Chapter 1

Introduction

1.1 Introduction

Carbon in the form of coal had been the driving force of the industrial revolution. Nowadays, the carbon nanostructures play a significant role in another technological/scientific revolution: nanotechnology. The research in the realm of carbon nanotechnology has been significantly contributed to the routes which the science has taken at the nanoscale. The carbon nanostructures include fullerenes, carbon nanotubes and recently prepared single layers of graphite; graphene [1]. Although, all of the above mentioned carbon advanced materials are composed of sp^2 carbon, the physical/chemical properties of them vary due to by versatile atomic structures. Carbon has four valence electrons with similar energies which can easily hybridize. In carbon atom, these valence electrons give rise to 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals while, the two inner shell electrons which belong to a spherically symmetric 1s orbital; are tightly bound and the energy level of them is far from the Fermi level of carbon. Thus, only the electrons corresponding to the 2s and 2p orbitals contribute to the solid-state properties of graphite. This unique capability for hybridization makes the carbon to form 0D, 1D, 2D, and 3D structures (Fig. 1.1).
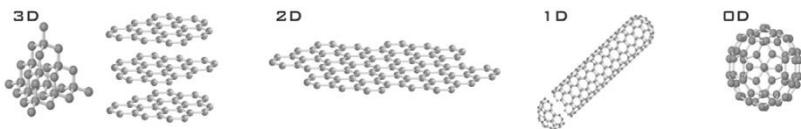

Fig. 1.1 *Different structures of carbon allotropes [2].*

During the 1960s and 1970s, carbon fibers became an important industrial material [3] and today, they employs in variety fields from sports equipment to vehicle parts, anywhere where the low weight together with high strength is required. Fibrous carbon materials are as part of everyday life in the form of

carbon fiber reinforced composites [3]. Carbon nanotubes and graphene promise even greater benefits if their extraordinary properties can be harnessed. In the last few years graphene, which consists of a single layer of carbon atoms arranged in a honeycomb lattice, has become one of the most interesting and controversial topics in physics and material science [4, 5]. The word of graphene is derived from the word graphite and the suffix-ene that is used for polycyclic aromatic hydrocarbons such as naphthalene, anthracene, coronene and benzene [6]. Thus, the term graphene refers to one strictly two-dimensional monolayer of graphite in the (0001)-plane.

The hexagonal structure is also a well-known for carbon nanotubes and, somehow, for fullerenes [7]; i.e. this structure has been theoretically studied for a long time as a building block of graphite and carbon nanotubes (Fig. 1.2) [7].
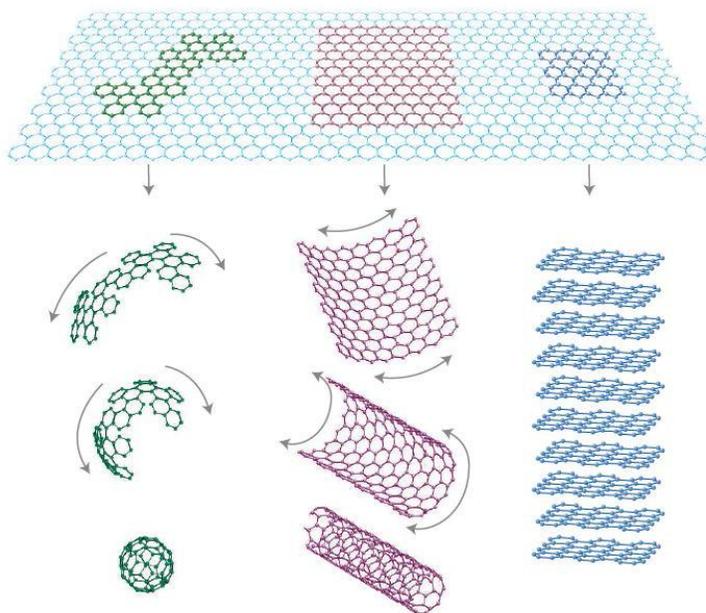

*Fig. 1.2 Graphene, a single sheet of graphite, can be considered as a
building block of all these carbon structures [8].*

