

Synthesis and Fabrication of Graphene and Graphene Oxide: A Review

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Abstract

The field of nanotechnology has advanced following the discovery of a two-dimensional material of sp^2 hybridized carbon atoms, graphene in 2004 by Geim and Novoselov. Graphene has received so much attention due to its exceptional electronic, thermal, mechanical, and optical properties in addition to its large surface area and single-atom thickness. This has led to the discovery of several techniques to obtain graphene such as chemical exfoliation, chemical vapor deposition (CVD), chemical synthesis etc. However, these techniques are majorly challenged with developing graphene with fewer defects and in large scale; thus, there is an increasing need to produce graphene in large quantities with high quality. Several studies have been carried out to find routes to producing high-quality graphene. This paper focuses majorly on the synthesis and fabrication methods of producing graphene and its derivative, graphene oxide. Characterization techniques to identify graphene such as optical microscopy, scanning electron microscopy (SEM), Raman spectroscopy, scanning probe microscopy (SPM) used to determine number of layers, quality, atomic structures, and defects in graphene is also briefly discussed. This article also covers a short description of graphene applications in transparent electrodes, composites and energy storage devices.

Keywords

CVD, Exfoliation, Graphene, Graphene Oxide, Synthesis

1. Introduction

The field of nanotechnology has blossomed following several studies on carbon. Carbon exists in three-dimensional (3D) forms (regarded as allotropes) as diamond and graphite. Evidence of the 3D graphitic form of carbon dates as far back to 1500s [1] [2]. This brought about its use as a writing material in the

1900s as the pencil industry was developed [3]. Other carbon allotropes, such as zero-dimensional (0D) fullerene [1] and one-dimensional (1D) carbon nanotubes [2] were discovered in the 1980s and 1990s (Figure 1). However, there remained an argument on the existence of two-dimensional (2D) allotrope of carbon until 2004, when a publication by Andre Geim and Konstantin Novoselov documented a successful isolation of a single layer of graphite (graphene) on a sticky tape by micromechanical cleavage (scotch tape method) of highly ordered pyrolytic graphite (HOPG) [4].

Graphene is a two dimensional (2D) single layer structure of covalently bonded sp^2 -hybridized carbon atoms arranged in a hexagonal honeycomb network. It is a single-atom thick allotrope of carbon which serves as the basic structural unit for other carbon allotropic forms: 1) 0D fullerenes formed by wrapping up graphene sheet to form a sphere (Bucky ball), 2) 1D carbon nanotube (CNT) formed by rolling of a graphene sheet to form a cylindrical structure, and 3) 3D graphite formed by stacking several layers of individual graphene sheet held together by van der Waals bonds as shown in Figure 1 [5].

Single, double, and triple graphitic layers are commonly known as monolayer, bilayer, and trilayer graphene's respectively. Graphene layers exceeding 5 and up to 30 are generally called multilayer graphene/thick graphene [6]. In graphene, the carbon-carbon bond distance is about 0.142 nm (1.42 Å) with the layer height (thickness) of about 0.33 nm (3.3 Å) (Figure 2) [3].

Graphene shows exceptional properties including a large theoretical specific surface area ($2630 \text{ m}^2\text{g}^{-1}$) [7], high intrinsic mobility ($200,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [8] [9], high Young's modulus ($\sim 1.0 \text{ TPa}$) [10], and thermal conductivity ($\sim 5000 \text{ Wm}^{-1}\text{K}^{-1}$) [11]. It also has good optical transmittance ($\sim 97.7\%$), good electrical conductivity, and ability to withstand current density of 108 A/cm^2 [12]. Graphene is also known to be a zero-bandgap semiconductor; therefore, the band gap can be tuned through simple physicochemical processes [13].

Owing to its exciting properties, study on graphene and its derivatives in the field of materials science and condensed-matter physics has generated immense attention over the past few years with various applications including membranes [14] [15], nanoelectronics [16] [17] [18], Li-ion batteries [19], electrodes [20] [21] [22], supercapacitors [23], sensors [24], drug delivery [25], etc.

Graphene produced through micromechanical cleavage of graphite was pure with high quality, although it was time consuming and incapable of mass scale production. Recently, several other techniques have been reported for the fabrication and synthesis of graphene, such as epitaxial growth by chemical vapor deposition on copper (Cu) substrate [26] [27], epitaxial growth by thermal deposition of Si atom from SiC surface [28], colloidal suspension from graphite oxide [29], and many others.

2. Synthesis of Graphene

The process of fabricating or extracting graphene based on desired size and quality is regarded as synthesis of graphene. So far, numerous approaches to

synthesis of graphene and graphene derivatives have been established. Mechanical cleaving (exfoliation) [4], chemical synthesis [30], chemical exfoliation [31] [32], epitaxial growth [33], and thermal chemical vapor deposition (CVD) [34] methods have been extensively studied. Other methods including electrochemical exfoliation [35], microwave synthesis [36], and unzipping of CNT [37] [38] [39] have been reported. Generally, graphene synthesis methods for large scale production, including single layer graphene (SLG), bilayer graphene, and few layer graphene (FLG) can be broadly classified into two types: 1) top-down process, and 2) bottom-up process. The classification of each technique is shown in the flow chart in **Figure 3**.

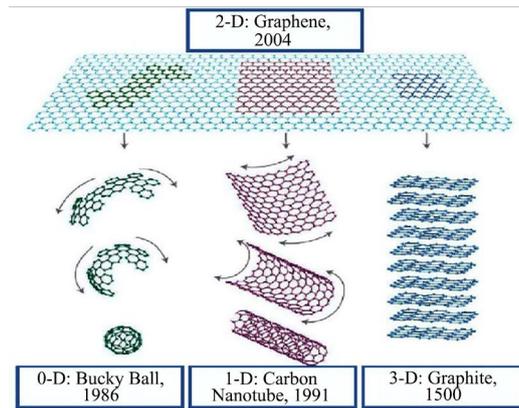


Figure 1. The 2D hexagonal nanosheets of graphene as a building block of other forms. An illustration of different allotropes of carbon arising from a graphene sheet [5].

