

GRAPHENE: A REVIEW ON ITS RESEARCH TRENDS AND SYNTHESIS TECHNIQUES.

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Abstract- Graphene, the first 2D material on earth, considered as the unique and the smartest material in the field of materials science. It gathers a set of unique physico-chemical properties, ranging from its extreme mechanical behavior to its exceptional electrical and thermal conductivities, which are making graphene as a major alternative to replace many conventional materials for various applications. This review demonstrates on recent trends in graphene research, analyzes the various synthesis techniques and attempts to identify the suitable techniques which could be used commercially in future.

Keywords: Graphene, 2D material, Properties, Synthesis.

1. INTRODUCTION

No one had ever wondered that a mere tip of pencil that is graphite would be the most talked material among the researchers this decade. This has become possible because of the groundbreaking work by the noble laureates (2010) Andre Geim and Konstantin Novoselov back in 2004. They successfully exfoliated a single layer of carbon from the graphite which was later named as “Graphene” by the IUPAC commission [1,2]. So basically graphene is a 2D crystalline form of carbon; more precisely a one atom thick, sp² bonded planar sheet of carbon arranged in a hexagonal honeycomb like structure [3,4] (Fig.1). The main reason of roar about graphene is its extraordinary combination of electrical [5], mechanical [6], optical [7], thermal [8] and sensing properties [9], which had been thought impossible to be found in a single material.

Considering the electrical properties, the electron mobility of graphene is $2.5 \times 10^5 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ (theoretical limit is $2 \times 10^5 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) the reason of which is its unusual energy band structure and it is nearly independent of temperature between 10k to 100k [5,10,11]. Electron acts as massless relativistic particle in graphene which is why high integer quantum hall effect is seen even at room temperature [2,11]. It also has the ability to sustain extremely high densities of electric current (a million times higher than copper). These properties along with its high surface area ($2630 \text{m}^2 \text{g}^{-1}$) make it compatible to use in energy production and storage applications such as Li-ion batteries, super-capacitors, solar cells, fuel cells

etc [10,12]. In addition, graphene has the potential to be used in transistor as a distinct band gap can be generated if the dimension of graphene is reduced into narrow ribbons with a width of 1-2nm [13,14].

Graphene has a Young's modulus of 1 TPa and an intrinsic strength of 130 GPa [2,6]. A single layer of graphene absorbs 2.3% of incident light over a broad wavelength range in spite of being just a monolayer. This high transparency and flexibility make it a potential candidate for flexible electronics [7, 155-163]. As graphene can readily be chemically functionalized [171], several researches are going on to modify its electrical, mechanical and optical properties and this combination have opened new avenues for various applications in photonics and optoelectronics which includes photodetectors, touch screens, light emitting devices, photovoltaics, transparent conductors, terahertz devices and optical limiters [2].

Graphene also has the highest thermal conductivity (3000 W/mK) and impermeability to any gases, making it an excellent candidate for the applications in electronic circuit boards, heat sink and light weight high performance thermal management systems [2,8,15]. These wide range of superior properties and applications justify its nickname as a “miracle material” [10].

Despite having such extraordinary properties, the commercial application of this miracle material is limited and the reason behind this is the limitation in bulk synthesis processes. Another limitation playing key role behind this problem is the limitation of producing highest

quality samples because some of the superior properties are only found in the highest quality grades [10,16]. Thus extreme researches are going on for the betterment in the mass production process to get the highest quality graphene at lower cost. Current graphene synthesis methods such as exfoliation (mechanical or chemical) [17,18], epitaxial growth via Chemical Vapor Deposition (CVD) [19,20], reduction of graphene oxide (GO) [21,22], unzipping of CNTs, reduction of sugars (such as glucose or sucrose) [23,24,25] etc can be classified into two broad categories i.e. top down and bottom up methods. However, it needs to be mentioned that there is no single synthesis method that yields graphene exhibiting the optimum properties for all potential applications [16].

This review is intended to address the ongoing development in the graphene research, highlight and analyze the fundamental understanding of synthesis procedures as well as projecting the commercially viable ones.

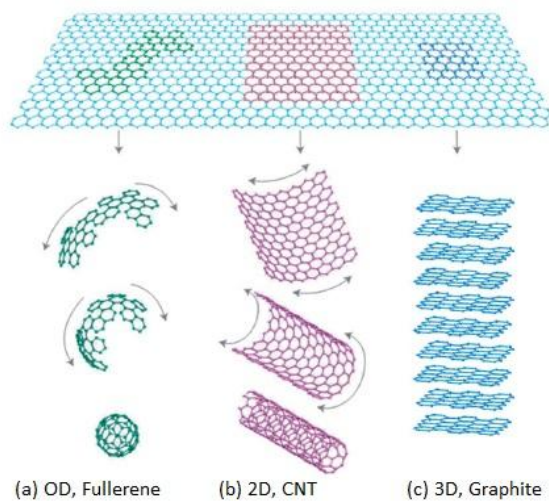


Fig.1: Graphene: Mother of all carbon nanostructures. (a) Wrapped up into 0D fullerenes, (b) rolled into 2D CNTs, and (c) stacked into 3D graphite. Reproduced from ref. [1]