Since in graphite the distance between the graphite planes is high in compared to that of carbon atoms within the same plane (3.37 Å versus 1.42 Å), graphene serves as a model particularly for the description of such 3D material [9, 10]. In 1937 Landau had theoretically stated that 2D crystals were thermodynamically unstable [11], and consequently, the 2D crystal system such as graphene was only theoretically discussed. Still, many experimentalists have acquired graphene as an unwanted byproduct during experimental runs in the laboratory. In fact, the structural study on the other forms of carbon nanostructures, fullerenes and carbon nanotubes, helped to the rapid development of the graphene identification and characterization. Graphene as a thin film over the metallic substrates was produced and studied at the 1970s when Blakely and colleagues worked on the single layer graphite growth over the various transition-metal substrates [12, 13, 14]. Van Bommel et al. developed graphene/thin graphite films by silicon evaporation of SiC in 1974 [15] even former, the separation of graphene layers via the intercalation/exfoliation of graphite and so called graphene oxide were investigated [16, 17]. However, the first documented graphene synthesis as a carbon monolayer was recorded in 1977 by Oshima et al. It is worthy of note that acquiring a clean crystal surface was difficult in the case of materials which tend to dissolve carbon atoms; as a result, it was usually more convenient to study the carbon covered clean surfaces [17, 18, 19]. Since the most research on graphene was practically conducted over the metal substrates, the properties of graphene were not completely preserved in such systems. At 1986, Till Boehm et al. proposed the term "graphene" for the description of a single atomic sheet of graphite [6]. Finally, Novoselov et al. at 2004 could produce free-standing graphene flakes from the graphite crystals by mechanical exfoliation [20]. Following these findings, Novoselov et al. [20, 21], Zhang et al. [23] and Berger et al. [23] have quantified very unique properties of graphene. However, despite

many fundamental researches on the graphene, the production of high quality graphene for applied purposes has been still a challenging issue.

1.2 Graphene Properties

At a glance, Graphene is immediately considered as the successor of current silicon-based technology due to the 2D honeycomb carbon structure, which makes it ideal as a computing element. Therefore, graphene sheets can be potentially used in computer technology. Moreover, pure graphene exhibits exceptional mechanical, physical and chemical properties such as Young's modulus ($\sim$1000) [24], thermal conductivity ($\sim$5000 $Wm^{-1}K^{-1}$) [25], mobility of charge carriers ($\sim$200 000 $cm^2V^{-1}s^{-1}$) [26], and specific surface area ($\sim$2630 m^2g^{-1}) [27] while, graphene derivatives like graphene oxide or other types of functionalized graphene display remarkable catalytic, mechanical, sensing and electronic properties.

One of the most important factors that enabled the discovery of single layer graphite among these crystallites is that even graphene, not to mention bilayer graphene, can be seen with a conventional optical microscope on top of a wafer with carefully chosen SiO_2 thickness [20, 28]. This effect arises because graphene has certain opacity and it also adds to the optical path of the light traversing the SiO_2 capping layer [28]. Together, these effects are enough to give graphene a well discernible contrast in an optical microscope. This technique simplifies the process of finding single graphene sheets but obviously limits this fabrication scheme to devices for research purposes.
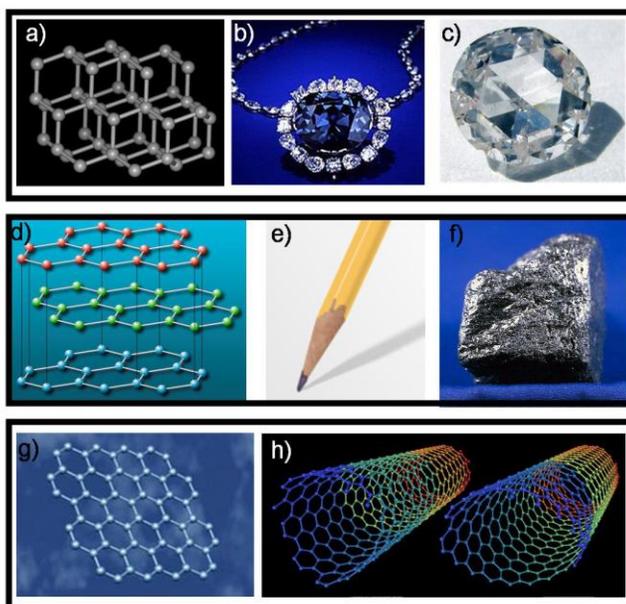
Fig. 1.3 *(a) Diamond lattice. Picture taken from http://mrsec.wisc.edu (b) Hope Diamond. Image from Smithsonian. (c) Lab grown diamond. Image from Apollo diamond, Inc. (d) Graphite lattice. Image from. http://www.scifun.ed.ac.uk/ (e) Pencil. Image from www.xara.com. (f) Graphite. Image from U.S. Geological Survey. (g) single layer of graphene. Image from http://ewels.info.com.(h) Single walled carbon nanotubes. Image created by Michael Ströck from Wikipedia.*

Fig. 1.3 shows the 2D sp2 hybridized structure of Graphene and Graphite. Actually, Graphite is the stacks of graphene sheets with 0.3 nm distance between the layers. These layers held together by weak Van Der Waals forces (Fig. 1.3 d) [9]. Thus, they can slide relatively easily across each another. It has been known that the presence of water molecules reduce the frictional force considerably [29, 30]. Another frictional effect which is believed to be important is the registry of the lattice between the layers. A mismatch in this registry gives graphite the property of superlubricity where the frictional force reduces significantly [31]. Mechanical experiments based on few layer graphene may help to elucidate some of these mechanisms clearly [32].