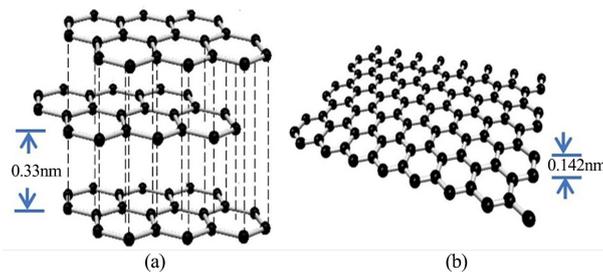


Figure 2. Schematic diagram of (a) Graphite and (b) Single layer of graphene from graphite.

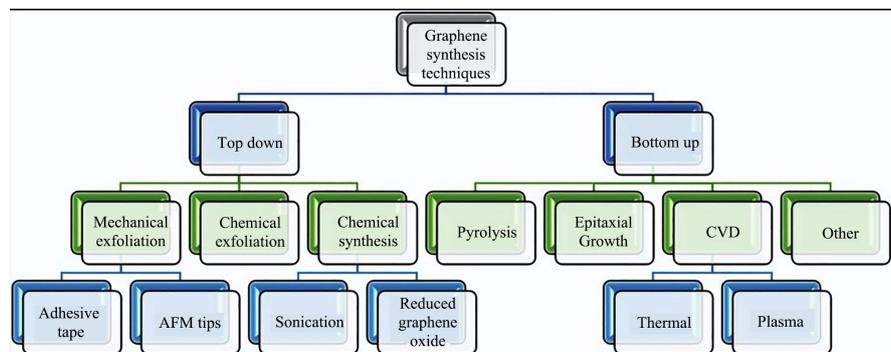


Figure 3. Graphene synthesis processes flow chart [47].

2.1. Top-Down Process

In the top-down process, graphene sheets are produced by exfoliation or separation of highly ordered pyrolytic graphite (HOPG) or its derivative, graphene oxide (GO).

2.1.1. Mechanical Exfoliation

Mechanical exfoliation is the first established method of extraction of graphene flakes on a substrate [4]. In nanotechnology, it is a top-down method of graphene synthesis, by which a stress (longitudinal or transverse) is applied to layered graphite surface using a simple adhesive tape (scotch tape) or AFM tip. Graphite structure is composed of several single-atomic layers of graphene stacked and held together by weak van der Waals forces. Between each layer is an interlayer distance of 3.3 Å (0.33 nm) and interbond energy of 2 eV/nm². Single layer graphene (SLG) to few layer graphene (FLG) can be produced through mechanical cleaving by slicing down the layers from graphitic materials such as HOPG, single-crystal graphite or natural graphite [40] [41]. This method requires an external force of about ~300 nNµm⁻² to separate a single graphene layer from graphite [42]. Mechanical exfoliation can be achieved using several agents including scotch tape [4], electric field [43], and ultrasonication [44]. Prior to the first production of a single layer graphene by Novoselov *et al.*, Ruoff *et al.* [41] first produced thin multilayered graphite with about 200 nm thickness by mechanical exfoliation using AFM tip (Figure 4(a)). Figure 4(b) shows the micro-graph of fabricated thin multilayered graphite consisting of 500-600 layers of monolayer graphene.

Novoselov *et al.* [4] utilized adhesive tape to produce single graphene layer (thickness < 10 nm) by exfoliation from 1 mm thick HOPG mesa. This involved compressing dry etched graphite mesa (by oxygen plasma) against a 1 mm thick wet photoresist layer over a glass substrate. Baking was done to attach the HOPG mesa to the layer of photoresist and exfoliation of the graphite flakes was achieved by using the scotch tape. Dispersed graphite flakes in acetone was transferred onto a cleaned SiO₂/Si substrate. Figure 4(c) shows optical micro-graph of multilayer graphene flakes produced via mechanical exfoliation on top of SiO₂/Si substrate while Figure 4(d) shows the identification of single graphene flakes with different number of layers.

The problem with the exfoliation process is scalability and reproducibility. Though it produces high quality graphene layers, there is still a need for further improvement to produce large-scale, high quality, and defect-free graphene for use in nanotechnology.

2.1.2. Chemical Exfoliation

Chemical exfoliation is another route to obtaining monolayer graphene. This method involves production of suspension which changes graphite to form graphene through the formation of graphene-intercalated compounds (GICs). This involves the introduction of alkali metals into a graphite solution to increase the

interlayer spacing, thereby reducing the van der Waals forces between the layers and forming GICs which are then dispersed in a liquid medium through sonication to form single-layer graphene [45]. Alkali metals are the only choice of materials as they easily form GICs on reaction with graphite due to the difference in ionization potential between graphite and alkali metals. Chemical exfoliation methodology was used by Viculis *et al.* to obtain graphene nanoplatelets (GNP) using potassium alkali metal [46]. Potassium graphite (KC_8) intercalated compound was formed when potassium reacted with graphite at 200°C under inert atmosphere. Dispersion of the GIC in aqueous ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) resulted in an exothermic reaction as shown in (1) and produced GNP.



Potassium ions dissolve into the ethanol solution forming potassium ethoxide (KOCH_2CH_3) and hydrogen gas is formed to aid the separation of the layers of graphene. Precaution must be taken during this reaction as alkali metals vigorously react with water and alcohol, as such there is a need for an ice bath to dissipate heat during reaction. The main advantage of alkali metals, such as potassium, is their relatively small atomic radius which is smaller than the interlayer spacing in graphite and hence fits the interlayer spacing easily as shown in **Figure 5(a)**.

