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Review Article

A review on appropriate graphene synthesis methods for diverse applications

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ABSTRACT

After exfoliation of graphite and discovered graphene in 2004 by Novoselov and Geim, the attention of graphene by the global scientific community enhanced progressively as a multi-functional wonder material in the world due to its unique extraordinary properties. Numerous methods apart from the discovered method have been investigated to synthesize the graphene in mass scale for variety of applications. Consequently, we believe that an adequate knowledge is necessary to choose a proper method of synthesis for a particular application. The main objective of the present review is to summarize the feasible methods followed in synthesis of graphene, discussing their properties, applications, advantages, and disadvantages for future prospects.

Keywords: graphene, exfoliation, CVD, epitaxial growth.

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1. INTRODUCTION

Graphene is fundamentally a single layer of graphite which is arranged in a two-dimensional hexagonal lattice [1]. It has been identified as a multifunctional wonder material due to its extraordinary physical and chemical properties[2]. Each atom in a graphene sheet is connected to its three adjacent atoms by a σ-bond and one out-of-plane π-bond [3]. In this bonding, the bond angle between adjacent carbon atoms identified as 120^0 and the length of the σ[c-c] bond is about 0.142 nanometers [4-5].

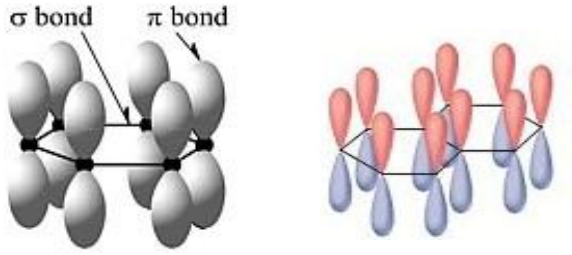

Figure 1: Arrangement of carbon atoms in graphite

This arrangement of sp^2 hybridization of carbon atoms gives graphene its unique properties [6]. Graphene sheets are arranged to form graphite with an inter planar spacing of 0.335 nm [7]. One graphitic layer is commonly prefixed by single-layer graphene or monolayer graphene. Two and three graphitic layers are called as bilayer and tri-layer graphene, respectively. Up to 10 graphitic layer is known as few-layer grapheme [8]. Each graphene layer in graphite is bound by a weak van der Waals force [9]. Excellent thermal conductivity of ~5000 W m^{-1} K^{-1}[10], high specific surface area of about 2630 m^2/, highest intrinsic electron mobility (200,000 cm^2), high optical transmittance (97.7 %), high Young's modulus (1.0 TPa), high mechanical strength are the merit attention properties of graphene[11-16]. As well as several superior properties can be produced by graphene composited with other elements [17]. A wide range of potential applications for graphene including batteries, transistors, supercapacitors, sensors, DNA sequencing, water filters, antennas, touchscreens, LCD displays, solar cells, etc. have been investigated [18-25].

Specific properties of graphene are required for particular applications, for example, high-performance batteries and supercapacitors require a large specific area, high electrical conductivity, good chemical stability, and large quantities of graphene amount [26-27]. High electron mobility is required for producing sensing devices and transistors [28]. High electrical conductivity and optical transmission are required to make transparent electrodes, photonic devices, liquid crystal displays (LCD), touch screens, etc. [29].

Defects in the material help enhance the electrochemical properties [30]. Significant improvement in electrochemical applications has not been shown from few-layer graphene compared with multilayer stacked grapheme [31]. Specific properties of graphene are favored and selected should for each application. Therefore the quantity, quality, and form of graphene could vary according to the application type.

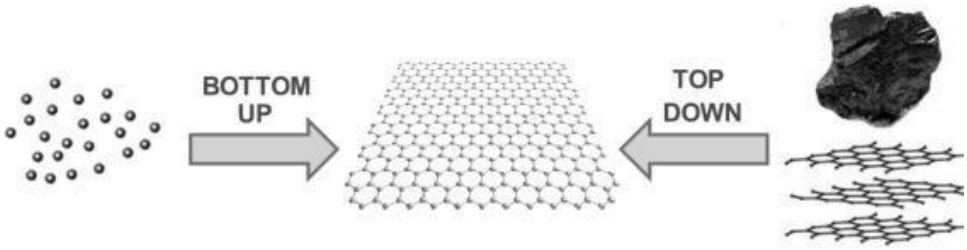

Figure 2: Schematic illustration of bottom-up and top-down graphene synthesis approaches Source [32].

A number of different methods have been reported to synthesize graphene in recent years. Micromechanical exfoliation, chemical synthesis, electrochemical exfoliation, pyrolysis, chemical vapor deposition, are the commonly used technics for graphene synthesis. Graphene synthesis can be classified basically into two different mechanisms, called top-down and bottom-up approach [33]. Exfoliation of stacked layers of graphite into single graphene sheets is called the top-down approach [34]. Van der Waals forces need to be overcome for the top-down approach [35]. Graphene produced through molecular growth from small molecular carbon precursors is known as the bottom-up approach [36]. Here we review extensively used graphene synthesis methods for better use of appropriate technology in diverse applications.

2. TOP-DOWN APPROACH

2.1. Mechanical exfoliation

The mechanical or micro-mechanical discharge system has become a milestone in Graphene history. It was developed by Novoselov and Geim in 2004 using a simple adhesive tape [37]. As a result, the method is also called as “scotch tape method”. They have successfully exfoliated graphite all the way down to few-layer and even single-layer graphene. A piece of tape has been used to remove the graphene sheets from the graphite stack. Which should be removed after exfoliation of graphite by dissolving in a solvent. This method can be used to make high-quality, defect-free graphene without specialized equipment. The scotch tape method is still the key synthesis technique to obtain high-

quality graphene for research purposes [38]. Low yields and high production costs make this method unusable for large-scale production [39].