2. SYNTHESIS OF GRAPHENE

2D crystal lattices are always thought to be an integral part of 3D structures. About 70 years ago Landau and Peierls had proved the thermodynamically unstableness of 2D crystals in favor of the previous statement [26,27]. This had been strengthened by the work of Mermin who reported that the melting temperature of thin film decreases with the reduction of thickness and become unstable (segregated into islands or decompose) when the thickness reduced to a level of dozens of atomic layer [28]. This was valid until 2004 when a stable 2D layer of carbon that is graphene was first isolated from graphite by the mechanical exfoliation method by Andre Geim and Konstantin Novoselov at the University of Manchester [1]. But before that several theory on graphene was proposed by various researchers across the globe [29] and several researches also reported on the production of mono and multilayered graphite on various

substrates [30,31]. However, after 2004 widespread researches have been going on to develop the exfoliation method as well as to develop new processing routes for efficient and large scale synthesis of graphene. The synthesis pattern of graphene can be categorized into following sections (Fig.2) as stated below.

2.1 Top-down approach:

Top down approach is a very common nanostructure synthesis technique. This technique is defined by the peeling off or separation of individual layers from the host material [32].

2.1.1 Mechanical Exfoliation:

Mechanical exfoliation (ME) is the first recognized method of graphene synthesis. Various graphene layers stacked on one another and bonded by weak van der Waals force to form graphite [33]. If this weak force can be overcome by normal or shear force then layers of graphene can be separated [34]. This principle is utilized in mechanical exfoliation method. The first mechanical exfoliation of graphene involves the use of scotch tape. This scotch tape is applied on the highly ordered pyrolytic graphite sample (HOPG) and peeled it off. This way a normal force is exerted on the sample and a layer from graphite will be adhered on the tape as shown in fig.3. If this process can be repeated several times then a very thin layer of graphite will be found finally having a thickness of several monolayer of graphene [1]. Though this method produces a high quality graphene flakes, the repeating process makes the production rate very low. To overcome this trouble Jayasena et al. made a mechanical setup where an ultrasharp single crystal diamond wedge along with the aid of ultrasonic oscillation is used to cleave a HOPG sample to generate the graphene layers. This method produces graphene flakes 10nm of thickness [35]. Fukuda et al. produces few-layer graphene flakes by mechanically exfoliating SbCl_5 -graphite intercalation compounds (GICs) and the resultant flakes are reported to have higher electric mobility than that produced by the conventional ME method. Although all these type of mechanical exfoliation processes provide graphene of best quality in terms of purity, defects, electrical and optical properties, but use are limited to fundamental researches only as all are impractical of bulk production for industrial applications [36, 37].

2.1.2 Chemical Exfoliation:

Chemical exfoliation is a slightly different approach where exfoliation is done by using solvents (organic or ionic) with the aid of sonication [39] or rapid heating [38]. These solvents produce strong interaction with the graphitic basal planes which reduces the interlayer van der Waals forces to increase the interlayer spacing and later by sonication or rapid heating exfoliation occurs [40]. Solvents such as N-methyl-pyrrolidone (NMP)[41], sodium dodecylbenzene sulfonate (SDBS) [42], dimethyl formamide (DMF)[43] are the most commonly used in this case. But all these solvents are toxic and have high boiling points which limit their uses in many applications in particular thin film fabrications. Thus