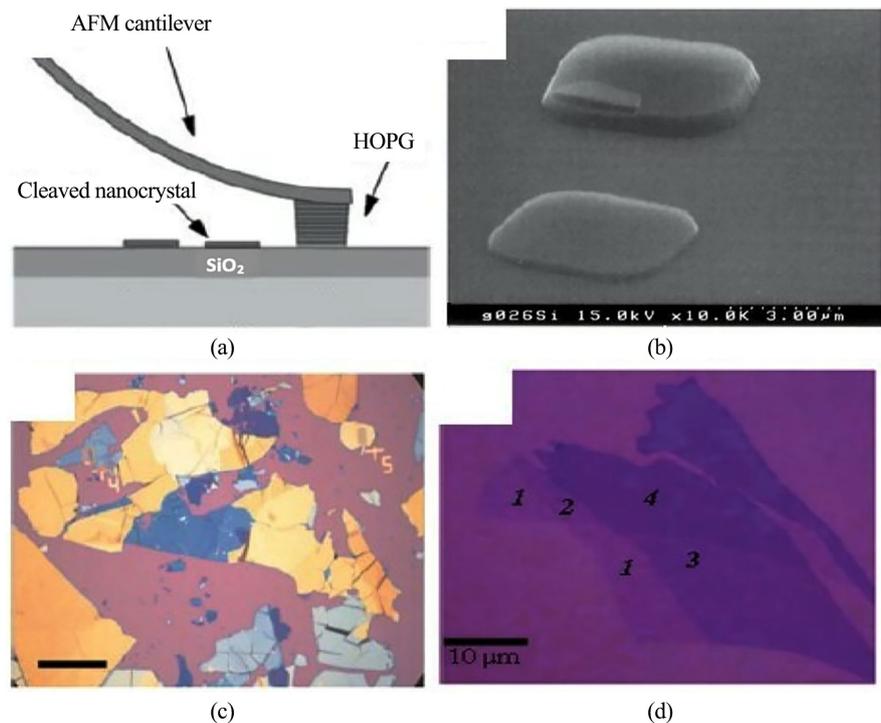


Figure 4. (a) Mechanical exfoliation process by using AFM; (b) SEM micrograph of mechanically exfoliated thin graphite layers from HOPG using AFM; (c) Optical micro-graph of few graphene flakes produced by the scotch tape method (scale bar $50\ \mu\text{m}$); (d) Graphene layer of various thickness on SiO_2/Si substrate.

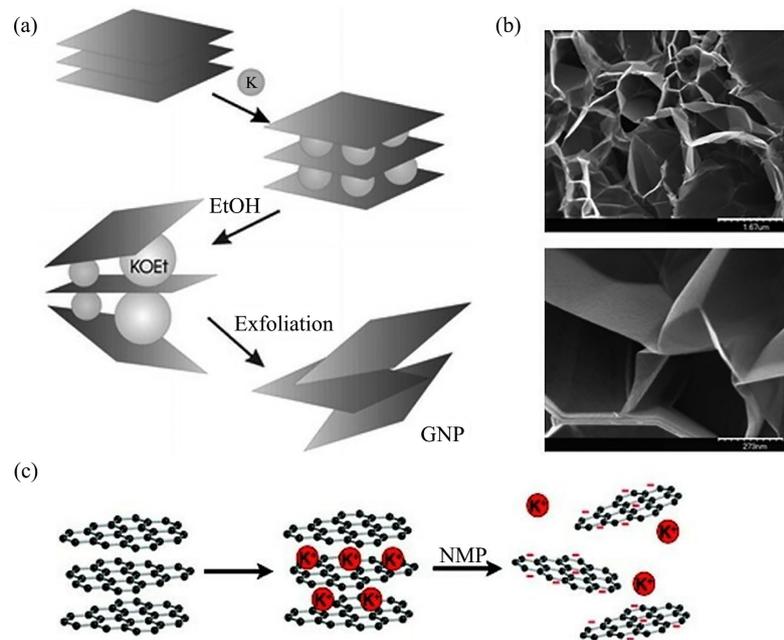


Figure 5. (a) Schematic showing the intercalation of potassium between layers during chemical exfoliation process [46]; (b) SEM micrographs of chemically exfoliated graphite nanoplatelets [46]; (c) Schematic illustrating the production of negatively charged graphene sheets [48].

Figure 5(b) shows SEM micrographs of the chemically exfoliated GNP with ~ 10 nm thickness and ~ 30 layers. Viculis *et al.* also carried out exfoliation via GIC formation using an alkali metal such as Cesium (Cs) and NaK₂ (sodium-potassium) alloy [32]. Work by Vallés *et al.* [48] utilized ternary potassium salt K(THF)_xC₂₄ tetrahydrofuran (THF) as the alkali metal to prepare potassium-intercalated GICs which was dispersed in N-methyl pyrrolidone (NMP) to yield a stable dispersion of negatively charged SLG as shown in **Figure 5(c)**.

One major challenge in this work was the reassembly of produced graphene back into graphite. Later studies have incorporated surfactants in the solvent used and utilized immiscible liquids such as heptane and water [48] [49]. Other studies have utilized ferric chloride, supercritical carbon dioxide, and nitromethane as the intercalation chemicals [50] [51] [52].

Graphene synthesis through chemical exfoliation is important and unique as it can produce a large amount of graphene at a low temperature. It is also scalable and can be extended to a wide range of functionalized graphene production.

2.1.3. Chemical Synthesis

Chemical reduction of graphite oxide (GO) is one of the conventional ways of preparing graphene in large quantities. The three routes available for GO synthesis; the Brodie method [5], Staudenmaier method [53], and Hummers method [54] consist of oxidation of graphite through strong acids and oxidants such as concentrated sulfuric acid (H₂SO₄), nitric acid, and potassium permanganate. Oxidation degree can be varied by the stoichiometry, reaction conditions

(pressure, temperature, etc.), and the graphite type (HOPG, pure graphite, etc.). The works of Brodie *et al.* [5] in 1859 first demonstrated the synthesis of GO by adding potassium chlorate (KClO_3) to a graphite slurry in the presence of fuming nitric acid (HNO_3). However, the process was time consuming, involved several steps, and hazardous. This brought about a modification to the process by Staudenmaier *et al.* in 1898 [53] with the inclusion of concentrated H_2SO_4 to the process and resulted in the production of highly oxidized GO in a single step process. A popular method used today was developed in 1958 by Hummers *et al.* [54]. This involves the oxidation of graphite by mixing the graphite slurry in sodium nitrite (NaNO_2), concentrated H_2SO_4 , and potassium permanganate (KMnO_4) without the use of HNO_3 . **Figure 6** shows a schematic diagram of GO synthesis from graphite method using the three methods explained.

