Graphene based materials: Past, present and future

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\textbf{A B S T R A C T}

Graphene, a two dimensional monoatomic thick building block of a carbon allotrope, has emerged as an exotic material of the 21st century, and received world-wide attention due to its exceptional charge transport, thermal, optical, and mechanical properties. Graphene and its derivatives are being studied in nearly every field of science and engineering. Recent progress has shown that the graphene-based materials can have a profound impact on electronic and optoelectronic devices, chemical sensors, nanocomposites and energy storage. The aim of this review article is to provide a comprehensive scientific progress of graphene to date and evaluate its future perspective. Various synthesis processes of single layer graphene, graphene nanoribbons, chemically derived graphene, and graphene-based polymer and nano particle composites are reviewed. Their structural, thermal, optical, and electrical properties were also discussed along with their potential applications. The article concludes with a brief discussion on the impact of graphene and related materials on the environment, its toxicological effects and its future prospects in this rapidly emerging field.

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\textbf{Contents}

1. Introduction .......................................................................................................................... 1181
2. History of graphene ............................................................................................................. 1181

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Nomenclature

Acronyms

AFM  atomic force microscopy
APTS  3-aminopropyltriethoxysilane
ATRP  atom transfer radical polymerization
CB  Coulomb blockade
CCG  chemically converted graphene
CNT  carbon nanotube
CRG  chemically reduced graphene oxide
CVD  chemical vapor deposition
DCC  N,N-dicyclohexylcarbodiimide
DGU  density gradient ultracentrifugation
DMF  N,N-dimethylformamide
DMSO  dimethyl sulfoxide
DP  Dirac point
EBL  electron-beam lithography
ECL  electrogenerated chemiluminescence
EDC  1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide
FET  field effect transistors
FQM  fluorescence quenching microscopy
GNR  graphene nanoribbon
GO  graphene oxide
GQD  graphene quantum dot
HATU  2-(7-aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate
HRTEM  high resolution transmission electron microscopy
ITO  indium tin oxide
LB  Langmuir-Blodgett
LED  light emitting diode
MOSFET  metal oxide semiconductor FET
NMP  N-methyl-2-pyrrolidone
NMR  nuclear magnetic resonance
NPs  nanoparticles
P3HT  poly(3-hexylthiophene)
PAH  polycyclic hydrocarbons
PAN  Polyacrylonitrile
PEN  poly (ethylene-2,6-naphthalate)
PET  polyethylene terephthalate
PECVD  plasma enhanced chemical vapor deposition
PL  photoluminescence
PMMA  poly(methylmethacrylate)
PS  polystyrene
PSS  poly(sodium 4-styrenesulfonate)
PU  polyurethane
PVA  poly(vinyl alcohol)
PVC  poly(vinyl chloride)
QD  quantum dot
QHE  quantum Hall effect
RGO  reduced graphene oxide
SC  sodium cholate
SEM  scanning electron microscope
SLG  single layer graphene
STEM  scanning transmission electron microscopy
STM  scanning tunneling microscopy
TBA  Tetrabutylamomium
1. Introduction