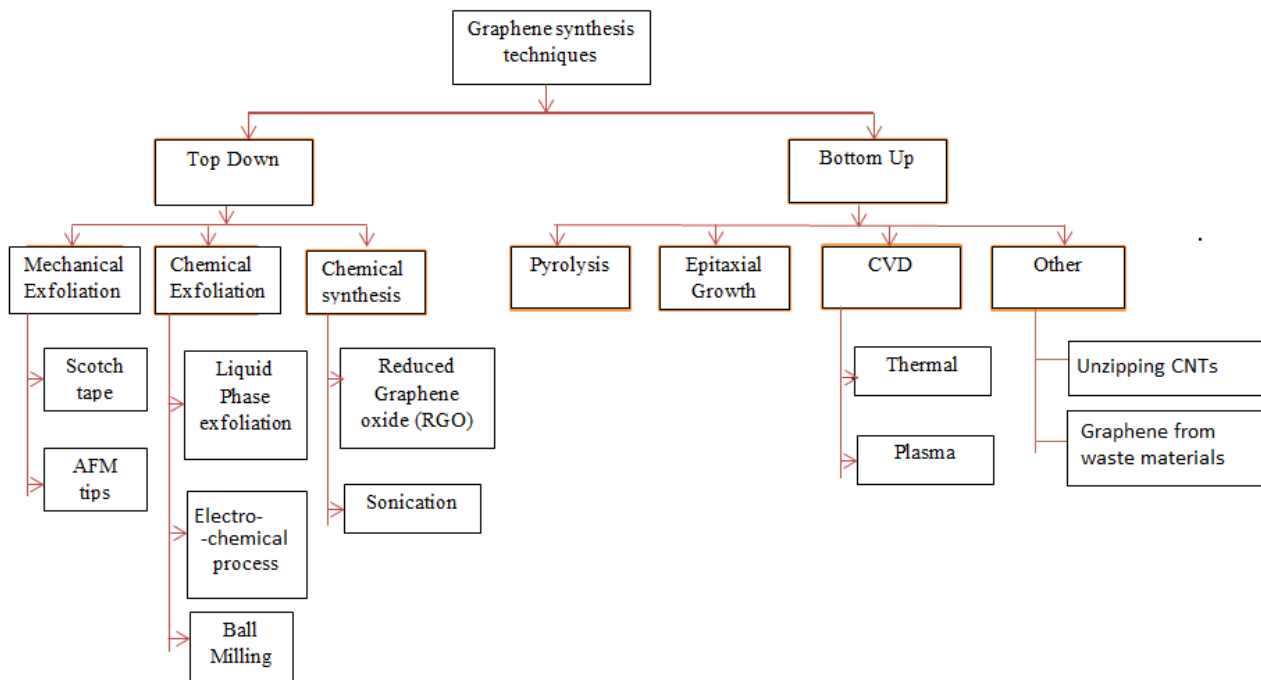


Fig.2: Classification of graphene synthesis techniques.

stable dispersions of graphene in low boiling point solvents such as water, ethanol etc is highly desirable. In recent years several researches have been reported on that issue. Zhang et al. successfully disperses graphene in ethanol by solvent exchange from NMP[44]. 4-dodecylbenzenesulfonicacid (SDBS) [42], sodium cholate (SC) [45] and sodium deoxy-cholate (SDC) [46,47] have also been reported to be used successfully to stably disperse graphene in water. Though chemical exfoliation method is a potentially scalable non-oxidative route, major problem lies in that the yield of thin graphene layers is very low [54].

A slight modification in chemical exfoliation process is done in electrochemical process where an electrolyte along with a power source is used to exfoliate graphene flakes from graphite which is usually act as electrode in this electrochemical system [48]. Electrochemical exfoliation process recently gained much attention because of its faster production rate (gram-scale quantity in tens of minutes), great ease of operation (operated at ambient temperature), easily controllable synthesis process and environment friendly method [49]. Two types of electrolytes are used in this method i.e. non-aqueous and aqueous [50]. It has been reported that various types of organic solvents (e.g., dimethylsulfoxide (DMSO) [51], 1-methyl-2-pyrrolidone (NMP) [52] or ace-tonitrile [53]) were used to disperse inorganic salts (e.g., lithiumsalts, small alkylammonium molecules or perchlorate salts) to act as non-aqueous electrolytes for electrochemical exfoliation. On the other hand water (solvent) along with hydrobromic acid(HBr), hydrochloric acid (HCl), perchloric acid (HClO₄), nitric acid (HNO₃), sulphuric acid (H₂SO₄) etc are used as aqueous electrolyte [50]. In this process, intercalation of molecules in between the graphene sheets occur and this result in expanded graphite (EG). These intercalated ions produce gaseous species by means of oxidation which

exert a large force on the graphite layers and thereby separate weakly bonded graphite layers from one another (Fig.4)[48,54]. It must be mentioned here that inspite of having several advantages discussed above, the ineffectiveness of this method lies in controlling the thickness of the flakes [54].

Another recent progress in exfoliation method is ball milling, a common milling method in powder processing technique [55]. In this primitive powder processing method, high quality large graphite flakes can be obtained by using shear force on graphite [56]. It needs to be mentioned that other forces i.e. collisions and vertical impacts involved in this process must be avoided to attain the best quality graphene. In general, there are two types of ball milling techniques i.e wet milling and dry milling [34]. In wet milling technique, a good solvent that can overcome the van der waals force between the adjacent graphite flakes such as DMF, NMP, tetramethyluren, 1-pyrene carboxylic acid [57], melamine [58] is used along with graphite [34] and