A single 2D sheet of graphene has hexagonal structure and each atom forms three bonds with each of its nearest neighbors (Fig. 1.3g). These are known as the bonds oriented towards the neighboring atoms. These covalent carbon-carbon bonds, the strongest bond in nature, lock these atoms in place giving them remarkable mechanical properties [33, 34]. In other words, the covalent C-C bonds in graphene are nearly similar to those present in diamond structure. Interestingly, a suspended single layer of graphene is one of the stiffest known materials with a Young's modulus of ~ 1 TPa. The fourth valence electron that does not participate in covalent bonding is located in the $2p_z$ state perpendicular to the sheet of graphite (a conducting π band).

The mechanical properties of graphene are still unexplored and it is the time to revise the old assumptions about bulk graphite for determination of the elastic constants by scaling down it to the atomic thicknesses. In this regard, production single atomic layers or few atomic layers of graphene can be useful for overcoming some of the uncertainties involved in working with large single crystals.

1.3 Fabrication Methods

1.3.1 Mechanical Exfoliation

The most widely used method is which the single layer graphene flakes are mechanically separated from the bulk graphite. Carbon layers in bulk graphite are held together by weak Van Der Waals energy of the order of 2 eV/nm^2 and a force about 300 nN/μm^2 is adequate for removing the monolayer of graphene [35]. Such small force can be easily produced by an adhesive tape. In 2004 Novoselov et al. used common "scotch" tape to peel off layers of graphite from HOPG [1].

This so called micromechanical cleaving technique consists of repeated peeling off the graphite crystallites stuck to the scotch tape, during which ever thinner crystals are produced on the tape surface. In fact, this method of graphene fabrication is exfoliation, the technique that has been employed for centuries; i.e. writing with a graphite pencil over a paper. During writing with a pencil, many graphene sheets spread over the paper but in an uncontrollable way. In this way, the graphite crystals separate very easily because of the weak Van Der Waals forces. After peeling, the tape is pressed against the surface of a silicon wafer having either a 90 or 300 nm of SiO_2 capping layer. While the tape is removed from the surface of the wafer the crystallites sticking to the SiO_2 surface cleave one last time and the result is an assortment of graphite crystals with varying thicknesses on the SiO_2 (Figure 1.4 b). To distinguish between layers of graphene, the thickness of SiO_2 is important because at the thickness of 90 nm or 280 nm, graphene contrast on SiO_2 is maximized by about 12% at 550 nm where the sensitivity of human eye is optimal [28].

To partially remove contamination from adhesive tape, heat treatment under Ar/H_2 atmosphere at 200 ℃ [36] or in situ Joule heating by the application of current of the order of micro amperes can be employed [37]. The size of graphene flakes obtained by this method is limited which is the main obstacle towards large scale graphene production. However, this method is the benchmark for the comparison of the electronic characteristics of the graphene obtained by other techniques.
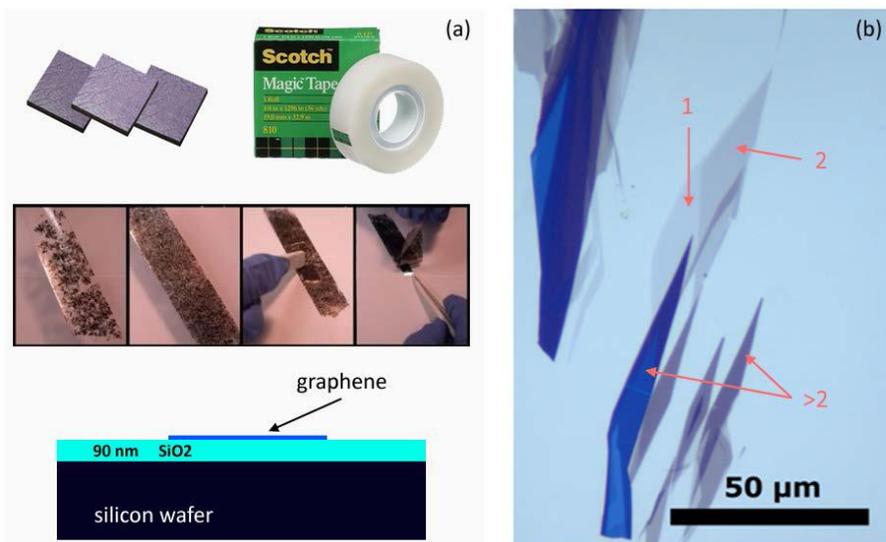
Fig. 1.4 *(a) Process of preparing graphene (b) Optical microscopy image of single layer graphene on 90 nm thick SiO$_2$ Single, bi- and multi layered graphite is highlighted by the red arrows.*

There are recent attempts to improve the quality and yield of exfoliation techniques. These include stamping methods which use silicon pillars to transfer graphene flakes and electrostatic voltage assisted exfoliation which uses electrostatic forces to controllably separate graphene from bulk crystals [38].