The 5th of October, 2010 was another beautiful day at Partin Elementary School in Oviedo. When Kaleb, a 6 year old kindergartener, took out his pencil and started writing letters on a piece of paper, he did not realize that he was using a material that caught the attention of all scientific community that same day. The Nobel Prize in Physics 2010 was awarded to Andre Geim and Konstantin Novoselov “for ground breaking experiments regarding the two-dimensional material graphene”, a layer of graphite in the pencil. Graphene, one of the allotropes (carbon nanotube, fullerene, diamond) of elemental carbon, is a planar monolayer of carbon atoms arranged into a two-dimensional (2D) honeycomb lattice with a carbon–carbon bond length of 0.142 nm [1]. Electrons in graphene behave like massless relativistic particles, which contribute to very peculiar properties such as an anomalous quantum Hall effect and the absence of localization [2,3]. Graphene [2] has demonstrated a variety of intriguing properties including high electron mobility at room temperature (250,000 cm²/Vs) [4,5] exceptional thermal conductivity (5000 W m⁻¹ K⁻¹) [6] and superior mechanical properties with Young’s modulus of 1 TPa [7]. Its potential applications include single molecule gas detection, transparent conducting electrodes, composites and energy storage devices such as supercapacitors and lithium ion batteries [7–20]. In addition, a distinct band gap can be generated as the dimension of graphene is reduced into narrow ribbons with a width of 1–2 nm, producing semiconductive graphene with potential applications in transistors [8–10]. There is no doubt that graphene has risen as a shining star in the horizon on the path of the scientists’ searching for new materials for future electronic and composite industry. This review article narrates the brief history of graphene related research, and presents the synthesis of graphene and its derivatives and various characterization techniques pertaining to 2D structure. Many extraordinary properties of graphene such as electrical, mechanical, anomalous quantum Hall effect, thermal, and optical are discussed. These properties have generated tremendous interest among material researchers. The recent applications in various fields such as in large scale assembly and field effect devices, sensors, transparent electrodes, photodetectors, solar cells, energy storage devices, polymer composites, nanocomposites will be reviewed with a brief update on toxicology. The conclusion and outlook summarizes the research activities and presents the possible future research directions.

2. History of graphene

Although the usage of graphite started 6000 years ago, when Marican in Europe used it to decorate pottery, the research about graphene, essentially an isolated single-atom plane of graphite, dates back to the 1960s when surprisingly higher basal-plane conductivity of graphite intercalation compounds were discovered compared to that of the original graphite [11–13]. While the scientific community was excited about the discovery that might lead to a lighter, cheaper substitute for existing metal conductors, they were puzzled by the cause of the high conductivity of graphite intercalation compounds and cautious about the future applications. The research of graphene has grown slowly in late 20th century with the hope to observe superior electrical properties from thin graphite or graphene layers while obtaining graphene was considered to be a formidable task in both theoretical and experimental aspect. In the graphite intercalation systems, large molecules were inserted between atomic planes, generating isolated graphene layers in a three-dimensional matrix. The subsequent removal of the larger molecules produced a mixture of stacked or scrolled graphene layers without the control of the
structure. It was generally believed that, based on both theoretical calculation and experimental observation, 2D materials did not exist without a 3D base. \textit{Ab initio} calculations showed that a graphene sheet was thermodynamically unstable with respect to other fullerene structures if its size was less than about 20 nm (“graphene is the least stable structure until about 6000 atoms” and becomes the most stable one (as within graphite) only for sizes larger than 24,000 carbon atoms) \cite{14}. Various attempts were made to synthesize graphene including using the same approach for the growth of carbon nanotubes (producing graphite with 100 layers of graphene) \cite{15}, chemical vapor deposition on metal surfaces (a few layers of graphene) \cite{16,17}, or the thermal decomposition of SiC \cite{18}. Although these approaches did not produce perfect monolayer graphene, the studies showed high-charge mobility of a few layers of graphene and the CVD approach has been optimized and become a major technique to produce graphene nowadays \cite{19–21}. It was until 2004 that Andre Geim and Konstantin Novoselov used a method to isolate graphene, a method similar to what young Kaleb did, drawing with a piece of graphite or peeling graphite with adhesive tape till the graphene is found. Such a “kindergarten” approach can provide high quality graphene with size in hundreds of microns \cite{22}. These high quality graphene crystals realize the investigation of their amazing properties. Since then, the research of graphene including the control of the graphene layers on substrates, functionalizing graphene and exploring the applications of graphene has grown exponentially. As shown in Fig. 2.1, the number of publications on graphene (according to ISI Web of Knowledge) increases dramatically after 2004.