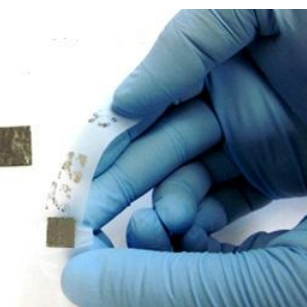


Fig.3: Scotch tape approach of graphene synthesis. Reproduced with the permission of ref. [2]

milled at a low speed (to ensure the maximum of shear force) [34] in a planetary ball mill [55-58] or stirred

media ball mill [59,60]. Among the exfoliating agents, melamine and 1-pyrene carboxylic acid are reported to be shown high degree of exfoliation than the others [57,58]. In dry ball milling process rather than using solvents, water soluble inorganic salts are used followed by the subsequent water washing or sonication of the milling products [61,62]. Some research has shown that elemental sulfur [63], commercially available solid melamine [64] and dry ice [65,66,67] can also be used instead of inorganic salts. These modifications sometimes lead to the formation of high quality edge functionalized graphene. Thus for the attainment of edge functionalized graphene dry milling is thought to be better than the wet milling process. Though both of the milling processes are favorable for combined functionalization and exfoliation, the major drawbacks lie in the long process time and sonication based post milling treatment. Another drawback is that fragmentation and defects are unavoidable due to the high energy collisions of grinding media.

In all types of chemical exfoliation processes discussed above, involve one common problem. The product graphene layers tend to agglomerate to form graphite through Van der Waals interactions. So the major challenge is to prevent this agglomeration and achieve complete and homogeneous dispersion of individual graphene sheets in various solvents. Sometimes intercalation of molecules between graphene layers is occurred and the product is termed as graphene intercalation compound (GIC). The molecules can be attached with the layers in two ways i.e. non-covalent attachment and covalent attachment. It has been reported that in case of non-covalent attachment electrical conductivity of the compound increases whereas in case of covalent attachment, conjugated sp^2 system disrupted and as a result, conductivity decreases [2]. GICs are another broad category under graphene related compounds and thus GICs aren't further discussed here.

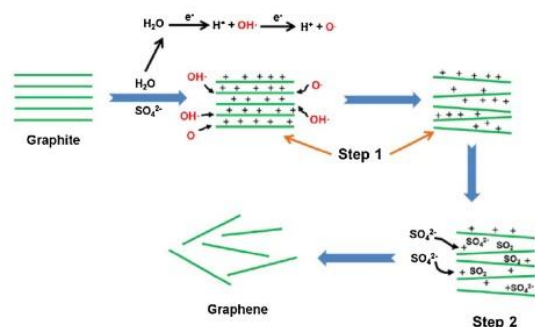


Fig.4: Separation of graphite layers (graphene) through the intercalation of ions. Reproduced with the permission of ref. [54]

2.1.3. Chemical Synthesis:

In a general sense chemical synthesis of graphene means the production of graphene oxide (GO) by oxidation and its subsequent reduction to graphene. This oxidation of graphite to GO can be done in various ways. From the nineteenth century graphene oxide has been producing by three methods i.e. Brodie [68], Staudenmaier [69] and Hummers [70] methods. Though

in all three methods, oxidation is done in the presence of strong acids and oxidants, among them hummers method gained huge attention. In the hummers method KMnO₄, H₂SO₄ and NaNO₃ are used to oxidize graphite flakes [70]. D. C. Marcano et. al had reported that more oxidized GO can be produced by increasing the KMnO₄ content in hummers method. Another improvement was done by the same author where NaNO₃ was excluded from the reaction, KMnO₄ content was increased and the reaction was performed in a 9:1 mixture of H₂SO₄/H₃PO₄. And in this improved hummers method, greater amount of hydrophilic oxidized graphene materials was found. The main advantages of this improved method are process temperature can be easily controlled, doesn't produce toxic gases and shows equivalent conductivity upon reduction [71].

Weiwei Cai, et al. have studied ¹³C-labelled graphene oxide using NMR and revealed that the basal plane of the sheets have hydroxyl and epoxy (1,2-ether) functional groups whereas carbonyl and carboxyl groups located at the edges [72]. These functional groups can react to form functionalized GO. These groups are also responsible for the disruption of conjugated electronic structure and make GO electrically insulating though the electronic structure can be partially restored by reduction [73,74]. Now the graphene oxide can be reduced chemically [75,76], thermally [77] or UV-assisted ways [78]. In chemical reduction process various reagents like hydrazine [79,81], sodium hydroborate [80] etc are used. Hydrazine are reported to be best among them as does not react with water and was found to be the best one in producing very thin and fine graphite-like sheets. But produced graphene sheets are hydrophobic in nature and tend to agglomerate. This problem can be minimized by decorating/stabilizing with various surfactants like gold nanoparticles, amphiphilic polymer, alkylamine etc [13,78,82,83]. Thermal reduction process involves heating GO upto 1050C. Heating at this temperature causes decomposition of the epoxies or hydroxyl functional groups as well as producing gaases. When the decomposition rate becomes greater than the diffusion rate of the evolved gases, a pressure generates that exceed the van der waals forces holdin the sheets together and thus reduced graphene oxide sheets are produced [2]. But recently a low temperature thermal reduction process is reported where reduction was done in ambient air at less than 300C [86]. Another improvement in the reduction process was done by Williams G et al. where reduction is accompanied by changes in the UV absorption of the graphene oxide, as the color of the suspension shifts from brown to black [78]. Nangamso Nathaniel Nyangiwe et al. has also reported a cost effective way of reducing GO sheets by using direct sunlight. This methodology provides an effective way for the bulk production of high quality graphene sheets from GO [87].