2.2. Sonication method

One of the most scalable graphene production routes is to exfoliate graphite using ultrasonication. Firstly, Hernandez et al. have reported a high yield production of graphene from graphite through sonication assisted liquid-phase exfoliation in 2008[40]. They have obtained a monolayer graphene dispersion by dispersing graphite in specified organic solvents, followed by sonication and centrifugation. Here the surface energy of graphene has been estimated to be 46.7 mN/m[41]. Therefore, the specific solvents with a surface tension of ~40 mN/m, such as N-methylpyrrolidone (NMP), N,N-dimethylformamide(DMF), γ- butyrolactone (GBLmN/m), and orthodichlorobenzene (o-DCB) are identified as the best solvents for the exfoliation of graphite because they minimize the interfacial tension between solvent and the graphene layers[42-44]. After this work, many researchers have paid attention in achieving high quality graphene by optimizing the sonication time, ambient conditions, increasing the initial graphite concentration, adding surfactants and polymer, solvent exchange method, mixing solvents, etc.[45-48]. Sonication assisted liquid-phase exfoliation of graphite can be employed to produce graphene-based composites or films to use numerous applications, including thin-film transistors, light-emitting diodes (LED), photovoltaic cells [49-52]. The graphene prepared through sonication has much more defects and disordering resulting major short comes in sonication-assisted production processes of graphene [49]. Cost-effectiveness, scalability, and easy production process are the advantages of this method [53].

2.3 Ball milling

Ball milling is a common technique in the powder production process and it can be used to exfoliate thick graphite flakes into graphene by the milling impact. Initially, ball milling was used to reduce the size of graphite [54]. In most ball-milling apparatuses, there are two possible exfoliation and fragmentation effects [55]. Both wet ball milling and dry ball milling have been followed to synthesize grapheme [56]. The former process to get graphene involves dispersing graphite in suitable solvents which have a matched surface tension to overcome the Vander Waals force of adjacent graphene flakes [57]. The dry ball milling process uses a mixture of graphite and chemically inert water-soluble inorganic salts [58]. In 2010, Knieke et al. have introduced a novel milling technique to produce

graphene by using planetary ball milling and obtained few-layer graphene sheets having a thickness of around

0.8–1.8 nm [59]. In 2017, C Teng et al. reported an ultrahigh conductive graphene paper by using ball milling exfoliated graphene [60]. The main advantage of ball milling production is the possibility of large-scale production, while a drawback is fragmentation and defects, long processing time, high energy consumption, etc. This method is suitable for the production of functionalized graphene for functional coating, energy storage, and electrochemical sensors [61-63].

2.4 Electrochemical exfoliation

Electrochemical exfoliation is a promising method for producing large-scale graphene from graphite. An applied voltage drives the ionic species in an electrolyte to intercalate into the graphite electrode and increase the inter-planer distance [64]. Graphite exfoliation can be divided into two-electrode and three-electrode exfoliation [65]. The most common exfoliation is two-electrode exfoliation, which involves the intercalation, oxidation and exfoliation steps of graphite [66]. The mechanism for the formation of electrochemically processed graphite oxide was first reported by F. Beck *et al.* in 1995[67]. They have found the oxidation of graphite by using potential oscillations galvanostatic techniques in aqueous sulphuric acids. In 2011, You *et al*.have successfully demonstrated the preparation of GO by using a two- electrode exfoliation method with KCl as the electrolyte and expanded graphite and platinum wire as the anode and cathode, respectively at a voltage of 4 V [68]. In 2018, S Pei *et al*. have reported a scalable, safe, ultrafast, and green method to synthesize clean GO sheets by water electrolytic oxidation of graphite [69]. They have found that, the pre intercalation of graphite efficiently inhibit the anodic electrocatalytic oxygen evolution reaction of water at high voltage enabling rapid synthesis.

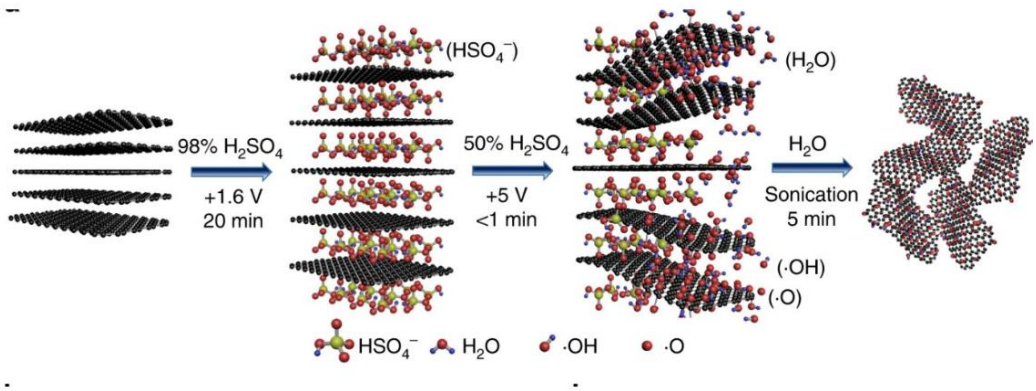

Figure 3: Three steps electro chemical graphene synthesis. Source: [34].

Single to few-layer graphene can be obtained from electrochemical exploitation [70]. High electrical conductivity of the functionalized graphene, environmental friendliness, high efficiency and relatively low cost are the advantages of the electrochemical synthesis method [65]. Electrochemically exfoliated graphene has been used in several applications such as supercapacitors, batteries, sensors, catalysts, hybrid membranes, anticorrosion coatings, and fire hazard suppression materials [71-74].

2.5 Chemical exfoliation

Chemical exfoliation of graphite has been carried out by B.C. Brodie in 1859 [1]. Hummer and Offeman have introduced the method to produce graphite oxide in 1958 [75]. In the chemical exfoliation methods, graphite is oxidized to graphite oxide first and then reduced to produce graphene. The Hummers method is the often used method for preparing graphene and its derivatives. They have used graphite powder, sodium nitrate, sulfuric acid, and potassium permanganate in the oxidation process. In order to get rid of the drawbacks of this method, in 2010 a new protocol called Tour's method was introduced where the oxidation reaction is carried out without sodium nitrate and increased amount of potassium permanganate along with phosphoric acid. They have reported a GO product with higher degree of oxidation by reacting graphite with six equivalents of $KMnO_4$ in a 9:1 mixture of H_2SO_4/H_3PO_4 where phosphoric acid is believed to offer more intact graphitic basal planes delivering much higher yield than Hummers method [76].