The term of “graphene” was recommended by the relevant IUPAC commission to replace the older term “graphite layers” that was unsuitable in the research of single carbon layer structure, because a three-dimensionally (3D) stacking structure is identified as “graphite”. The recent definition of graphene can be given as a two-dimensional monolayer of carbon atoms, which is the basic building block of graphitic materials (i.e. fullerene, nanotube, graphite).

3. Synthesis of graphene

3.1. Exfoliation and cleavage

Recent studies showed that graphite nanoplatelets (GNP) or graphene could be used as a viable and inexpensive filler substitute for carbon nanotubes (CNT) \cite{23} in nanocomposites owing to the
excellent in-plane mechanical, structural, thermal and electrical properties of graphite [24]. It is obvious that these excellent properties are relevant at the nanoscale and the manufacture of the conducting nanocomposites is highly dependent on the exfoliation of the graphite down to single graphene sheet in the matrices. However, the challenge remained to achieve complete and homogeneous dispersion of individual graphene sheets in various solvents [25]. Like CNT and other nanomaterials, the key challenge in synthesis and processing of bulk-quantity graphene sheets is aggregation. Graphene, a one-atom-thick planar sheet of sp$^2$-bonded carbon atoms densely packed in a honeycomb crystal lattice has very large specific surface area. Unless well separated from each other, graphene tends to form irreversible agglomerates or even restack to form graphite through Van der Waals interactions. The prevention of aggregation is essential for graphene sheets because most of their unique properties are only associated with individual sheets.

3.1.1. Mechanical exfoliation in solutions

Mechanical exfoliation is a simple peeling process where a commercially available highly oriented pyrolytic graphite (HOPG) sheet was dry etched in oxygen plasma to many 5 mm deep mesa (Fig. 3.1). The mesa was then stuck onto a photoresist and peeled off layers by a scotch tape. The thin flakes left on the photoresist were washed off in acetone and transferred to a silicon wafer. It was found that these thin flakes were composed of monolayer or a few layers of graphene. While the mechanical exfoliation of graphene used by Geim and coworkers [22] led to numerous exciting discoveries of graphene electronic and mechanical properties, such approach is limited by its low production.

On the other hand, although chemical oxidation of graphite and the subsequent exfoliation provide large amount of graphite oxide monolayer, the invasive chemical treatment inevitably generates structural defects as indicated by Raman spectroscopic studies [26,27]. These structural defects disrupted the electronic structure of graphene and change it to semiconductive. The subsequent chemical reduction or thermal annealing (up to 1000 °C) are virtually impossible to regenerate the graphene structures as indicated by XPS studies [28]. Therefore, physical exfoliation approaches are desirable where it is required to maintain the graphene structure. Blake et al. and Hernandez et al. have demonstrated that graphite could be exfoliated in N-methyl-pyrrolidone to produce defect-free monolayer graphene [29,30]. Such approach utilizes the similar surface energy of N-methyl-pyrrolidone and graphene that facilitates the exfoliation. However, the disadvantage of this process is the high cost of the solvent and the high boiling point of the solvent that makes the following graphene deposition difficult. Lotya and coworkers have used a surfactant (sodium dodecylbenzene sulfonate, SDBS) to exfoliate graphite in water to produce graphene. The graphene monolayers are stabilized against aggregation by a relatively large potential barrier caused by the Coulomb repulsion between surfactant-coated sheets. The dispersions are reasonably stable with larger flakes precipitating out

![Scotch tape method of making graphene from HOPG.](image-url)
over more than 6 weeks [31]. Similarly, Green and Hersam have used sodium cholate as a surfactant to exfoliate graphite and moved further to isolate the resultant graphene sheets with controlled thickness using density gradient ultracentrifugation (DGU) (Fig. 3.2). Since the exfoliation of the graphite yielded a dispersion of monolayer graphene and graphite with a few layers of graphene which have different buoyant density, DGU separations of such mixture produce graphene sheets with mean thicknesses that increase as a function of their buoyant density (Fig. 3.3) [32].