2.2 Bottom up approach

Bottom up approach is a method wherein there is a progression from the individual elements to the whole. Here in graphene synthesis CVD, epitaxial growth on various substrates, pyrolysis and some unconventional

synthesis procedures are considered as bottom up approaches.

2.2.1 Chemical vapor deposition (CVD):

Though graphene from monolayer to few layers are being synthesized by mechanical exfoliation and chemical reduction method since 2004, subsequently another promising type of synthesis method CVD came into the scenario in 2006. This process can be categorized into two types-I) Thermal CVD and II) Plasma enhanced CVD.

Somani et al first successfully synthesized fewlayer graphene using camphor as precursors on Ni foils [88]. In his work environment-friendly, cost effective camphor precursors was evaporated at 180 C further pyrolyzed in another chamber of CVD furnace using Ar as carrier gas at 700-850 C. This study opened a route of successful growth, etching and transferring processes of the CVD-grown large-scale graphene films from the substrate for their next researchers keeping behind some unsolved problems such as controlling the number of layers, minimizing the folds etc. Kim et al. successfully transferred the CVD grown films to target substrates (Fig.5) without intense mechanical and chemical treatments, to hold high crystalline quality of the graphene samples [89]. In 2010 Bae and his coworkers reported the synthesis of 30 inch graphene nonolayer film by the roll-to-roll production approach using chemical vapour deposition onto flexible copper substrates (Fig.6) [90]. They completed fabrication process by three steps-I) polymeric adhesion to the graphene on the Cu foil, II) etching of the Cu layer and III) transferring the graphene films to the target substrate. The film showed sheet resistances as low as $\sim 125\Omega/\text{square}$ with 97.4% optical transmittance, and exhibit the half-integer quantum Hall effect, indicating their high quality. By further process up gradation they reduced sheet resistance at values as low as $\sim 30/\text{square}$ at $\sim 90\%$ transparency, which may be emerged as potential replacement of commercial transparent electrodes such as indium tin oxides. In another work [91] synthesis of 1 to 2 nm thick graphene film by CVD method has been obtained on Ni substrate but not on Si substrate (Fig.7). Also another interesting matter found by researchers, is nitrogen (N₂) doped graphene synthesis via CVD method [92,93]. N graphene fabrication by this method drew the attention of scientific community because of its distinguishing electrical characteristics from pristine graphene (Fig.8)[93].

Another promising type of CVD method used for graphene synthesis is Plasma Enhanced Chemical Vapor Deposition (PECVD) technique. Synthesis of carbon films by d.c. discharge plasma-enhanced chemical vapor deposition (PECVD) using a hydrogen–methane gas mixture by Obraztsov et al. [94] is considered as pioneer experiment for subsequent graphene synthesis by PECVD method. For the first time graphene nano sheet was synthesized by Wang et al. [95] using radio frequency PECVD keeping behind process parameters as-CH₄ volume concentration range of 5–100% in an H₂ atmosphere temperature variation from 600 to 900 C.

This process used Si, SiO₂, Al₂O₃, Mo, Zr, Ti, Hf, Nb, W, Ta, Cu, 304 stainless steel as substrate and time duration of 5-40 min. Since then much effort and devotion has been given to control the graphene layer thickness by optimizing experimental conditions in this process.

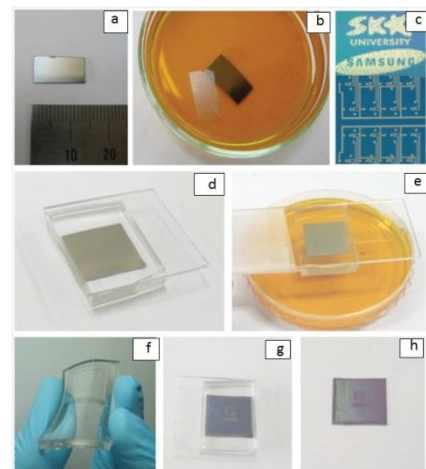


Fig.5: Transfer processes for large-scale graphene films: (a) A centimetre-scale graphene film grown on a Ni(300 nm)/SiO₂(300 nm)/Si substrate (b) A floating graphene film after etching the nickel layers in 1 M FeCl₃ aqueous solution. After the removal of the nickel layers, the floating graphene film can be transferred by direct contact with substrates (c) Various shapes of graphene films can be synthesized on top of patterned nickel layers. (d, e) The dry-transfer method based on a PDMS stamp is useful in transferring the patterned graphene films. (d) After attaching the PDMS substrate to the graphene, (e) the underlying nickel layer is etched and removed using FeCl₃ solution. (f) Graphene films on the PDMS substrates are transparent and flexible. (g, h) The PDMS stamp makes conformal contact with a silicon dioxide substrate. (g) Peeling back the stamp (h) leaves the film on a SiO₂ substrate. Reproduced with the permission of ref. [89]