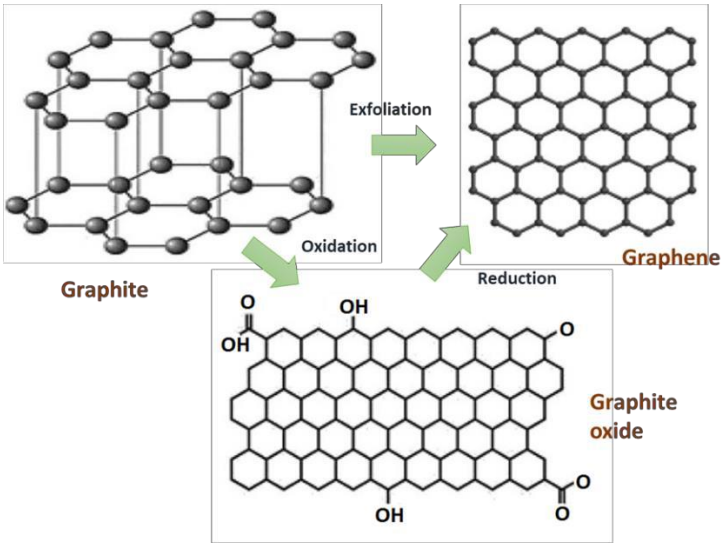

Figure 4: Schematic illustration of chemical exfoliation processing steps

Chemical exfoliation methods generally produce multi-layers or a few layers of graphene in flake types having a lateral length in the range of several hundred nanometers to several micrometers [77]. The method is suitable for mass production of graphene flakes with low purity for various applications including fillers, coating, conductive ink paste, batteries, etc. In addition, a low- temperature thermal method has been followed to synthesize graphene from GO which has been previously synthesized from graphite using the Hummer method [78]. They have revealed that few-layer of graphene can be produced in a short time.

In addition, a controlled hydrothermal method using ethylene glycol has been successfully used to synthesize graphene and composite from GO for fast charge-discharge application. They have found that, the method delivers high rate capability, good stability, and long cycle life as anode in Li-ion batteries [79]. Sharma N. *et al*. have investigated a method to prepare GO by exfoliation of graphite using modified Hummer's method and then reduced using hydrazine hydrate to produce rGO. The product is highly sensitive and more corrugated. They expect that the investigation would be useful to develop GO/rGO-based gas sensors [80]. Jayaweera *et al.* in 2014 have been successfully demonstrated a high-performing sensor consisting of SnO_2/Graphene nanocomposite by using a novel one-step in-situ sonochemical method [81]. They used reducing properties of $SnCl_2$ for reducing Graphite oxide (GO) to graphene. Recently, Jayaweera *et al*. have reported a novel symmetric supercapacitor electrode material using rGO-SnO_2-polyaniline nanocomposite [82]. They synthesized high current density, outstanding charge-discharge characteristic composite material using graphite oxide, $SnCl_2.2H_2O$, and pure Aniline as precursors in a scalable and straightforward one-pot process. [82-84]. GO has also been reduced to rGO using *coffea arabica* leave for bio-medical application for the first time which is referred as a green synthesis method [86]. But chemical exfoliation is not suitable for applications where high purity is mandatory such as in electronics. High scalability and low cost are the advantages of chemical exfoliation method. Disadvantages of this method are low purity, hazardous chemical use, product agglomeration etc. [87-89].

3 BOTTOM – UP APPROACH

3.1 Chemical Vapor Deposition (CVD)

CVD is the most effective bottom-up approach for the direct synthesis of high-quality, large scale single-layer graphene for use in a variety of applications. Many research studies have been focused on the development of a more efficient CVD system. As a result, recently

different types of CVD methods are available such as plasma-enhanced CVD, thermal CVD, hot/cold wall CVD and many others [90-92]. CVD is a thin film deposition technology of material onto substrates from vapor species through chemical reactions [93]. It is a two steps process, the molecules are heated at first to change into a gaseous state and secondly, it is deposited on the surface of a substrate [94]. There are many processing factors affecting on the quality of products such as pressure, temperature, depositing time, precursor nature, gas flow state and wall/substrate temperature, etc. [95]. Figure 5: shows the schematic diagram of thermal CVD growth of graphene.

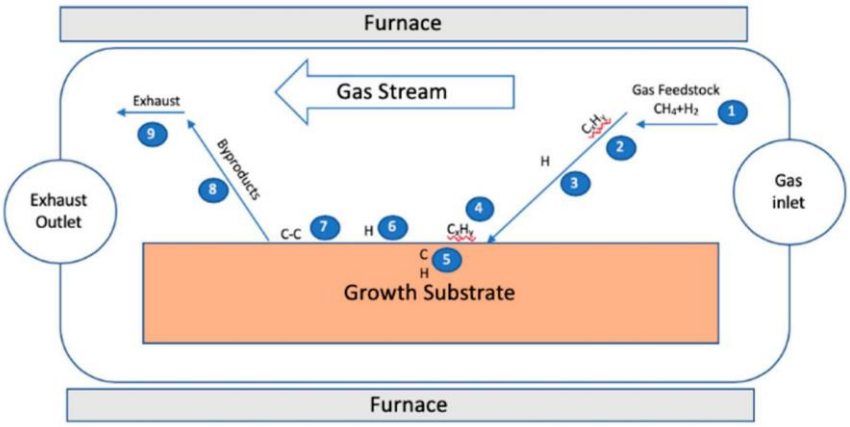

Figure 5: Schematic diagram of thermal CVD growth of graphene. Source [96].

For the first time, thermal CVD on metals was reported by A.E Karuin*et al*. in 1966. They have demonstrated highly crystalline graphite films on Ni substrates[97]. Deposition of single-layer graphene on Pt substrate using the hydrocarbon decomposition at 530 °C was successfully demonstrated by Land *at el.* in 1992[98]. Ni, Cu, Pd, Ru, Ir and Pt have been studied as a substrate for depositing single-layer graphene through CVD technology [99-100]. However, Ni and Cu are the most commonly used substrate for CVD deposition technology. Methane (CH_4), ethylene (CH_2=CH_2), and acetylene (C_2H_2) have been used as typical gaseous carbon precursors. Among them most widely used carbon precursor is methane (CH_4) gas [96]. Hydrogen, Argon, and Nitrogen have also been used as processing gases. Recently, Bointonet *et al.* have produced high-quality monolayer graphene by using resistive heating cold-wall CVD. They have found 100 times faster technology for 99% lower cost than standard conventional CVD [101]. High quality and large-scale production processes are the advantages of graphene synthesis using CVD. The disadvantages of CVD technology are toxic gas generation during the process, complex and expensive process

[102]. The CVD has been used for several high purity requisite applications such as touch screens, smart windows, flexible LCDs and solar cells etc[103-106].