When graphite turns to GO, the interlayer spacing is increased to between two to three times depending on the oxidation time. In the case of pristine graphite, interlayer spacing is increased from about 3.34 Å to 5.62 Å after an hour of oxidation, and then further expanded to about 7.35 Å upon prolonged oxidation of 24 hours [5]. Upon ultrasonication in a DMF/water (9:1) (dimethyl formamide), GO interlayer distance is further expanded, forming individual layer suspensions. With hydrazine hydrate treatment, GO reduces back to graphene or reduced graphene oxide (RGO). The chemical reduction process is done using dimethyl hydrazine or hydrazine in the presence of a surfactant or polymer to produce homogenous colloidal graphene suspensions [55]. **Figure 7** shows the process for chemical synthesis of graphene from graphite. Reduction of GO has also been performed using sodium borohydride (NaBH_4) [56], hydroxylamine [57], hydroquinone [58], ascorbic acid [59], etc. as reducing agents.

The use of toxic chemicals such as HNO_3 and KClO_3 has prompted researchers to develop new methods to graphene oxide synthesis [60] [61] [62]. However, the Hummer's method has been found to be quicker, safer, and more efficient method for graphene oxide synthesis used widely today with some modifications. Hummer's method was modified and further improved by Marcano *et al.* with the use of a larger amount of KMnO_4 , exclusion of NaNO_2 , and a 9:1 reaction mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ [61]. Compared to the Hummer's method, this improved method shows higher oxidation efficiency and production of better hydrophilic oxidized graphene product [61].

Various reports on the production of graphene by graphene oxide reduction exists. Some of the methods involve thermal reduction [63] [64] [65], electrochemical reduction [66] [67], photochemical reduction [68], hydrothermal reduction [69], microwave assisted reduction [70], and chemical reduction using reducing agents [71].

Paredes *et al.* [29] produced graphene nanosheet derived from graphene oxide using the Hummer's method with the reduced and unreduced aqueous dispersion drop casted onto freshly cleaved HOPG substrate. It was reported that the chemically reduced graphene oxide nanosheets were hardly distinguishable from

their counterparts in the topographic AFM images. However, they could be distinguished by their phase contrast with the unreduced graphene oxide showing a phase difference on the HOPG substrate while the RGO showed little phase contrast with the HOPG substrate (due to little defects). The thickness of the chemically reduced graphene oxide nanosheet was reported as ~1 nm using tapping mode AFM as shown in **Figure 8**. It was concluded that the chemically reduced graphene oxide still contained some oxygen functional groups [29].

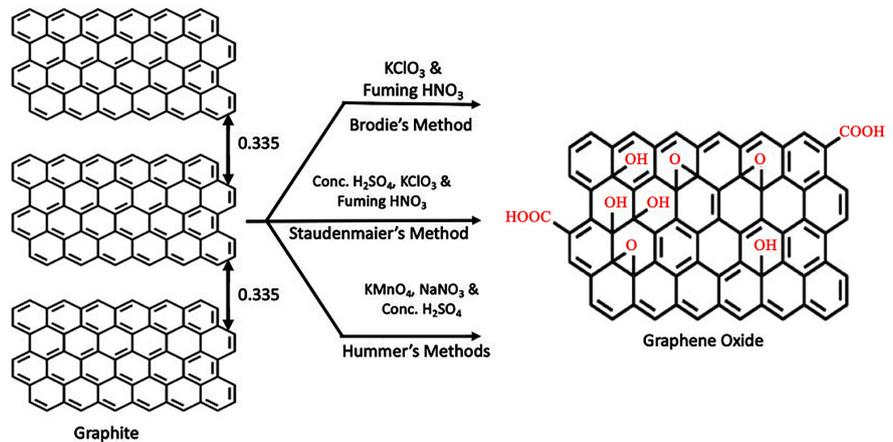


Figure 6. Schematic illustration of graphene oxide synthesis by chemical oxidation using Brodie's [5], Staudenmaier's [53], and Hummer's methods [54].

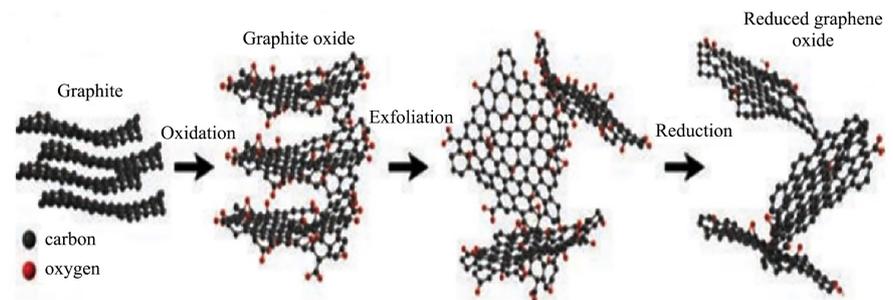


Figure 7. Synthesis route of graphene from graphite [72].

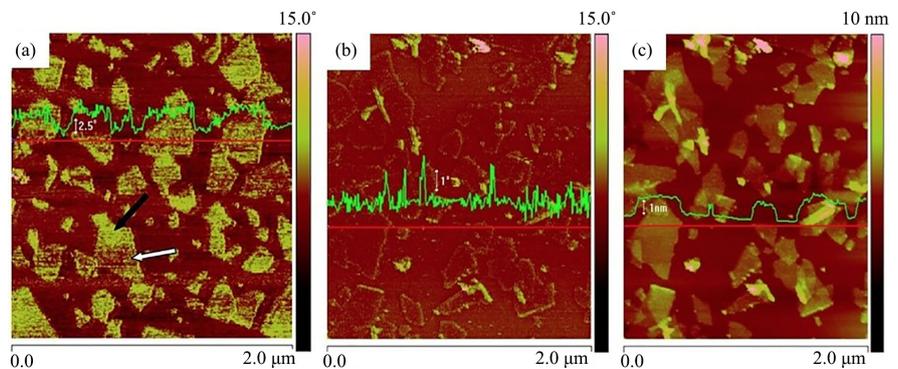


Figure 8. Tapping mode atomic force micrographs: (a) Phase image of unreduced graphene oxide nanosheet; (b) Phase image of chemically reduced graphene oxide nanosheet; (c) Height of chemically reduced graphene oxide nanosheet [29].

The chemical reduction method is the most useful method as it removes most of the functional groups present in the intermediate graphene oxide with the structure of the graphene surface restored after reduction. However, the produced graphene contains some defects due to the presence of remaining oxygen functional groups (such as –OH and –COOH) that causes some disorder in the graphene electronic structure. This results in reduced electrical conductivity of produced graphene as compared to that of pristine graphene (defect-free). These remaining functional groups on graphene and RGO can be used to tune their electrical and chemical properties for different applications.