An additional advanced research was reported by Malesev et al [96,97] to obtain 4 to 6 layers of graphene sheet using micro wave PECVD. In 2012 another report came by Nang and Kim [98] showed high quality graphene synthesis on Cu foil using inductively-coupled plasma chemical vapor deposition (ICPCVD). Therefore, it can be declared as a superior process over thermal CVD because of lower temperature and time requirement for film growth on substrate.

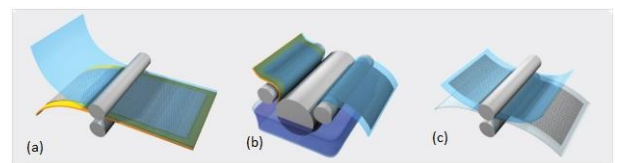


Fig.6: Schematic of the roll-based production of graphene films grown on a Cu foil. The process includes (a) adhesion of polymer supports, (b) copper etching (rinsing) (c) dry transfer-printing on a target substrate. Reproduced with the permission of ref. [90]

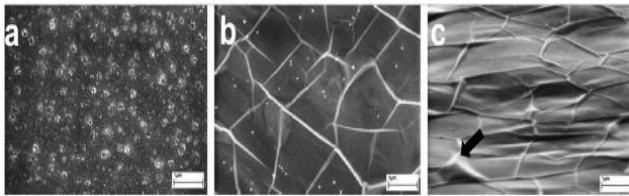


Fig.7: The SEM images films grown in identical CVD conditions on Si (a) and Ni (b and c) substrates. The image (c) has been obtained with the sample tilt of 75. Reproduced with the permission of ref. [91]

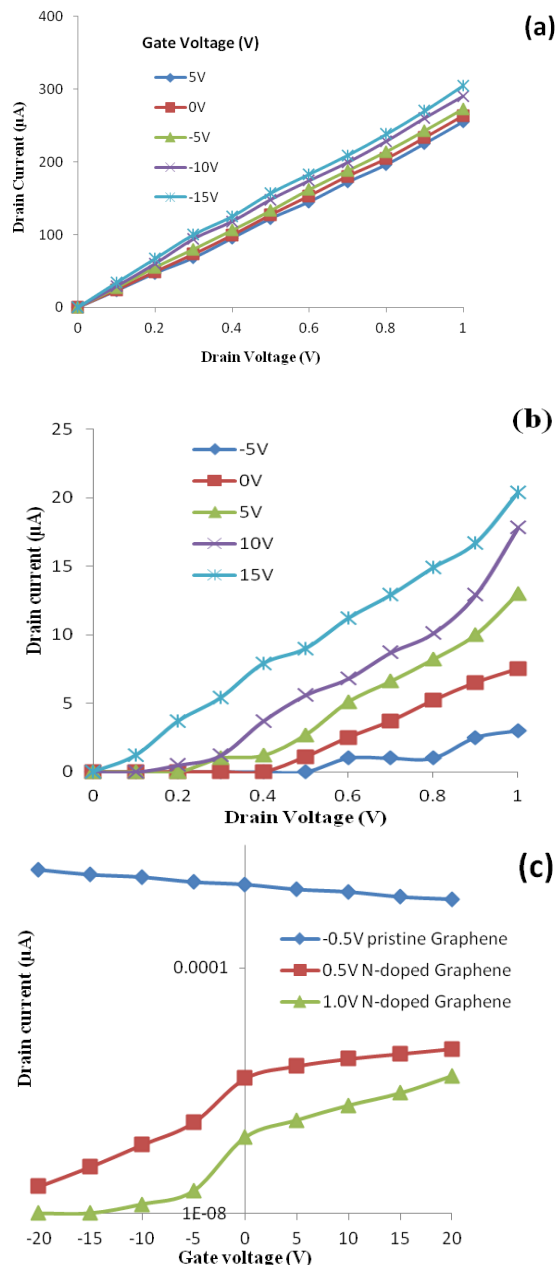


Fig.8: Electrical properties of the N-doped graphene. (a) & (b) I_{ds}/V_{ds} characteristics at various V_g for the pristine graphene and the N-doped graphene FET device, respectively. The insets are the presumed band structures. (c) Transfer characteristics of the pristine graphene (V_{ds} at -0.5 V) and the N-doped graphene (V_{ds} at 0.5 and 1.0 V). Reproduced with the permission of ref. [92]