3.2 Epitaxial growth of graphene

Epitaxial growth of graphene thin films on specific substrates is found to be a reliable method for graphene synthesis. The mechanism is based on the thermal decomposition of SiC in a high vacuum. Figure 6: shows the mechanism of epitaxial growth of graphene. Depending on the substrate material, the epitaxial growth process can be classified into two types, it is homo-epitaxial and heteroepitaxial [107]. The homoepitaxial process is the substrate material same as the deposited material. If these two materials become different, the process is called hetero-epitaxial. In 1893 Acheson *et al.* introduced the concept for producing silicon carbide by heating different carbonaceous sources [108]. Later A. Charrier *et al.* have successfully demonstrated that the thermal decomposition of an electronic-grade wafer of 6H-SiC after annealing at increasing temperature leads to the layer-by-layer growth of non-distractive heteroepitaxial single-crystalline graphite [109].

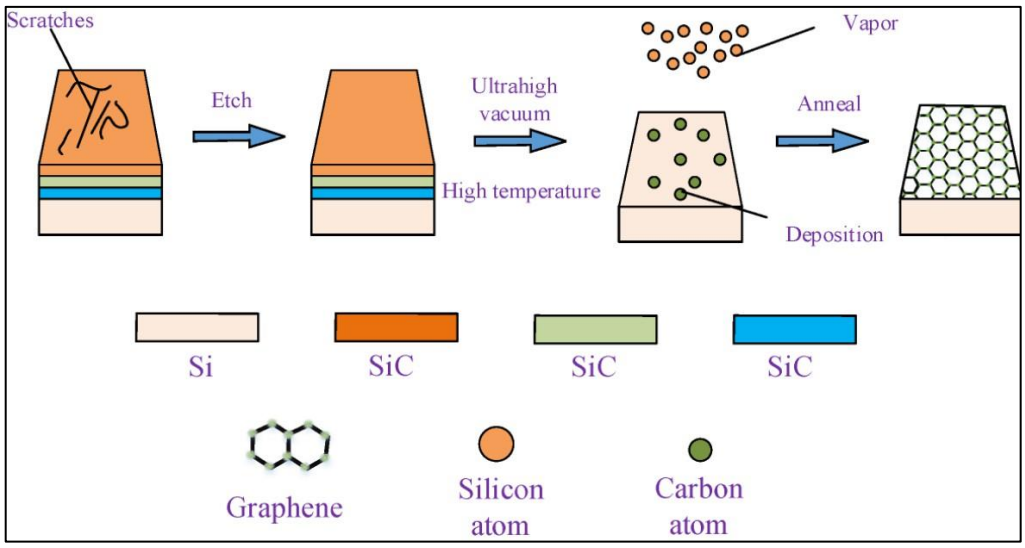

Figure 6: Mechanism of epitaxial growth of graphene. Source [110]

High-quality graphene can be produced by epitaxial growth and it is highly demanding in electronic related applications. Kim. *et al*. have successfully demonstrated ferroelectric nonvolatile memory devices that use graphene electrodes as the epitaxial growth substrate for crystalline polymer[111]. Hoang, *et al.* have reported a high-quality MoS_2/graphene hetero structure that was epitaxially grown on a transparent platform. They have found exhibiting inverse photo response with highly uniform photoresponsivity in the photodetector pixels fabricated across a full wafer [112]. The high production cost, low

yield, and inhomogeneity are the major limitations, therefore not suitable for large-scale manufacturing.

4. CONCLUSION

The present review enclosed an introduction of graphene and feasible methods followed holistically in graphene synthesis for different applications discussing their properties, advantages and limitations. Top-down methods such as mechanical exfoliation is suitable to synthesis mainly high quality defects free graphene for research purposes. Low yield and high production costs are the limitations in large-scale production. The graphene prepared through sonication or ball milling has much more defects and disordering and therefore can be employed to produce graphene-based composites for energy storage devices, gas sensors etc. Cost effectiveness, scalability, and easy production process are the advantages of these methods. Single to few-layer graphene can be obtained from electrochemical exfoliation which is more suitable for high electrical conductivity required applications such as in batteries. Environmental friendliness, high efficiency and relatively low cost are the advantages of the electrochemical method. The chemical exfoliation using Hummer method provides graphene oxide with more impurities and more suitable for low purity required applications such as in construction industry, sport equipment and vehicles etc. High scalability and low cost are the advantages. Disadvantages includes low purity and hazardous chemical usage. The chemical vapour deposition (CVD) is a common bottom up method to synthesize graphene. It provides relatively defect-free graphene suitable for high purity requirements such as electronics. High quality and large-scale production processes are the advantages. The disadvantages are toxic gas generation during the process, complexity and expensiveness. Epitaxial growth of graphene thin films are more suitable for transparent conductive thin film requirements such as electrodes. The high production cost, low yield, and inhomogeneity are the major limitations.

References

[1] M. J. Allen, V. C. Tung, and R. B. Kaner, "Honeycomb carbon: a review of graphene,"*Chem. Rev.*, vol. 110, no. 1, pp. 132–145, 2010.

[2] W. Wei and X. Qu, "Extraordinary physical properties of functionalized graphene," *Small*, vol. 8, no. 14, pp. 2138–2151, 2012.

[3] D. R. Cooper *et al.*, "Experimental review of graphene," *Int. Sch. Res. Not.*, vol. 2012,2012.

[4] Y. Zhu, D. K. James, and J. M. Tour, "New routes to graphene, graphene oxide and their related applications," *Adv. Mater.*, vol. 24, no. 36, pp. 4924–4955, 2012.

[5] A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, "The electronic properties of graphene," *Rev. Mod. Phys.*, vol. 81, no. 1, p. 109, 2009.

[6] M. Telychko *et al.*, "Electronic and chemical properties of donor, acceptor centers in graphene," *ACS Nano*, vol. 9, no. 9, pp. 9180–9187, 2015.