2.2. Bottom-up Process

In the bottom-up process, graphene sheets are produced by building up nanoscale material via atomic or molecular arrangement of carbon.

2.2.1. Pyrolysis of Graphene

This involves the solvothermal synthesis of graphene with the use of a solvent interacting with precursor [47]. This reaction is performed in a closed vessel under high pressure with a 1:1 molar ratio of ethanol and sodium. Using sonication, graphene sheets can be smoothly detached by pyrolysis of sodium ethoxide. The produced graphene sheets were determined to have dimensions up to 10 μm . Using Raman spectroscopy and transmission electron microscopy (TEM), the graphene sheets were characterized to determine the crystalline structure, number of layers, band structure, and the graphitic nature [73]. Raman spectra showed a broad D-band (defect) and G-band with the intensity ratio of ~ 1.16 (I_G/I_D), representative of single layer defective graphene. Though this process was less expensive, easy, and required low temperature, the presence of many defects reduced the graphene quality. This method of graphene production has not been widely explored.

2.2.2. Epitaxial Growth of Graphene on SiC Surface

Epitaxial thermal synthesis of graphene on the surface of single-crystalline silicon carbide (SiC) is one of the well-known synthesis techniques. The term “epitaxy” is a method that allows the deposition of a single-crystalline film (epitaxial film) on a single-crystal substrate. When an epitaxial film is of the same material as the substrate, it is known as homoepitaxial layer, and if the epitaxial film and the substrate have different material, then an heteroepitaxial film is formed. Epitaxial growth on SiC forms an heteroepitaxial layer of single-layer graphite or graphene. In 1975, Bommel *et al.* [74] first reported heat treatment between 1000°C and 1500°C under ultrahigh pressure produced graphite on both polar planes of SiC. Synthesis by de Heer *et al.* in 2004 [75] produced ultrathin (few layers between 1 to 3 monoatomic graphene layers) graphitic layers on Si-terminated (0001) face of single-crystal 6H-SiC. Using the same thermal decomposition method, they fabricated 1 to 2 layers of epitaxial graphene on the (0001) face of 6H-SiC [76]. Synthesized epitaxial graphene on SiC although had high quality,

they could not be transferred to other substrates.

In 2012, Juang *et al.* [77] reported a breakthrough with the growth of epitaxial graphene on SiC substrate coated with Ni catalyst thin film. This produced graphene which was easily transferable to other substrate for versatile applications [77]. Epitaxial growth of graphene on SiC is very promising due to its scalability, best electronic properties, and especially due to its high-quality graphene.

2.2.3. Chemical Vapor Deposition (CVD)

Thermal chemical vapor deposition process involves exposure of a substrate to thermally decomposed precursors in gaseous state resulting in the deposition of the product onto the surface of the substrate at a high temperature. In many cases, deposition at high temperature is not desired, plasma-assisted reaction and deposition have been utilized to reduce the temperature. This process will be explained later in this paper. Depending on the quality, type of precursor, desired thickness of product, and structure, several types of CVD processes can be utilized including thermal, plasma enhanced (PECVD), reactive, hot wall, cold wall, etc. In the hot wall process, the walls of the reactor are kept relatively constant all around the reactor while in the cold wall process, the walls never get heated. Thermal CVD and PECVD are the most commonly used types of chemical vapor deposition to produce graphene. **Figure 9** demonstrates the schematic of a thermal and plasma-enhanced CVD process.

1) Thermal chemical vapor deposition of graphene

This process of graphene production involves flowing of precursor gases such as methane, hydrogen and argon in certain ratios into a quartz tube containing a substrate such as Cu at high temperatures in a furnace (**Figure 9(a)**). Over time, there is a deposition of graphene comprising of either single layer, bilayer or multilayer depending on preset conditions such as gas flow rate, reaction time, pressure, and temperature. Deposition of high-quality graphene using CVD process is usually done on various transition-metal substrate (their surface acts as catalyst) such as Ni [78], Pd [73], Ru [79], Ir [80], and Cu [34] with different hydrocarbons such as methane, benzene, acetylene, and ethylene [34]. On exposure of the transition-metal to hydrocarbon gas at high temperature, there is carbon saturation on the substrate and a thin film of carbon is formed on cooling.

In 1966 [81], Ni was exposed to methane at a temperature of 900°C to form thin graphite. Formation of FLG was observed on the evaporation of carbon from a graphite rod in 1971 [82]. In 1975, Lang *et al.* [42] demonstrated the deposition of monolayer graphitic structure on Pt using ethylene for the first time. Eizenberg *et al.* [83] later reported the formation of graphitic layer on Ni (111) over a long reaction time. There was over two decades interval in single graphitic layer deposition research due to inadequacy in finding applications of thin graphite films. However, the discovery of graphene in 2004 [4] with potential application in graphene-based electronics, there arose wide interest in this material.

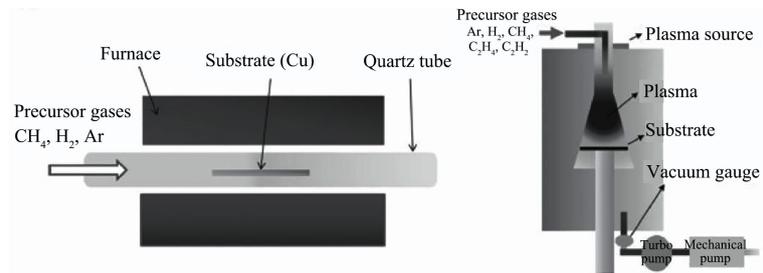


Figure 9. Schematic of (a) thermal CVD, and (b) plasma-enhanced CVD (PECVD) [5].