2.2.2 Pyrolysis method:

Along with other synthesis method, this process is also being experimented by the researchers. Worsley et al [99] reported the synthesis of graphene aerogel by pyrolysis at 1050°C . They carried out synthesis by sol-gel polymerization of resorcinol (R) and formaldehyde (F) with sodium carbonate as a catalyst (C) in an aqueous suspension of GO. Then the sol-gel mixture was cured in sealed glass vials at 85°C . As GO-RF gels formed it was washed in acetone to remove water from the pores. Using supercritical CO_2 , the GO-RF gels were dried, pyrolyzed at 1050°C under nitrogen yielded the final graphene aerogel. Another advanced work [100] revealed in 2015 using a simple method produced ultrathin (~ 1 nm) conducting carbon films and membranes based on molecular self-assembly, electron irradiation, and pyrolysis. Also a contemporary work [101] published a report of synthesizing graphene-like materials by pyrolysis of hydrocarbons in thermal plasma. By slight modification in it, recently a report [102] showed the synthesis of graphene films by Nebulized spray pyrolysis method. Hopefully modification if necessary in this process will bring productive outcome in future.

2.2.3 Epitaxial Growth on substrates:

Simply the term ‘‘Epitaxial Growth’’ means ordered or arranged atomic growth in single crystalline manner over a single crystalline substrate. When the substrate deposited material on it are of same type, then it is called homo epitaxial growth. If substrate differs from the deposited materials then it is defined as hetero epitaxial growth. Though epitaxial growth of graphite on semiconducting substrates ($\text{SiC}\{0001\}$) was known since 1975 [103], outstanding outcome of this process has come to light in the recent decade. Notable milestones in this prospect for opening the potential of recent studies are the possibility to grow single crystal SiC on Si substrates invented by Matsunami et al. in 1981 [104] and the high-quality epitaxy at low-temperatures on off-axis SiC substrates in 1987 [105]. Recently researchers are preparing good quality monolayer, bilayer and three layer epitaxial graphene samples on $6\text{H-SiC}\{0001\}$ substrate [106,107]. Epitaxial graphene sheet was successfully synthesized by Berger’s group [106] using Si terminated (0001) face of single-crystal 6H-SiC by thermal desorption of Si. A more later study [107] produced single layer graphene by thermal decomposition of the (0001) face of a 6H-SiC wafer. After surface preparation, samples were heated by electron bombardment in ultrahigh vacuum (UHV; base pressure 1×10^{-10} Torr) to $\sim 1000^\circ\text{C}$. More productive a new ‘‘face to face’’ method introduced the way to synthesize high quality epitaxial graphene, has been reported by Yu et al [108]. To conclude, this is a promising method and may be scalable commercially, though still it is an expensive approach.

2.2.4 Unzipping CNTs:

Carbon nanotubes (CNTs) are actually rolled graphene sheets. Thus by unzipping these nanotubes, graphene can be formed. Usually graphene nanoribbons

with a large number of exposed edges are formed by various unzipping techniques. These edges are highly susceptible for chemical attacks and thus can be easily functionalized or modified to improve its properties. Due to the zero bandgap of pure graphene sheets, they hadn't considered potential for semiconductor appliances. But these nanoribbons have a notable bandgap and this way has opened up a dimension in semiconductor world. Many researchers around the globe followed different routes to unzip the CNT. Tour et al. followed a simple solution based oxidative process (suspension of MWNTs in concentrated sulphuric acid followed by treatment with 500 wt% KMnO₄ for 1 h at room temperature and 1 h at 55–70C) which yield nanoribbons by longitudinally unzipping multiwalled carbon nanotubes (MWNTs) [24]. Abraham G. Cano-Ma´rquez et al. reported that MWNTs can be unzipped longitudinally by intercalation of lithium ions and ammonia followed by exfoliation with acid treatments and abrupt heating [109]. Both of these processes have limitations of producing heavily oxidized and defective wide ribbons. This problem was overcome by Jiao et al. who reportedly produced narrow ribbons (10-20nm) by plasma etching of CNTs partly embedded in a polymeric film [23]. Another facile synthesis route is developed by the same authors in which MWNTs was first calcined in 500C and then dispersed in a 1,2-dichloroethane (DCE) organic solution of poly(m-phenylenevinylene-co-2,5-dioctoxy-p phenylenevinylene) (PmPV) by sonication [110]. By this way large scale of high quality products can be obtained. AFM images of unzipped CNTs on SiO₂/ silicon substrate shows the narrow width and smooth edges of the nanoribbons (Fig.9). A very recent approach is the use of transition metal nanoparticles (Ni or Co) to longitudinally cut MWNTs to form GNRs. The main advantage of this route is its simplicity. As no chemical treatment is involved, the edges of the ribbons are cleaner compared to the other methods addressed above [111]. Not only nanoribbons but also graphene sheets can also be produced by unzipping CNTs. Jung et al. reported a way where graphene sheets was produced by calcination of aluminum sulfide (Al₂S₃) under a mixed gas flow of carbon monoxide (CO) and argon. But by this method not all evolved gaseous carbons are crystallized in the graphene sheets [112]. Recently another approach was reported by Kuang Bo Shim et al. where graphene sheets were found from MWNTs with a high direct current pulse through a pulsed current sintering process [113]. Major advantage of this process is it can produce graphene sheets very quickly compared to other methods. Though many routes on CNTs unzipping is discussed above, but still high-purity, defect-free controlled synthesis process are yet to come to convert it as a boon in electronic industries.