### 3.1.2. Intercalation of small molecules by mechanical exfoliation

Agglomeration in graphite can be reduced appreciably by incorporating small molecules between the layers of graphite or by non-covalently attaching molecules or polymers onto the sheets, generating graphite intercalation compounds (GICs). In GICs, the graphite layers remains unaltered with guest molecules located in the interlayer galleries. When the layers of graphite interact with the guest molecules by charge transfer, the in-plane electrical conductivity generally increases but when the molecules form covalent bonds with the graphite layers as in fluorides or oxides the conductivity decreases as the conjugated sp$^2$ system is disrupted. The first graphite intercalation compound, (GIC), or commonly known as expandable graphite was prepared by Schafhautl in 1841 while analyzing crystal flake of graphite in sulfuric acid solution. In the laboratory, flake graphite was subjected to shear intensive mechanical stirring with ultrasonic solvent in the ultrasonic cleaning bath at room
temperature to prepare expandable graphite. Experimental conditions could be tuned by changing ultrasonic solvent, ultrasonic power (nominal power of 500 W and 250 W) and ultrasonic time. After the treatment, the mixture was washed thoroughly with water to neutrality and dried below 60°C for 60 min. The expandable graphite was then expanded at 900°C to obtain the expanded graphite (EG).

The choice of ultrasonic solvent depended on the oxidation ability and water content of the solvents, which affected the volume of expanded graphite. Acetic acid, acetic acid anhydride, concentrated sulfuric acid and hydrogen peroxide were the examples of few ultrasonic solvents. Among all those, concentrated sulfuric acid had been proved to be the best ultrasonic solvent to provide optimum condition for preparing the expandable graphite with ultrasound irradiation. Such sulfuric acid intercalated graphite compound consisted of layers of hexagonal carbon structure within which H2SO4 was intercalated. EG could be prepared either by oxidation with a chemical reagent or electrochemically in the intercalating acid [33,34]. Graphite could expand up to a hundred times in volume at high temperature [35] due to the thermal expansion of the evolved gases trapped between the graphene sheets. So it was reasonably assumed that oxidants and other molecules could enter in the interlayer space of EG more easily compared to natural graphite. The influence of ultrasonic solvent and ultrasonic power on the volume of expanded graphite could be analyzed from the data listed in Table 3.1.

Li et al. reported the exfoliation–reintercalation–expansion of graphite to produce high quality single layer graphene sheets stably suspended in organic solvents [36]. Commercial expandable graphite was subjected to brief heating (60s) at 1000 °C in forming gas. It was then grounded with NaCl crystals and reintercalated with oleum. The exfoliated graphite was then dispersed in N,N-dimethylformamide (DMF) and treated with tetrabutylammonium (TBA). TBA could insert into and increase the distance between adjacent layers of graphite facilitating the separation of graphene sheets in surfactant solutions. The reintercalation and the rapid, brief heating of EG enabled the preparation of highly conducting graphene sheets without functionalizing the graphite.
3.2. Chemical vapor deposition (CVD)

3.2.1. Thermal CVD

Besides mechanical exfoliation and chemical reduction methods to produce graphene sheets, several promising approaches including epitaxial growth from SiC, and chemical vapor deposition (CVD) on metal surfaces have been reported. Among them, the CVD growth appears to be the most promising technique for large-scale production of mono- or few-layer graphene films. Although the formation of “monolayer graphite” was mentioned in early CVD studies on metal single crystals [37–39], the first successful synthesis of few-layer graphene films using CVD was reported in 2006 by Somani and coworkers using camphor as the precursor on Ni foils [40]. This study opened up a new graphene synthesis route with several unsolved issues like controlling the number of layers, and minimizing the folding of graphene. Since then, much progress has been made to obtain graphene layers on several types of metal substrates with controlled thickness [26,41–47]. After a chemical etching of the metal substrate, the graphene layers detach and can be transferred to another substrate, providing high quality graphene layers without complicated mechanical or chemical treatments.