[7] A. Saini, A. Kumar, V. Kumar, and S. Chander, "Synthesis of graphene oxide using modified Hummer's method and its reduction using hydrazine hydrate," *Int. J. Eng. Trends Technol*, vol. 40, pp. 67–71, 2016.

[8] W. Choi and J. Lee, *Graphene: synthesis and applications*. CRC press, 2019.

[9] C. R. C. Rêgo, L. N. Oliveira, P. Tereshchuk, and J. L. F. Da Silva, "Comparative study of van der Waals corrections to the bulk properties of graphite," *J. Phys. Condens. Matter*, vol. 27, no. 41, p. 415502, 2015.

[10] A. A. Balandin, "Thermal properties of graphene and nanostructured carbon materials," *Nat. Mater.*, vol. 10, no. 8, pp. 569–581, 2011.

[11] S. Zhang, H. Wang, J. Liu, and C. Bao, "Measuring the specific surface area of monolayer graphene oxide in water," *Mater. Lett.*, vol. 261, p. 127098, 2020.

[12] P. Gori, O. Pulci, R. de Lieto Vollaro, and C. Guattari, "Thermophysical properties of the novel 2D materials graphene and silicene: insights from ab-initio calculations," *Energy Procedia*, vol. 45, pp. 512–517, 2014.

[13] S.-Y. Yang *et al.*, "A powerful approach to fabricate nitrogen-doped graphene sheets with high specific surface area," *Electrochem. commun.*, vol. 14, no. 1, pp. 39–42, 2012.

[14] K. I. Bolotin *et al.*, "Ultrahigh electron mobility in suspended graphene," *Solid State Commun.*, vol. 146, no. 9–10, pp. 351–355, 2008.

[15] Y. U. Jung, K.-W. Park, S.-T. Hur, S.-W. Choi, and S. J. Kang, "High-transmittance liquid-crystal displays using graphene conducting layers," *Liq. Cryst.*, vol. 41, no. 1, pp. 101–105, 2014.

[16] S. Wan *et al.*, "High-strength scalable graphene sheets by freezing stretch-induced alignment," *Nat. Mater.*, vol. 20, no. 5, pp. 624–631, 2021.

[17] B. Wang *et al.*, "Graphene-based composites for electrochemical energy storage," *Energy storage Mater.*, vol. 24, pp. 22–51, 2020.

[18] M. F. El-Kady, Y. Shao, and R. B. Kaner, "Graphene for batteries, supercapacitors and beyond," *Nat. Rev. Mater.*, vol. 1, no. 7, pp. 1–14, 2016.

[19] F. Schwierz, "Graphene transistors," *Nat. Nanotechnol.*, vol. 5, no. 7, pp. 487–496, 2010.

[20] W. K. Chee, H. N. Lim, Z. Zainal, N. M. Huang, I. Harrison, and Y. Andou, "Flexible graphene-based supercapacitors: a review," *J. Phys. Chem. C*, vol. 120, no. 8, pp. 4153–4172, 2016.

[21] C. I. L. Justino, A. R. Gomes, A. C. Freitas, A. C. Duarte, and T. A. P. Rocha-Santos, "Graphene based sensors and biosensors," *TrAC Trends Anal. Chem.*, vol. 91, pp. 53–66, 2017.

[22] S. J. Heerema and C. Dekker, "Graphene nanodevices for DNA sequencing," *Nat. Nanotechnol.*, vol. 11, no. 2, pp. 127–136, 2016.

[23] A. Kovtun *et al.*, "Graphene oxide–polysulfone filters for tap water purification, obtained by fast microwave oven treatment," *Nanoscale*, vol. 11, no. 47, pp. 22780–22787, 2019.

[24] A. I. Vlasov, D. S. Terent'ev, and V. A. Shakhnov, "Graphene flexible touchscreen with integrated analog-digital converter," *Russ. Microelectron.*, vol. 46, no. 3, pp. 192–199, 2017.

[25] D. H. Shin and S.-H. Choi, "Use of graphene for solar cells," *J. Korean Phys. Soc.*, vol. 72, no. 12, pp. 1442–1453, 2018.

[26] Q. Ke and J. Wang, "Graphene-based materials for supercapacitor electrodes – A review," *J. Mater.*, vol. 2, no. 1, pp. 37–54, 2016.

[27] R. Signorelli, D. C. Ku, J. G. Kassakian, and J. E. Schindall, "Electrochemical Double-Layer Capacitors Using Carbon Nanotube Electrode Structures," *Proc. IEEE*, vol. 97, no. 11, pp. 1837–1847, 2009.

[28] T.-H. Tsai *et al.*, "Hydrogen sensing properties of a metamorphic high electron mobility transistor," *Appl. Phys. Lett.*, vol. 94, no. 1, p. 12102, Jan. 2009.

[29] K. Rana, J. Singh, and J.-H. Ahn, "A graphene-based transparent electrode for use in flexible optoelectronic devices," *J. Mater. Chem. C*, vol. 2, no. 15, pp. 2646–2656, 2014.

[30] N. Jia, Z. Wang, G. Yang, H. Shen, and L. Zhu, "Electrochemical properties of ordered mesoporous carbon and its electroanalytical application for selective determination of dopamine," *Electrochem. commun.*, vol. 9, no. 2, pp. 233–238, 2007.

[31] M. S. Goh and M. Pumera, "The electrochemical response of graphene sheets is independent of the number of layers from a single graphene sheet to multilayer stacked graphene platelets," *Chem. Asian J.*, vol. 5, no. 11, pp. 2355–2357, 2010.

[32] S. Chaitoglou, "Growth Study and Characterization of Single Layer Graphene Structures Deposited on Copper Substrate by Chemical Vapor Deposition," 2016.

[33] J. M. Tour, "Top-down versus bottom-up fabrication of graphene-based electronics," *Chem. Mater.*, vol. 26, no. 1, pp. 163–171, 2014.

[34] N. Kumar *et al.*, "Top-down synthesis of graphene: A comprehensive review," *FlatChem*, p. 100224, 2021.

[35] A. Sharma, P. Harnish, A. Sylvester, V. N. Kotov, and A. H. C. Neto, "Van der Waals forces and electron-electron interactions in two strained graphene layers," *Phys. Rev. B*, vol. 89, no. 23, p. 235425, 2014.