1.3.2 Graphitization of Silicon Carbide

Another route for the production of graphene sheets is the graphitization of silicon carbide. In this method the SiC wafer, a highly resistive material, is heated up to 1200-1400 ℃. This heat treatment results in the removal of surface silicon and a carbon rich phase is left which consists of graphene layers [39]. This process is ideally suited for future electronics applications since graphene covers the entire surface of the SiC wafer and the substrate. However, the graphene prepared via this method has higher crystal defects than the cleaved graphene [23].

It is should be noted that direct growth of graphene currently has the highest potential for mass production purpose. Typically, this technique is accomplished by heating a SiC wafer resulting in the partial graphitization of the upper layers [40, 23]. However, the control over the number of layers together with the grain size is difficult [23]. Furthermore, lithography is required for the isolation of the single sheets to pattern the electrostatic gates on top of the graphene surface. Another disadvantage of the high temperature vacuum annealing of SiC is the highly corrugated surface covered by small graphene regions with various thickness [41]. In order overcome this problem, the use of carbon terminated SiC has been proposed instead of previously used Si terminated SiC [42]. However higher graphene coverage via this method has been achieved by graphitization near atmospheric pressure (Ar atmosphere at ambient temperature) resulting in a smooth surface with graphene coverage (50 μm) [43]. The problem with this technique is the initial costs of the SiC wafer and high operational temperature (1400-1600 ℃).

1.3.3 Chemical Vapor Deposition (CVD)

Carbon nanotubes and diamond are successfully grown via CVD methods. Similar to the CNTs, CVD methods are one of the most important methods for graphene preparation which enable the growth of graphene samples of macroscopic size [44, 45].

This technique is based on the usage of precursors in the vapor phase which adsorb and react over the substrate surface at elevated temperatures under low pressure or atmospheric pressure; this results in the deposition of thin film through the chemical reactions. In case of graphene, the precursors are typically carbon containing gas/vapors such as methane and alcohols that react over the transition metal surface under the ambient environment in which the deposition

of amorphous carbon is avoided. The transition metals serve as the efficient catalysts in transformation of hydrocarbons into the graphitic materials [46], for instance, in early 1960's graphite layers were obtained over nickel surface from hydrocarbon gases (vapors) or evaporated carbon [47]. The solubility of carbon in transition metal during CVD process has an important role in growth mechanism and the number of graphene layers [47]. Recent research on graphene growth over the copper substrate (Fig. 1.5) indicates that CVD can result in the growth of monolayer graphene with high coverage; this is due to the negligible solubility of carbon in copper even at 1000 ℃ [50].
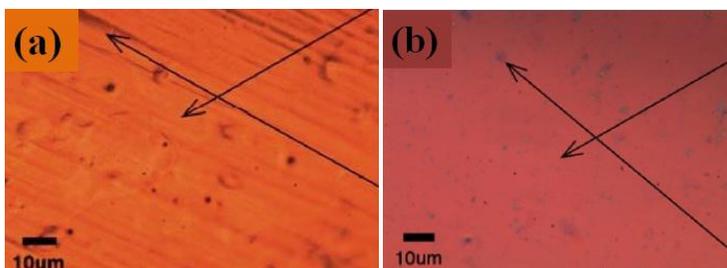

Fig. 1.5 *CVD grown graphene on copper. Optical images of (a) as-grown graphene and (b) transferred to 300 nm SiO₂. Black arrows in (a) show corrugations on copper surface that result in multilayer graphene highlighted by black arrows close to purple regions in (b) [48].*

Since the graphene growth on copper is surface limited, the smoothness of copper surface plays very significant role in obtaining monolayer coverage across entire surface of the substrate [49]. Using this process, the size of graphene is only limited by the size of the metal substrate. Additionally, it should be mentioned that graphene obtained by CVD is inferior in compared to graphene obtained by mechanical exfoliation in terms of above mentioned parameters. One reason for such inferiors is that the graphene obtained via CVD is a continuous sheet which is inherently polycrystalline because the different orientated domains of graphene merge to form a graphene sheet. Also, due to the presence of grain boundaries,

the electrical properties of the film are poor [50]. Many efforts have been devoted to obtain the single crystal isolated graphene domains with improved electrical properties [51]. Another major problem with CVD is that graphene is located over a metal surface and for the electronic devices, it is necessary to have graphene on an insulating substrate such as SiO_2. During the transfer of graphene from a conducting substrate to an insulating one, unavoidable structural damages occur for graphene, which can degrade its electronic/ electrical properties [52].

1.3.4 Annealing Solid Carbon Sources

In this method, the carbon precursor is solid such as PMMA [53], amorphous carbon [54] on copper surface, PAN, PS, PMMA [55], C60 [56] on nickel surface which is usually evaporated or spin coated over the metal surface. Another implementation method of this process is the deposition of carbon source on SiO_2/Si and then metal thin film is evaporated/annealed at elevated temperatures. The advantage of such method is that there is no need to transfer graphene to an insulating substrate. This has been also demonstrated in the case of C60 [56] and SAM [57] on nickel thin film evaporated on SiO_2/Si.