2.2.5 Others:

Extracting out good things from waste has been running on from the beginning of civilization. As usual after the discovery of graphene, some researchers have been focused on the production of graphene from various types of wastes. In 2011 tour et al. successfully developed graphene on the back side of Cu foil at 1050°C

under H₂/Ar flow by using six carbon-containing materials without prepurification i.e.cookies, chocolate, grass, plastics, roaches, and dog feces [114]. Monolayer graphene of high quality is reported to be produced by this method. Klita et al. produced high quality single crystal graphene on polycrystalline Cu foil using solid waste plastic as carbon source in an ambient pressure (AP) chemical vapor deposition (CVD) process [115]. A couple of researches also done to fabricate graphene from agrowastes.Patil et al. demonstrated an ecofriendly approach to develop silver-reduced graphene oxide nanocomposites using Moringa oleifera fruit shell extracts [116]. Somanathan et al. uses sugarcane bagasses as a raw material to produce GO by oxidation under muffled atmosphere conditions [117]. Goswami et al. reported a cost effective wide scale synthesis of Graphene oxide Nanoplatelets using biochar obtained from rice straw biomass as a green precursor [118]. Zhou et al. developed a combined hydrothermal and graphitization approach to synthesis high-quality graphene sheets from wheat straw. They also reported that produced graphene sheets have the relatively flat voltage profiles with a negligible charge/discharge voltage hysteresis which makes the wheat straw derived graphene as a potential candidate for Li-ion batteries [119]. As a source of graphite, spent batteries can also be used as raw material for graphene production. Graphite powder can be produced from the electrode of the waste batteries by acid treatment and can then be used as the starting material for GO production [120]. Badawy also reported a similar approach of producing graphite powder with its subsequent oxidation to GO from spent Li-ion batteries [121]. Though all these process discussed above are costeffective, but satisfactory synthesis of GO from different wastes is yet to be achieved.

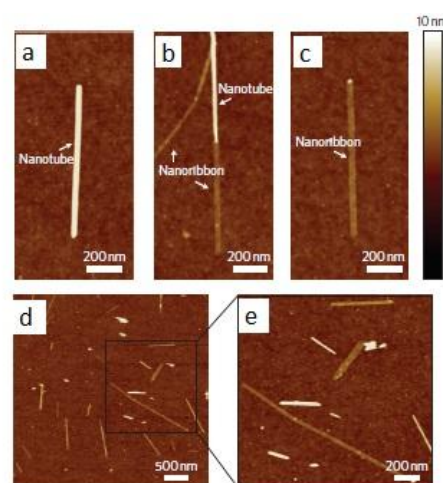


Fig.9: AFM image of (a) Pristine CNT (CNT height 9nm) (b) partially zipped CNT (GNR height 1.4nm) (c) fully zipped CNT (GNR height 1.6 nm) (d) unzipped CNTs deposited on a SiO₂/silicon substrate, showing a high percentage of single-, bi- and trilayer GNRs (e) enlarged image of the marked area showing the smooth edges of GNRs. Reproduced with the permission of ref. [110]

There are other minor ways of producing graphene. Subrahmaniyam et al. reported an arc discharge method of producing graphene flakes using high discharge pressure [122]. He and NH₃ are also reported to be used in the same method [123]. Thermal fusion of PAHs [124], electron beam irradiation of PMMA nanofibres [122] and conversion of nanodiamond [125] are also reported to be the possible ways of graphene production

3. CONCLUSION

Graphene, though emerging in the field of material science with its amazing properties, still so many works remaining to be done for its commercialization. Numerous studies are going on to improve its properties as well as materialize its cost effective bulk production. In this review we have tried to summarize the notable research works done on this prospect around the globe. To conclude, if the shortcomings highlighted in this review can be surpassed in the upcoming days, it will revolutionize the field of energy and electronics.

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