[36] D. X. Luong *et al.*, "Gram-scale bottom-up flash graphene synthesis," *Nature*, vol. 577, no. 7792, pp. 647–651, 2020.

[37] K. S. Novoselov *et al.*, "Electric field effect in atomically thin carbon films," *Science (80-.).*, vol. 306, no. 5696, pp. 666–669, 2004.

[38] R. C. Sinclair, J. L. Suter, and P. V Coveney, "Micromechanical exfoliation of graphene on the atomistic scale," *Phys. Chem. Chem. Phys.*, vol. 21, no. 10, pp. 5716–5722, 2019.

[39] C. Gao, B. Zhan, L. Chen, and X. Li, "A micromechanical model of graphene-reinforced metal matrix nanocomposites with consideration of graphene orientations," *Compos. Sci. Technol.*, vol. 152, pp. 120–128, 2017.

[40] Y. Hernandez *et al.*, "High-yield production of graphene by liquid-phase exfoliation of graphite," *Nat. Nanotechnol.*, vol. 3, no. 9, pp. 563–568, 2008.

[41] A. Kozbial *et al.*, "Study on the surface energy of graphene by contact angle measurements," *Langmuir*, vol. 30, no. 28, pp. 8598–8606, 2014.

[42] C. Liu, G. Hu, and H. Gao, "Preparation of few-layer and single-layer graphene by exfoliation of expandable graphite in supercritical N, N-dimethylformamide," *J. Supercrit. Fluids*, vol. 63, pp. 99–104, 2012.

[43] I. V Antonova, I. A. Kotin, R. A. Soots, V. A. Volodin, and V. Y. Prinz, "Tunable properties of few-layer graphene–N-methylpyrrolidone hybrid structures," *Nanotechnology*, vol. 23, no. 31, p. 315601, 2012.

[44] S. Wang, Y. Zhang, N. Abidi, and L. Cabrales, "Wettability and Surface Free Energy of Graphene Films," *Langmuir*, vol. 25, no. 18, pp. 11078–11081, Sep. 2009.

[45] S. Wang *et al.*, "Room-temperature synthesis of soluble carbon nanotubes by the sonication of graphene oxide nanosheets," *J. Am. Chem. Soc.*, vol. 131, no. 46, pp. 16832–16837, 2009.

[46] R. Mirzajani and S. Karimi, "Ultrasonic assisted synthesis of magnetic Ni-Ag bimetallic nanoparticles supported on reduced graphene oxide for sonochemical simultaneous removal of sunset yellow and tartrazine dyes by response surface optimization: Application of derivative spectrophotometry," *Ultrason. Sonochem.*, vol. 50, pp. 239–250, 2019.

[47] M. Yi, Z. Shen, S. Ma, and X. Zhang, "A mixed-solvent strategy for facile and green preparation of graphene by liquid-phase exfoliation of graphite," *J. Nanoparticle Res.*, vol. 14, no. 8, pp. 1–9, 2012.

[48] M. P. Lavin-Lopez, J. L. Valverde, L. Sanchez-Silva, and A. Romero, "Solvent-based exfoliation via sonication of graphitic materials for graphene manufacture," *Ind. Eng. Chem. Res.*, vol. 55, no. 4, pp. 845–855, 2016.

[49] A. Ciesielski and P. Samorì, "Graphene via sonication assisted liquid-phase exfoliation," *Chem. Soc. Rev.*, vol. 43, no. 1, pp. 381–398, 2014.

[50] E. Tavakolian and J. Tashkhourian, "Sonication-assisted preparation of a nanocomposite consisting of reduced graphene oxide and CdSe quantum dots, and its application to simultaneous voltammetric determination of ascorbic acid, dopamine and uric acid," *Microchim. Acta*, vol. 185, no. 10, pp. 1–8, 2018.

[51] J. K. Wassei and R. B. Kaner, "Graphene, a promising transparent conductor," *Mater. today*, vol. 13, no. 3, pp. 52–59, 2010.

[52] H. Y. Abbasi, A. Habib, and M. Tanveer, "Synthesis and characterization of nanostructures of ZnO and ZnO/Graphene composites for the application in hybrid solar cells," *J. Alloys Compd.*, vol. 690, pp. 21–26, 2017.

[53] T. Soltani and B.-K. Lee, "A benign ultrasonic route to reduced graphene oxide from pristine graphite," *J. Colloid Interface Sci.*, vol. 486, pp. 337–343, 2017.

[54] N. J. Welham, V. Berbenni, and P. G. Chapman, "Effect of extended ball milling on graphite," *J. Alloys Compd.*, vol. 349, no. 1–2, pp. 255–263, 2003.

[55] M. Yi and Z. Shen, "A review on mechanical exfoliation for the scalable production of graphene," *J. Mater. Chem. A*, vol. 3, no. 22, pp. 11700–11715, 2015.

[56] P. Chaiwan and J. Pumchusak, "Wet vs. dry dispersion methods for multiwall carbon nanotubes in the high graphite content phenolic resin composites for use as bipolar plate application," *Electrochim. Acta*, vol. 158, pp. 1–6, 2015.

[57] Y. Yao, Z. Lin, Z. Li, X. Song, K.-S. Moon, and C. Wong, "Large-scale production of two-dimensional nanosheets," *J. Mater. Chem.*, vol. 22, no. 27, pp. 13494–13499, 2012.

[58] T. Lin *et al.*, "Scotch-tape-like exfoliation of graphite assisted with elemental sulfur and graphene–sulfur composites for high-performance lithium-sulfur batteries," *Energy Environ. Sci.*, vol. 6, no. 4, pp. 1283–1290, 2013.

[59] C. Knieke, A. Berger, M. Voigt, R. N. K. Taylor, J. Röhrl, and W. Peukert, "Scalable production of graphene sheets by mechanical delamination," *Carbon N. Y.*, vol. 48, no. 11, pp. 3196–3204, 2010.

[60] C. Teng, D. Xie, J. Wang, Z. Yang, G. Ren, and Y. Zhu, "Ultrahigh conductive graphene paper based on ball-milling exfoliated graphene," *Adv. Funct. Mater.*, vol. 27, no. 20, p. 1700240, 2017.