One advantage of this method is that in situ doped graphene can be obtained by using solid carbon precursors that also contains desired dopant element [57]. The limitations of the method are similar to those corresponding to CVD. It is worthy of note that this method is relatively new and the physicochemical aspects of graphene formation are still the topic of active research.

1.3.5 Graphene Dispersion from Graphite

In this method graphite flakes are sonicated in a solution and then dispersed onto a wafer. AFM analysis is used to locate individual sheets [58]. This tech-

nique is very time consuming compared to the optical detection. Long sonication time is required to break the graphite and obtain small flakes [59]. One difficulty in dispersing graphene in the solution is the careful separation of the layers without destroying. The intercalation of graphite and dispersing in a solvent is one method to prevent such destruction. This technique is effective for graphene oxide. However, the aggregation of graphene sheets is another problematic issue.

1.3.6 Chemical Preparation of Graphene

Among the above mentioned methods for the synthesis of graphene sheets, the chemical production routes are the most promising in terms of controlling the process parameters and quality/quantity of the layers (transparency, sheet size and related features such as defect/impurity levels and reinforcing role in polymer matrix). In fact, while, micromechanical cleavage is very successful in producing samples for fundamental studies, the extremely low yield and lack of control in placement of the sheets, limits its application. Other methods based on the use of SiC as a substrate and as a precursor have excellent potential in the pursuit of the best quality synthetic graphene but they are too expensive. For large scale production of GSs, graphite is used as starting material and delaminating is carried out by various means such as chemical functionalization, oxidation or intercalation. The idea behind this technique is to intercalate different reactants among the bulk graphite which results in the separation of graphite layers. In some of these methods, chemical oxidation of graphite precursor occurs and graphene oxide forms; the subsequent exfoliation and reduction lead to reduced graphene oxide nanosheets [60].

The challenge to this approach is that the original sp^2 network of graphite is not restored even after the treatment with reducing agents. To overcome this problem, non-covalent functionalization of conjugated carbon network can be a

proper alternative. The advantage of this scheme is that the external functional groups attach to carbon network through π-π stacking rather covalent bond formation. These improvements are the basis of other methods which employ direct intercalation and exfoliation of graphite (electrochemical methods) and produce a suspension of graphene sheets.

(a) Synthesis of Graphene from Graphene Oxide

In the first report on the production of GO [61], natural graphite (Ceylon) was treated by an oxidative mixture of potassium chlorate and fuming nitric acid for 3–4 days at 60 ℃ until no change was observed. After many years, Hummers and Offeman developed a method in which the oxidation of graphite was accomplished by treating a mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate (Fig. 1.6). This process required less than 2 h for completion at lower temperatures (below 45 ℃) [16].
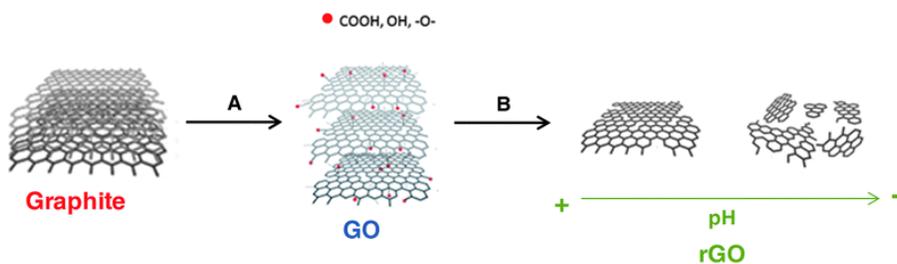

Fig. 1.6 *Hummer's method to produce graphene sheet [16].*

Based on the results obtained with a variety of modern analysis techniques such as NMR, XPS, TEM and Raman, the most recent model of GO structure is schematically depicted in Figure 1.7, where hydroxyl and epoxide groups are randomly grafted to the carbon mesh and alter the sp^2-bonded carbon network of pure graphene sheets.
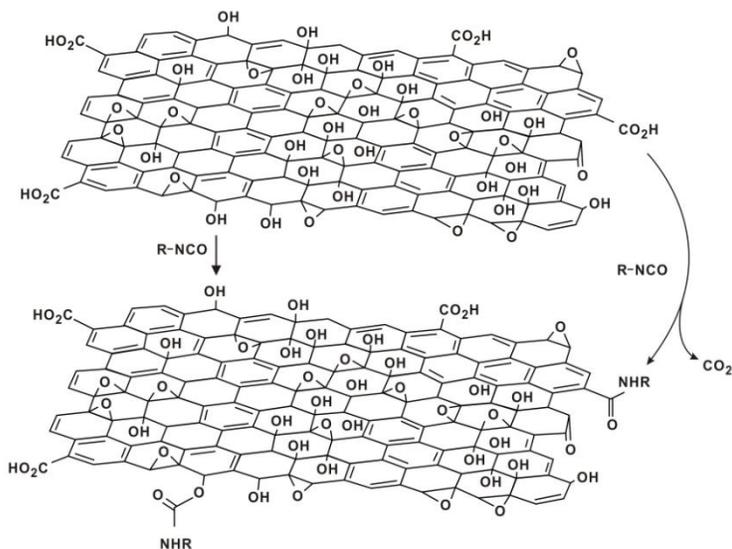
Fig. 1.7 *Structure of graphene oxide [62].*