In 2006, the first attempt at synthesis of graphene on Ni foil via CVD method was found using camphor (terpenoid, a white transparent solid of chemical formula C₁₀H₁₆O) as the precursor [84]. When viewed with the TEM, the product was found to have a hexagonal planar few-layer graphite-like structure consisting of almost ~35 layers of stacked SLG with interlayer spacing of 0.34 nm. However, the first evidence of large-scale monolayer graphene using CVD growth was discovered by Obratzsov *et al.* [85] in 2007. The growth was achieved using precursors of methane and hydrogen under direct current (DC) discharge of ~0.5 Acm⁻². The as-deposited graphene structure shown in **Figure 10** shows the anomalous surface ridges which can be described as graphene folding lines [85]. The ridge formation in the graphene was due to the thermal expansion coefficient difference between graphene and Ni. Raman spectroscopy and scanning tunneling microscopy (STM) confirmed the presence of about ~1 - 2 nm thick FLG [85].

Successively, other reports have demonstrated synthesis of single-to few-layer graphene on Ni substrate. In 2009, Reina *et al.* [34] utilized e-beam evaporated Ni on SiO₂/Si substrate to grow graphene using diluted hydrocarbon gas. About 1 - 10 layers of graphene were observed using high resolution transmission electron microscopy (HRTEM) as shown in **Figures 11(a)-(c)**. Raman spectroscopy was used to confirm the number of layers by the intensity ratio of the G'(2D) to G bands. The Raman signature were found around ~1342 cm⁻¹, ~1581 cm⁻¹, and ~2677 cm⁻¹ corresponding to the D, G, and G'(2D) bands of produced graphene respectively as shown in **Figure 11(b)** [34].

Graphene growth on Cu substrate displays another method towards scalability of graphene growth with increased single layer coverage [86]. Li *et al.* in 2009 demonstrated large-scale graphene synthesis on copper foils by thermal CVD of methane at 1000 °C [86]. The deposition of carbon on copper was described as a high-temperature surface catalyzed process due to the limited solubility of carbon in copper [86]. Additionally, graphene growth on Cu occurs by segregation of supersaturated carbon and adsorbed carbon on copper surface during the rapid cooling process in CVD copper [86] [87]. Following growth of graphene on Cu foil, grown graphene was transferred onto another surface through copper etching yielding several chemically unaffected layers of graphene confirmed by Raman spectroscopy and HRTEM [86].

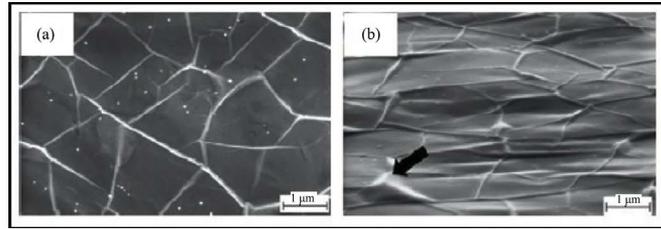


Figure 10. SEM images of graphene synthesis on Ni (111) by CVD method using DC discharge [85].

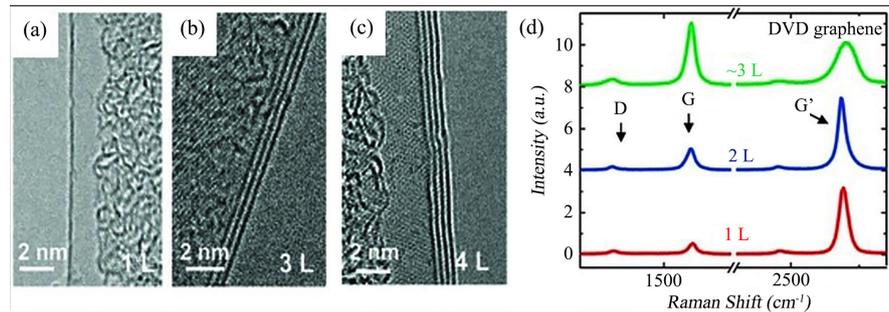


Figure 11. (a)-(c) HRTEM images of one to few layers of graphene grown on Ni using thermal CVD process; (d) Raman spectroscopy displaying the successive graphene layers and intensities [34].

Similarly, Lee *et al.* [87] developed optimized condition for synthesis of graphene produced by CVD process on Cu foil. It was observed that high pressure, low hydrogen to methane ratio, with reduced growth time produced graphene layers with improved quality [87]. As shown in **Figure 12**, there was formation of large Cu grains due to Cu grain coalescence during pre-annealing step, formation of copper grain boundary (Cu GB) separating the regions of small and big grains, and the presence of graphene folding lines like those obtained by Obraztsov *et al.* [85] [87].

Furthermore, grown graphene was transferred to a 290 nm-thick SiO₂/Si substrate. The produced graphene on Cu substrate was first coated with polymethyl methacrylate (PMMA) on the graphene side to provide strength and serve as protection to avoid graphene damage during the transfer process. In order to etch away the Cu foil, the PMMA/graphene/Cu structure was placed in Fe(NO₃)₃ solution (**Figure 13(b)**) with the PMMA side facing up. PMMA/graphene heterostructure was removed from the solution (**Figure 13(c)**) and rinsed severally in deionized (DI) water to remove residual Cu etchant solution (**Figure 13(d)**). The SiO₂/Si substrate was dipped in DI water (**Figure 13(e)**) and the PMMA/graphene structure. Through van der Waals forces, the graphene surface adhered to the SiO₂/Si substrate and the PMMA support was rinsed with solvents (acetone and isopropyl alcohol) (**Figure 13(f)**). The transferred graphene was distinguishable by the difference in color and contrast compared to the SiO₂/Si substrate as observed by the naked eye (**Figure 13(g)**) [87]. Transferred graphene displaced some wrinkles introduced during the transfer process as evidenced by scanning electron microscopy [87].

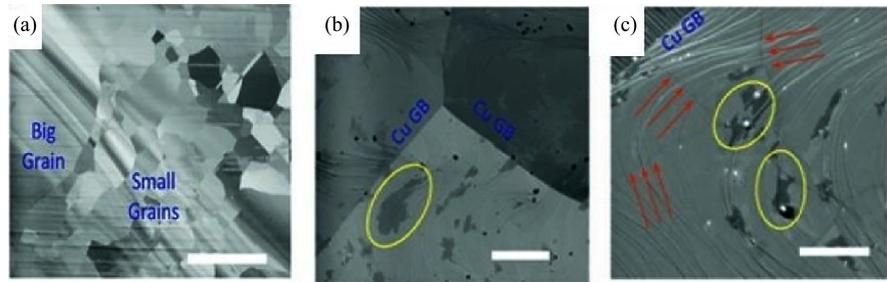


Figure 12. SEM micrographs of graphene via thermal CVD on Cu substrate: (a) Big and small Cu grains coexisting. Scale bar is 300 μm ; (b) & (c) Image showing Cu grain boundary (Cu GB), multilayer graphene (yellow circles), and graphene folding lines (red arrows). Scale bars are 5 μm [87].