[61] Q. Yang *et al.*, "High-Yield Production of Few-Layer Graphene via New-fashioned Strategy Combining Resonance Ball Milling and Hydrothermal Exfoliation," *Nanomaterials* , vol. 10, no. 4. 2020.

[62] X. Fan, D. W. Chang, X. Chen, J.-B. Baek, and L. Dai, "Functionalized graphene nanoplatelets from ball milling for energy applications," *Curr. Opin. Chem. Eng.*, vol. 11, pp. 52–58, 2016.

[63] X. Li, J. Shen, C. Wu, and K. Wu, "Ball-Mill-Exfoliated Graphene: Tunable Electrochemistry and Phenol Sensing," *Small*, vol. 15, no. 48, p. 1805567, 2019.

[64] A. M. Abdelkader, A. J. Cooper, R. A. W. Dryfe, and I. A. Kinloch, "How to get between the sheets: a review of recent works on the electrochemical exfoliation ofgraphene materials from bulk graphite," *Nanoscale*, vol. 7, no. 16, pp. 6944–6956, 2015.

[65] L. Li *et al.*, "Review—Progress of Research on the Preparation of Graphene Oxide via Electrochemical Approaches," *J. Electrochem. Soc.*, vol. 167, no. 15, p. 155519, 2020.

[66] Y. Yang *et al.*, "Electrochemical exfoliation of graphene-like two-dimensional nanomaterials," *Nanoscale*, vol. 11, no. 1, pp. 16–33, 2019.

[67] F. Beck, J. Jiang, and H. Krohn, "Potential oscillations during galvanostatic overoxidation of graphite in aqueous sulphuric acids," *J. Electroanal. Chem.*, vol. 389, no. 1–2, pp. 161–165, 1995.

[68] X. You, J.-H. Chang, B. K. Ju, and J. J. Pak, "An electrochemical route to graphene oxide," *J. Nanosci. Nanotechnol.*, vol. 11, no. 7, pp. 5965–5968, 2011.

[69] S. Pei, Q. Wei, K. Huang, H.-M. Cheng, and W. Ren, "Green synthesis of graphene oxide by seconds timescale water electrolytic oxidation," *Nat. Commun.*, vol. 9, no. 1, p. 145, 2018.

[70] G. M. Morales *et al.*, "High-quality few layer graphene produced by electrochemical intercalation and microwave-assisted expansion of graphite," *Carbon N. Y.*, vol. 49, no. 8, pp. 2809–2816, 2011.

[71] R. Zhai, Y. Xiao, T. Ding, Y. Wu, S. Chen, and W. Wei, "Construction of NiCo2S4 heterostructure based on electrochemically exfoliated graphene for high-performance hybrid supercapacitor electrode," *J. Alloys Compd.*, vol. 845, p. 156164, 2020.

[72] A. Ejigu, L. W. Le Fevre, K. Fujisawa, M. Terrones, A. J. Forsyth, and R. A. W. Dryfe, "Electrochemically exfoliated graphene electrode for high-performance rechargeable chloroaluminate and dual-ion batteries," *ACS Appl. Mater. Interfaces*, vol. 11, no. 26, pp. 23261–23270, 2019.

[73] X. Yuan, J. Li, C. Zhang, and W. Yue, "Fabrication of Pt3Ni catalysts on polypyrrole-modified electrochemically exfoliated graphene with exceptional electrocatalytic performance for methanol and ethanol oxidation," *Electrochim. Acta*, vol. 340, p. 135969, 2020.

[74] Z. Ji *et al.*, "A structured catalyst support combining electrochemically exfoliated graphene oxide and carbon black for enhanced performance and durability in low-temperature hydrogen fuel cells," *Energy*, vol. 226, p. 120318, 2021.

[75] W. S. Hummers Jr and R. E. Offeman, "Preparation of graphitic oxide," *J. Am. Chem. Soc.*, vol. 80, no. 6, p. 1339, 1958.

[76] D. C. Marcano *et al.*, "Improved synthesis of graphene oxide," *ACS Nano*, vol. 4, no. 8, pp. 4806–4814, 2010.

[77] K. Parvez, S. Yang, X. Feng, and K. Müllen, "Exfoliation of graphene via wetchemical routes," *Synth. Met.*, vol. 210, pp. 123–132, 2015.

[78] I. R. M. Kottegoda *et al.*, "Comparison of Few-layer Graphene Prepared from Natural Graphite through Fast Synthesis Approach," *J. Mater. Sci. Technol.*, vol. 31, no. 9, pp. 907–912, 2015.

[79] I. R. M. Kottegoda, N. H. Idris, L. Lu, J. Z. Wang, and H. K. Liu, "Synthesis andcharacterization of graphene-nickel oxide nanostructures for fast charge-discharge application," *Electrochim. Acta*, vol. 56, no. 16, pp. 5815–5822, 2011.

[80] N. Sharma *et al.*, "Synthesis and characterization of graphene oxide (GO) and reduced graphene oxide (rGO) for gas sensing application," in *Macromolecular Symposia*, 2017, vol. 376, no. 1, p. 1700006.

[81] M. T. V. P. Jayaweera, R. C. L. De Silva, I. R. M. Kottegoda, and S. R. D. Rosa, "Synthesis, characterization and ethanol vapor sensing performance of SnO2/Graphene composite film," *Sri Lankan J. Phys.*, vol. 15, no. 0, p. 1, 2015.

[82] V. Jayaweera and W. L. N. C. Liyanage, "Material Science Research India Composite for High-Performance Supercapacitors," vol. 18, no. 2, 2021.

[83] I. R. M. Kottegoda, N. H. Idris, L. Lu, J.-Z. Wang, and H.-K. Liu, "Synthesis and characterization of graphene–nickel oxide nanostructures for fast charge–discharge application," *Electrochim. Acta*, vol. 56, no. 16, pp. 5815–5822, 2011.

[84] M. T. V. P. Jayaweera, R. C. L. De Silva, I. R. M. Kottegoda, and S. R. D. Rosa, "Synthesis , characterization and ethanol vapor sensing performance of SnO 2 / Graphene composite films," vol. 15, pp. 1–10, 2014.