Regarding the desired properties depending on the application, graphene/graphene oxide is processed by several steps. On the other hand, the fabrication of graphene and/or graphene oxide composites coupled with a polymer or other layered material such as clay is another important goal of research. Some of these composite materials do not require any reduction process and the graphene oxide is utilized; for instance, the GO paper introduced by Ruoff and coworkers [63] is a well-known example of such composite films.

Nowadays the most efficient procedure for the reduction of GO seems to be the H plasma reduction method proposed by Kern et al [64]. Another efficient method is the thermal treatments or heat treatments in the vacuum or controlled atmosphere conditions [65]. Moreover, another alternative approach is the reduction of graphene oxide using electrical energy [66].

(b) Liquid-Phase Exfoliation of Graphite

Chemical preparation of graphene without oxidation is the way for the production of graphene sheets. A very influential method for the exfoliation of graphite is the use of organic solvents such as NMP, DMA, GBL and DMPU [67] (see appendix A). Such solvents have interaction energy with graphene equal to graphene–graphene interaction energy which results in a minimal energy to overcome the Van Der Waals forces between the graphene sheets.

In the liquid-phase exfoliation method for producing graphene which it was employed by Lotya et al. [68], there is no need to oxidation or high temperatures which avoids using expensive solvents. In this technique, graphite is dispersed in surfactant aqueous solutions similar to surfactant aided carbon nanotube dispersion. The dispersed graphitic/graphene flakes are stabilized against re-aggregation by Coulomb Repulsion between the adsorbed surfactant molecules.

It is worthy of note that the aqueous systems has some specific advantages. Generally, the majority of the few-layer flakes have a lateral dimension of ~ 1 μm.

Considerable efforts have been dedicated to the chemical exfoliation of graphite without the oxidation of the graphene flakes which prevents severe damage of the graphene structure. A scalable and facile technique for non-covalent functionalization of graphene was proposed by An et al. [69] based on the π-stacking bond of this molecule with the graphitic surfaces. In this technique, the single-, few-, and multilayered graphene flakes are exfoliated in a stable aqueous with the help of 1-pyrenecarboxylic acid. The -COOH groups present in the 1-pyrenecarboxylic acid structure desire the polar medium

and in this way, they keep the graphene flakes as a stabl suspension in water
[74].

(c) Electrochemical Method

The electrochemical intercalation and exfoliation of graphite has recently
grabbed many attentions because of various advantages compared to other
methods.

The term intercalation refers to the accommodation of guest molecules or
ions (called intercalants) into a host lattice possessing, in most of the cases, a
layered structure. The insertion of guest species into the host matrix is exploited
by the well-known 'intercalation chemistry'. According to the type of
interaction between intercalant and host material, intercalation may occur
through (a) electrostatic interaction, due to ion exchange of interlayer metal
cations with organic/inorganic cations (usually in clay minerals), (b) covalent
binding via chemical grafting reactions within the interlayer space (e.g. of
graphite) or (c) weaker interactions like Van Der Waals forces, hydrogen
binding, ion dipole and coordination, electron transfer, through absorption of
neutral molecules by interaction with external or internal surfaces [70]. Graphite
occupies a dominant space among the host matrixes due to the high degree of
structural ordering leading to well defined structures. The first synthesis of
intercalated graphite was reported by Schaffäult in 1841. However detailed
studies of graphite intercalation compounds (GIC) began in the 1930s, with
Hoffman; they introduced X-ray diffraction for the study of hybrid compounds
structures [71]. During recent years GIC have attracted the scientists' interest
due to their fascinating applications in high electrical conductors [72],
lithium-ion battery anodes [73], hydrogen storage materials, electrochemical
storage media [74], separation processes and gas sensors. GICs are being used

extensively as the starting materials for obtaining colloidal dispersions of single-layer graphene sheets [75]. Ideally the use of a GIC allows the production of high quality graphene.