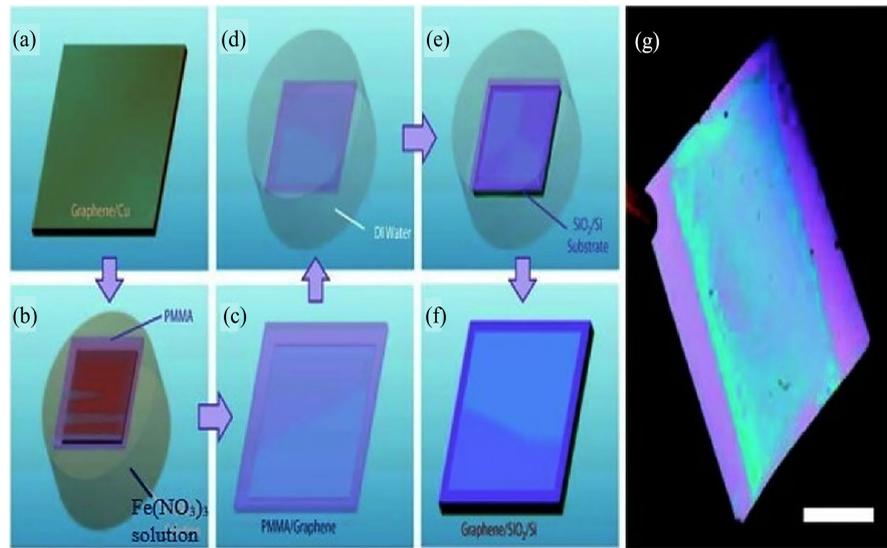


Figure 13. Graphene transfer process (a)-(f) from Cu substrate to SiO_2/Si substrate: (a) Graphene synthesized on Cu foil; (b) Graphene/Cu substrate coated with PMMA in $\text{Fe}(\text{NO}_3)_3$ solution; (c) Graphene on PMMA; (d) Cu etchant solution cleaning using DI water; (e) Contacting SiO_2/Si substrate with graphene on PMMA in DI water; (f) Final sample by removing PMMA using solvents; (g) Photograph of transferred CVD graphene on SiO_2 -on-Si substrate. Scale bar is 1 cm [87].

Numerous reports have shown graphene synthesis on other metal thin films and metal foils [34]. However, graphene growth by CVD method has been mostly done on Cu [27] [34] and Ni substrates [34]. The problem of producing graphene on Ni substrate included the time consuming non-self-limiting growth, and the production of large number of wrinkles and folds. Copper substrates have demonstrated more favorable CVD growth of graphene [86].

2) Plasma-Enhanced Chemical Vapor Deposition

This process of graphene production involves chemical reactions of reacting gases inside a vacuum chamber in the presence of plasma resulting in deposits of thin film on the surface of the substrate (Figure 9(b)), thus, the name, plasma-enhanced chemical vapor deposition (PECVD). Sources of plasma in PECVD can include radio frequency (RF), microwave, and inductive coupling (electrical

currents produced by electromagnetic induction). PECVD process of graphene synthesis is performed at a relatively lower temperature and shorter deposition time than other CVD techniques and as such is more feasible for large scale industrial applications. By controlling the process parameters, catalyst-free growth can be achieved [88]. RF plasma-enhanced chemical vapor deposition has been achieved using substrates such as Ti, SiO₂, Si, Al₂O₃, Mo, Hf, Zr, Nb, Cr, W, Ta, and 304 stainless steel [5]. This method reduces energy consumption and prevents the formation of unwanted products or amorphous carbon [89].

Thin graphitic layer was first synthesized using PECVD by Obratzsov *et al.* [90] through DC discharge CVD of a methane and hydrogen mixture. Nanocrystalline graphite growth was observed on silicon wafer, Ni, Mo, and Ni substrates. A thick layer of graphene was produced by this process [90]. Wang *et al.* [91] deposited graphene on different substrates using PECVD method with RF power of 900 W while varying methane concentration at different temperatures. Increase in graphene growth rate with increase in temperature and methane concentration was observed [91]. Other studies on graphene synthesis using PECVD were done, such as atmospheric pressure process [92], microwave plasma [93], nitrogen-doped graphene/CNT hybrid structure [94], and many others. PECVD method has been confirmed to produce high-crystalline graphene with high-purity; however, extensive research is ongoing in the production of uniform large-scale and single layer graphene through this technique.

2.2.4. Other Methods

Several other ways to produce graphene exists including: arc discharge of graphite [23], electron beam irradiation of PMMA nanofibers [95], and conversion of nanodiamond [96]. Graphene can be synthesized by unzipping of multi-walled carbon nanotubes (MWCNTs) using highly oxidative KMnO₂ and concentrated H₂SO₄ [38], laser irradiation [38], Li in liquid ammonia [10], and plasma etching [39] to open up the carbon nanotubes for graphene nanoribbons (GNR) production. Arc discharge methods are also commonly used to synthesis boron- and nitrogen-doped graphene [97] [98]. Arc discharge between carbon electrodes and pyridine or ammonia in the presence of nitrogen has yielded nitrogen-doped graphene sheets [97]. Boron-doped graphene sheet have been synthesized in the presence of hydrogen-diborane vapor mixture or boron-stuffed graphite electrodes [98].

3. Characterization of Graphene

Several microscopic and spectroscopic techniques are used to characterize graphene to determine the morphology, structure, quality, presence of defects, and number of layers. The most commonly used characterization techniques are optical microscopy, scanning probe microscopy (SPM), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), and Raman spectroscopy.

3.1. Optical Microscopy

Optical microscopy technique is an easy, straightforward, and effective method for non-destructive characterization of graphene. It is primarily used to determine the number of layers in graphene by using the contrast difference between graphene layers and the substrate. Size and shape of the graphene structure is also obtained from this technique. **Figure 14(a)** shows the optical micrograph with different graphene layers of graphene on SiO₂/Si substrate [99].