[86] D. S. M. Perera, R. C. L. De Silva, L. D. C. Nayanajith, H. C. D. P. Colombage, T. S. Suresh, and W. P. K. M. Abeysekera, I. R. M. Kottegoda,"Anti-Inflammatory and Antioxidant Properties of Coffea Arabica/Reduced Graphene Oxide Nanocomposite Prepared by Green Synthesis," *Mater. Sci. Res. India*, vol. 18, no. 3, pp. 305–317, 2021.

[87] I. R. M. Kottegoda *et al.*, "Comparison of Few-layer Graphene Prepared from Natural Graphite through Fast Synthesis Approach," *J. Mater. Sci. Technol.*, vol. 31, no. 9, pp.907–912, 2015.

[88] A. Amiri, M. Naraghi, G. Ahmadi, M. Soleymaniha, and M. Shanbedi, "A review on liquid-phase exfoliation for scalable production of pure graphene, wrinkled, crumpled and functionalized graphene and challenges," *FlatChem*, vol. 8, pp. 40–71, 2018.

[89] J. Luo, J. Kim, and J. Huang, "Material processing of chemically modified graphene: some challenges and solutions," *Acc. Chem. Res.*, vol. 46, no. 10, pp. 2225–2234,2013.

[90] D. W. Hess, "Plasma-enhanced CVD: Oxides, nitrides, transition metals, and transition metal silicides," *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, vol. 2, no. 2, pp. 244–252, 1984.

[91] H. An, W.-J. Lee, and J. Jung, "Graphene synthesis on Fe foil using thermal CVD," *Curr. Appl. Phys.*, vol. 11, no. 4, pp. S81–S85, 2011.

[92] M. Faisal *et al.*, "Cold wall CVD (CWCVD) in the synthesis of few layered graphene on Ni," 2017.

[93] A. T. Hunt, W. B. Carter, and J. K. Cochran Jr, "Combustion chemical vapor deposition: A novel thin-film deposition technique," *Appl. Phys. Lett.*, vol. 63, no. 2, pp. 266–268, 1993.

[94] R. Munoz and C. Gómez-Aleixandre, "Review of CVD synthesis of graphene," *Chem. Vap. Depos.*, vol. 19, no. 10-11–12, pp. 297–322, 2013

[95] A. C. Ferrari *et al.*, "Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems," *Nanoscale*, vol. 7, no. 11, pp. 4598–4810, 2015.

[96] S. M. Kim *et al.*, "The effect of copper pre-cleaning on graphene synthesis," *Nanotechnology*, vol. 24, no. 36, p. 365602, 2013.

[97] A. E. Karu and M. Beer, "Pyrolytic formation of highly crystalline graphite films," *J. Appl. Phys.*, vol. 37, no. 5, pp. 2179–2181, 1966.

[98] T. A. Land, T. Michely, R. J. Behm, J. C. Hemminger, and G. Comsa, "STM investigation of single layer graphite structures produced on Pt (111) by hydrocarbon decomposition," *Surf. Sci.*, vol. 264, no. 3, pp. 261–270, 1992.

[99] M. H. Ani *et al.*, "A critical review on the contributions of chemical and physical factors toward the nucleation and growth of large-area graphene," *J. Mater. Sci.*, vol. 53, no. 10, pp. 7095–7111, 2018.

[100] J. Wintterlin and M.-L. Bocquet, "Graphene on metal surfaces," *Surf. Sci.*, vol. 603, no. 10–12, pp. 1841–1852, 2009.

[101] T. H. Bointon, S. Russo, and M. F. Craciun, "High quality monolayer graphene synthesized by resistive heating cold wall chemical vapour deposition," no. July, 2015.

[102] M. I. Kairi, M. Khavarian, S. A. Bakar, B. Vigolo, and A. R. Mohamed, "Recent trends in graphene materials synthesized by CVD with various carbon precursors," *J. Mater. Sci.*, vol. 53, no. 2, pp. 851–879, 2018.

[103] U. Khan, T. Kim, H. Ryu, W. Seung, and S. Kim, "Graphene tribotronics for electronic skin and touch screen applications," *Adv. Mater.*, vol. 29, no. 1, p. 1603544, 2017.

[104] J. Sun *et al.*, "Graphene glass from direct CVD routes: production and applications," *Adv. Mater.*, vol. 28, no. 46, pp. 10333–10339, 2016.

[105] A. Moreno-Bárcenas, J. F. Perez-Robles, Y. V Vorobiev, N. Ornelas-Soto, A. Mexicano, and A. G. García, "Graphene Synthesis Using a CVD Reactor and a Discontinuous Feed of Gas Precursor at Atmospheric Pressure," *J. Nanomater.*, vol. 2018, p. 3457263, 2018.

[106] N. Wei *et al.*, "Direct synthesis of flexible graphene glass with macroscopic uniformity enabled by copper-foam-assisted PECVD," *J. Mater. Chem. A*, vol. 7, no. 9, pp. 4813–4822, 2019.

[107] M. Bhuyan, S. Alam, M. Uddin, M. Islam, F. A. Bipasha, and S. S. Hossain, "Synthesis of graphene," *Int. Nano Lett.*, vol. 6, no. 2, pp. 65–83, 2016.

[108] E. G. Acheson, "Carborundum: Its history, manufacture and uses," *J. Franklin Inst.*, vol. 136, no. 4, pp. 279–289, 1893.

[109] A. Charrier *et al.*, "Solid-state decomposition of silicon carbide for growing ultra-thin heteroepitaxial graphite films," *J. Appl. Phys.*, vol. 92, no. 5, pp. 2479–2484, Aug. 2002.

[110] H. Tan, D. Wang, and Y. Guo, "Thermal Growth of Graphene: A Review," *Coatings* , vol. 8, no. 1. 2018.

[111] K. L. Kim *et al.*, "Epitaxial Growth of Thin Ferroelectric Polymer Films on Graphene Layer for Fully Transparent and Flexible Nonvolatile Memory," *Nano Lett.*, vol. 16, no. 1, pp. 334–340, Jan. 2016.

[112] A. T. Hoang *et al.*, "Epitaxial Growth of Wafer-Scale Molybdenum Disulfide/Graphene Heterostructures by Metal–Organic Vapor-Phase Epitaxy and Their Application in Photodetectors," *ACS Appl. Mater. Interfaces*, vol. 12, no. 39, pp. 44335–44344, Sep. 2020.