Liu et al. [66] showed the ionic-liquid-functionalized graphite sheets with the assistance of an ionic liquid and water are accessible through a mild one-step electrochemical process (Fig. 1.8). During this process the ionic-liquid-treated graphite sheets can be exfoliated into functionalized graphene nanosheets; this means that not only an individual and homogeneous distribution in polar aprotic solvents is achieved, but also there is no need to further deoxidization.
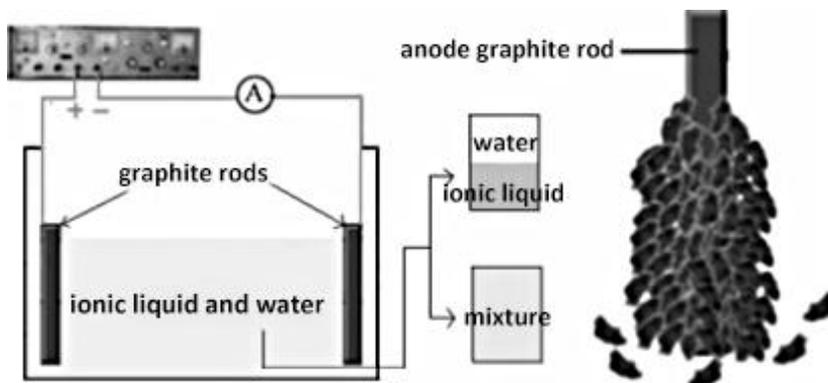

Fig. 1.8 *Experimental set-up diagram (left) and the exfoliation of the graphite anode (right) [66].*

One year later, highly efficient and large-scale synthesis of graphene from graphite was conducted by Wang et al. [76] via electrolytic exfoliation using poly (sodium-4-styrenesulfonate) (Fig. 1.9). Their results confirmed the existence of monolayer graphene sheets and presence of few graphene sheets in the stacks.

In other study, high-yield synthesis of few-layer graphene flakes through electrochemical expansion of graphite in propylene carbonate electrolyte has been carried out by Wang et al. [77]. A negative graphite electrode was

electrochemically charged and expanded in an electrolyte of Li salts and organic solvents under high current density; this led to efficient exfoliation of graphite into few-layer graphene sheets with the aid of sonication (Fig. 1.10).
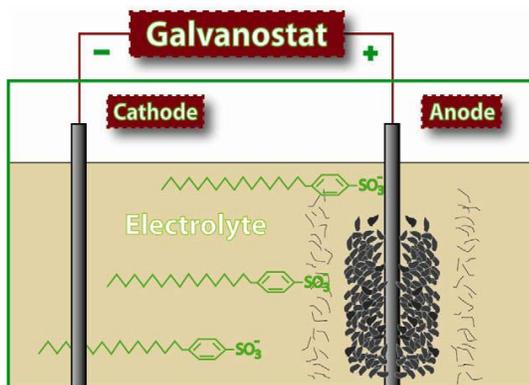

Fig. 1.9 *Diagram of the apparatus for graphene synthesis via electrolytic exfoliation [77].*
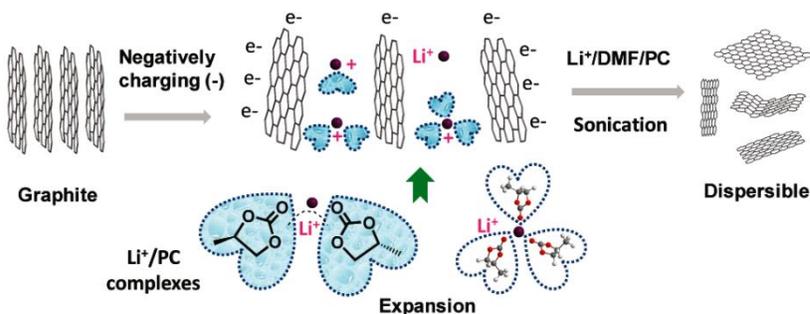

Fig. 1.10 *Exfoliation of graphite into few layer graphene via Intercalation of Li^+ Complexes [77].*

The one-step process for the production of high quality thin graphene films from a rapid electrochemical exfoliation has been reported by Su et al. [78] (Fig. 1.11). Their findings show that the lateral size of the exfoliated graphene sheets is in the range of several up to 30 μm, which significantly reduces the number of intersheet junctions for making percolative transparent conductive films.
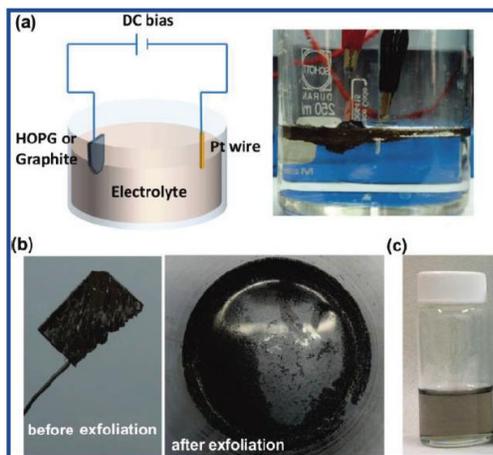
Fig. 1.11 *(a) Schematic illustration and photo for electrochemical exfoliation of graphite. (b) Photos of the graphite flakes before and after electrochemical exfoliation. (c) Photo of the dispersed graphene sheets in a DMF solution [78].*
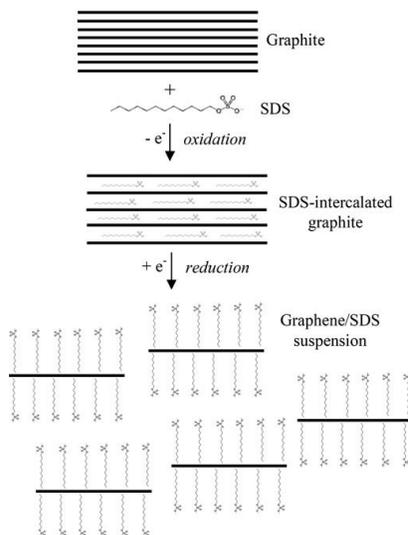

