raghu, H.M. Jeong, C.M. Shin, B.K. Kim,  
5 Morphological and physical properties of a thermoplastic polyurethane reinforced with  
6 functionalized graphene sheet, *Polym. Int.* 58 (2009) 412-417.
- 7 [285] J. Du, L. Zhao, Y. Zeng, L. Zhang, F. Li, P. Liu, C. Liu, Comparison of  
8 electrical properties between multi-walled carbon nanotube and graphene nanosheet/high  
9 density polyethylene composites with a segregated network structure, *Carbon.* 49 (2011)  
10 1094-1100.
- 11 [286] V.H. Pham, T.V. Cuong, T.T. Dang, S.H. Hur, B. Kong, E.J. Kim, E.W.  
12 Shin, J.S. Chung, Superior conductive polystyrene – chemically converted graphene  
13 nanocomposite, *Journal of Materials Chemistry.* 21 (2011) 11312.
- 14 [287] J. Li, L. Shao, L. Yuan, Y. Wang, A novel strategy for making poly(vinyl  
15 alcohol)/reduced graphite oxide nanocomposites by solvothermal reduction, *Materials &  
16 Design* (1980-2015). 54 (2014) 520-525.
- 17 [288] O. Park, S. Kim, N. You, B. Ku, D. Hui, J.H. Lee, Synthesis and properties of  
18 iodo functionalized graphene oxide/polyimide nanocomposites, *Composites Part B:  
19 Engineering.* 56 (2014) 365-371.
- 20 [289] L. Tang, Y. Wan, D. Yan, Y. Pei, L. Zhao, Y. Li, L. Wu, J. Jiang, G. Lai, The  
21 effect of graphene dispersion on the mechanical properties of graphene/epoxy composites,  
22 *Carbon.* 60 (2013) 16-27.
- 23 [290] L. Nguyen Dang, J. Seppälä, Electrically conductive nanocellulose/graphene  
24 composites exhibiting improved mechanical properties in high-moisture condition,  
25 *Cellulose.* 22 (2015) 1799-1812.
- 26 [291] I. Kim, Y.G. Jeong, Polylactide/exfoliated graphite nanocomposites with  
27 enhanced thermal stability, mechanical modulus, and electrical conductivity, *Journal of  
28 Polymer Science Part B: Polymer Physics.* 48 (2010) 850-858.
- 29 [292] X. Yang, S. Shang, L. Li, Layer-structured poly(vinyl alcohol)/graphene  
30 oxide nanocomposites with improved thermal and mechanical properties, *J Appl Polym  
31 Sci.* 120 (2010) 1355-1360.

32