3.2. Scanning Probe Microscopy

Scanning probe microscopy (SPM) is a popular technique used to characterize the topography of nanomaterials such as graphene by scanning the sample with a probe. Two SPM commonly used techniques for graphene characterization are atomic force microscopy (AFM) and scanning tunneling microscopy (STM). In the AFM mode, scanning is done in either the contact or noncontact tapping mode of the probe tip with the deflection of the cantilever probe based on the topography of the graphene structure to form 2D and 3D images. **Figure 14(b)** shows the AFM image of mechanically exfoliated graphene flake with atomic-level thickness [100]. STM utilizes tunneling current between the SPM probe and graphene to form similar pattern of the topography of the sample. **Figure 14(c)** shows high contrast atomic resolution of obtained using STM for graphene hexagonal structure [101].

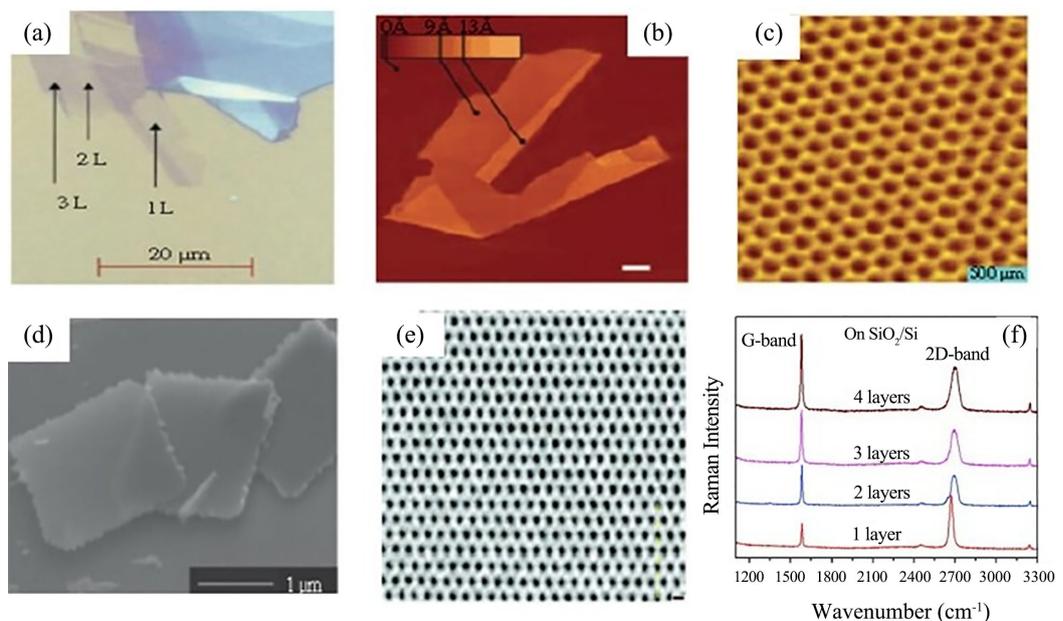


Figure 14. (a) Optical micrograph showing single-(1L), bi-(2L), and trilayer (3L) graphene on SiO₂/Si substrate [99]; (b) AFM image of mechanically exfoliated graphene (Scale bar is 1 μm) [100]; (c) STM micrograph showing atomic resolution of graphene with hexagonal close-packed lattice structure [101]; (d) SEM micrograph showing exfoliated graphene layers [102]; (e) The hexagonal honeycomb lattice of SLG under HRTEM (Scale bar is 0.2 nm) [103]; (f) Raman spectra of one to four layers of graphene on SiO₂/Si substrate [104].

3.3. Scanning Electron Microscopy

Scanning electron microscopy (SEM) technique is used to determine surface morphology and number of layers of graphene. This is achieved through focusing a beam of energetic electrons on the sample. Like optical microscopy, there is a contrast difference between graphene layers and the substrate. **Figure 14(d)** shows a micrograph from SEM for mechanical exfoliated graphene layers [102].

3.4. High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM is a very powerful characterization technique for graphene's structural characterizations. Its mode of operation is very similar to the SEM, but in this, the electron beam transmitted through the ultrathin sample. Atomic resolution images can be obtained using the HRTEM. **Figure 14(e)** shows the atomic arrangement of graphene structure and interfaces using HRTEM [103].

3.5. Raman Spectroscopy

Raman spectroscopy is one of the most important technique used today for graphene characterization. It is a nondestructive technique which reveals bonding information. It displays this information as unique fingerprints of graphene in Raman spectra. Information relation to the graphene quality, number of graphene layers, induced strain, presence of defects, and the lattice mismatch can be determined by this technique. Raman spectra of monolayer graphene displays characteristics D-band, G-band, and 2D band at its respective positions of $\sim 1350\text{ cm}^{-1}$, $\sim 1580\text{ cm}^{-1}$, and $\sim 2690\text{ cm}^{-1}$ respectively [5]. **Figure 14(f)** shows the Raman spectra of different layers of graphene on SiO_2/Si substrate using a laser power of $\sim 532\text{ nm}$ [104].

Several other characterization techniques for graphene exist, the mostly used methods have been discussed in this paper.

4. Application

Since the ground-breaking discovery of the wonder material, graphene, there has been numerous outstanding roles of the material in this century. There are so many areas of application of the novel material. Recent progress in green technology has emerged from the exceptional mechanical, electronics, magnetic, optical, and surface area of functionalized graphene bringing about commercialization and innovative solutions to existing problems such as electronic and photonic applications for ultrahigh-frequency graphene-based devices, anode for li-ion battery [19], sensors [24], nanosized graphene in physics and materials science [21], supercapacitors [23], in ceramics [105], membranes [14], lightweight gas tanks, solar cells, flexible electronics, composite materials, and so many others [105]. Vast areas of research and development continue to open in the area of graphene applications to numerous fields including medicine, electronics, and energy [106] [107] [108].

5. Conclusion

Discovery of the novel 2D material has revolutionized the nanoelectronics industry by providing an alternative to silicon, which has been used for decades. This contribution has also expanded to bio-medicine, nanorobotics, and energy. However, the issue yet to be resolved is scaling up production of graphene with high quality and uniformity. This is the goal to overcome in the years to come.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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