Fig. 1.12 *Representative view of electrochemical route to produce graphene/SDS suspension [70].*

Alanyalıoğˇ lu et al. [79] employed a two steps electrochemical route with a three electrodes system for the production of graphene sheets (Fig. 1.12); first

step is the electrochemical intercalation of SDS into graphite and electrochemical exfoliation of a SDS-intercalated graphite electrode is the second one. This tow-step process yielded a stable colloidal graphene/SDS suspension.

In the first part of this research, Graphene sheets were produced by elechtrochemical method and then in the second part of our experiments, we focused on usage and application of the graphene sheets produced by electrochemical way. Recent advances in the bulk production of the exfoliated GSs from graphite bring the possibility of GSs application in the molecular gas sensors [80], energy storage materials [81] and composite materials [82]. Also, the synergistic combination of the high specific surface area and strong nano-filler-matrix adhesion as well as the exceptional mechanical properties of the sp^2 carbon network in GSs [83] improves the mechanical properties of polymer nanocomposites [82]. On the other hand, the electrochemical production of graphene sheets in the presence of a surfactant is known as one of the facile and controllable method for the fabrication of high quality and stable GSs in a large scale.

Graphene can be well dispersed in poly (styrene), poly (acrylonitrile) and poly (methyl methacrylate) matrices and accordingly it improves the Young's modulus and the ultimate strength [84, 91]. For instance, Liang evaluated the molecular-level dispersion of the graphene oxide sheets in PVA matrix and observed a 62% and 76% increase in the young's modulus and tensile strength, respectively [85]. Additionally, Zhao and co-workers reported 150% improvement in the tensile strength and a nearly 10 times increase in Young's modulus of the PVA/GSs nanocomposite loaded by 1.8 vol% GSs [86]. It is worthy of note that in the electrochemical method the re-stacking and agglomeration of the obtained GSs is prevented by the use of surfactants; this results in an

efficient dispersion of GSs which is beneficial in the development of some composites as the reinforcement species [94].

It should be noted that the product of the electrochemical method is a mixture of mono and multilayer GSs and according to Gong and co-workers report, there is a relation between the layer numbers of GSs and reinforcing role of them in polymer matrix. Gong and co-workers have shown that the optimum layer numbers of GSs for reinforcing polymers is related to the polymer layer thickness. According to their results by increasing the polymer layer thickness, maximum composite modulus will obtain by multi-layer GSs (Fig. 1.13) [87].
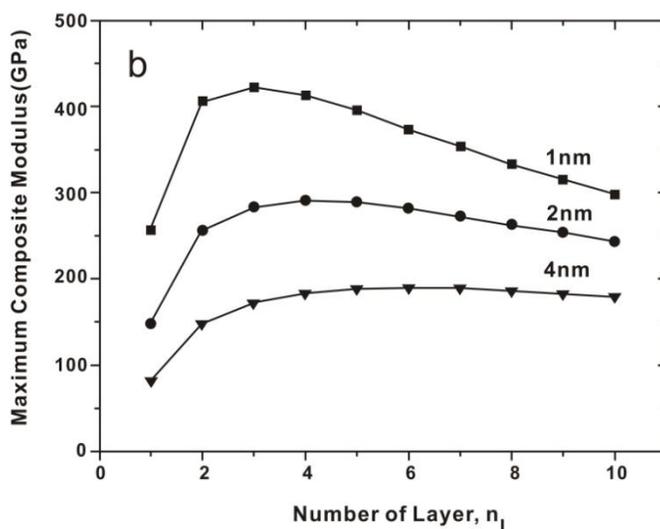

Fig. 1.13 *Maximum nanocomposite modulus predicted for different indicated polymer layer thicknesses as a function of the number of layers, n_l, is the number of graphene flakes [87].*

In fact, multi-layer SWGSs limit the viscose movement of the polymer chains and improve the elastic movements of them. Thus, for each polymer matrix the gyration radius and its relation with the number of GS's layers should be considered. As a result, it is rational that the SWGSs produced by electrochemi-

cal method be a perfect candidate to improve mechanical properties of the polymers with big gyration radius like PVA.