The growth mechanism of graphene on substrates with mediate-high carbon solubility (>0.1 atomic %) such as Co and Ni is through the diffusion of the carbon into the metal thin film at the growth temperature and the subsequent precipitation of carbon out of the bulk metal to metal surface upon the cooling [43,48]. A typical CVD process (i.e. using Ni as a substrate) involves dissolving carbon into the nickel substrate followed by a precipitation of carbon on the substrate by cooling the nickel. The Ni substrate is placed in a CVD chamber at a vacuum of 10⁻³ Torr and temperature below 1000 °C with a diluted hydrocarbon gas. The deposition process starts with the incorporation of a limited quantity of carbon atoms into the Ni substrate at relatively low temperature, similar to the carburization process. The subsequent rapid quenching of the substrate caused the incorporated carbon atoms to out-diffuse onto the surface of the Ni substrate and form graphene layers. Therefore, the thickness and crystalline ordering of the precipitated carbon (graphene layers) is controlled by the cooling rate and the concentration of carbon dissolved in the nickel which is determined by the type and concentration of the carbonaceous gas in the CVD, and the thickness of the nickel layer.

In contrast, the graphene growth on low carbon solubility (<0.001 atomic %) substrate like Cu mainly happens on the surface through the four-step process described by Li and coworkers as following [49]:

1. Catalytic decomposition of methane on Cu to form CₓHᵧ upon the exposure of Cu to methane and hydrogen. In this process, the Cu surface is either undersaturated, saturated, or supersaturated with CₓHᵧ species, depending on the temperature, methane pressure, methane flow, and hydrogen partial pressure.
2. Formation of nuclei as a result of local supersaturation of CₓHᵧ where undersaturated Cu surface does not form nuclear.
3. Nuclei grow to form graphene islands on Cu surface saturated, or supersaturated with CₓHᵧ species.
4. Full Cu surface coverage by graphene under certain temperature (T), methane flow rate (JₓMe), and methane partial pressure (PₓMe).

Table 3.1
The influence of ultrasonic solvent and ultrasonic power on the volume of expanded graphite.

<table>
<thead>
<tr>
<th>Ultrasonic power (W)</th>
<th>Ultrasonic solvents</th>
<th>Ultrasonic time (min)</th>
<th>Expanded volume (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>Acetic acid</td>
<td>60</td>
<td>150</td>
</tr>
<tr>
<td>500</td>
<td>Conc. sulfuric acid</td>
<td>60</td>
<td>500</td>
</tr>
<tr>
<td>500</td>
<td>Alcohol</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>250</td>
<td>Hydrogen peroxide</td>
<td>60</td>
<td>140</td>
</tr>
<tr>
<td>250</td>
<td>Acetic acid</td>
<td>60</td>
<td>140</td>
</tr>
<tr>
<td>250</td>
<td>Conc. sulfuric acid</td>
<td>60</td>
<td>380</td>
</tr>
<tr>
<td>250</td>
<td>Alcohol</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td>250</td>
<td>Hydrogen peroxide</td>
<td>60</td>
<td>100</td>
</tr>
</tbody>
</table>
If the amount of available $C_3H_6$ on the exposed Cu surface is insufficient to expand the C to the island edges, the Cu surface is only partially covered with graphene islands. Otherwise, if there is always enough methane to form sufficient $C_3H_6$ to drive the reaction between the $C_3H_6$ at the surface and the edges of graphene islands, graphene islands would grow until to connect neighboring islands and fully cover the Cu surface. With the understanding of the graphene growth mechanism, various approaches were applied to control the graphene growth rate to obtain monolayer graphene. Lee and coworkers have used SiO$_2$/Si substrates, coated with 300 nm thick Ni or 700 nm thick Cu to produce graphene layers [47]. The average number of graphene layers grown on a Ni catalyst ranged from three to eight, depending on the reaction time and cooling rates. On the other hand, the mono- and bilayer graphene grows predominantly on a Cu catalyst. The low solubility of carbon in Cu is believed to induce the self-limiting graphene growth process [44]. To prevent the formation of multilayer graphene on medium-high carbon solubility (>0.1 atomic %) substrates such as Co and Ni, the thin layers of Ni of thickness less than 300 nm were deposited on SiO$_2$/Si substrates to produce graphene monolayer [43]. Recently, Bae and coworkers reported a roll-to-roll production of 30-inch graphene films using the CVD approach [50]. Their fabrication process including three steps after the synthesis of graphene on copper substrates: (i) adhesion of polymer supports to the graphene on the copper foil; (ii) etching of the copper layers; and (iii) release of the graphene layers and transfer onto a target substrate (Fig. 3.4). The obtained graphene monolayer films have sheet resistances as low as ~125 Ω/square with 97.4% optical transmittance, and exhibit the half-integer quantum Hall effect, indicating their high quality. In addition, a layer-by-layer stacking of doped four-layer film has sheet resistance as low as ~30 Ω/square with ~90% transparency, demonstrating great potential to replace commercial transparent electrodes such as indium tin oxides.

An interesting feature of the CVD approach to synthesize graphene is the possibility for substitutional doping by introducing other gases, such as NH$_3$, during the growth [51–53]. The nitrogen atoms can be doped into graphene as “pyridinic”, “graphitic” and “pyrrolic” forms. These nitrogen doped graphene (N-graphene) layers have demonstrated interesting properties. For example, Dai’s group have used nitrogen doped graphene for oxygen reduction in fuel cells where the N-graphene electrode demonstrate a steady-state catalytic current to be calculated three times higher than the Pt/C electrode over a large potential range. The long-term stability, tolerance to crossover, and poison effect of the N-graphene electrode are also better than Pt/C for oxygen reduction in alkaline electrolyte [52]. Reddy and coworkers have reported that the reversible discharge capacitance of N-graphene

![Fig. 3.4](image_path)
in lithium ion batteries is almost double compared to pristine graphene because the surface defects induced by nitrogen doping [53].

3.2.2. Plasma enhanced CVD

Plasma enhanced chemical vapor deposition (PECVD) offers another route of graphene synthesis at a lower temperature compared to thermal CVD. Thick graphite structures were observed during the fabrication of “nanostructured graphite-like carbon” using a dc discharge PECVD. The first report of the production of mono- and few layer of graphene by PECVD involved a radio frequency PECVD system to synthesize graphene on a various substrates where graphene sheets were produced from a gas mixture of 5–100% CH₄ in H₂ (total pressure 12 Pa), at 900 W power and 680 °C substrate temperature [54,55]. Since then, much effort have been devoted to understand the graphene growth mechanism and to optimize experimental conditions to control the thickness of graphene films [56–58]. The advantages of the plasma deposition include very short deposition time (<5 min) and a lower growth temperature of 650 °C compared to the thermal CVD approach (1000 °C). The growth mechanism involved a balance between the graphene deposition through the surface diffusion of C-bearing growth species from precursor gas and etching caused by atomic hydrogen. The verticality of the graphene sheets, produced through this method, is caused by the plasma electric field direction [56,58].

3.2.3. Thermal decomposition on SiC and other substrates

Producing graphite through ultrahigh vacuum (UHV) annealing of SiC surface has been an attractive approach especially for semiconductor industry because the products are obtained on SiC substrates and requires no transfer before processing devices [18,59–61]. When SiC substrate is heated under UHV, silicon atoms sublimate from the substrate. The removal of Si leaves surface carbon atoms to rearrange into graphene layers. The thickness of graphene layers depends on the annealing time and temperature. The formation of “few-layer graphene” (FLG) typically requires few minutes annealing of the SiC surface at temperature around 1200 °C [62]. More recently, vapor phase annealing has been used to produce FLG on SiC. At the expense of a higher temperature (typically 400 °C above UHV temperature), [63] this method leads to the formation of FLG on SiC with an improved thickness homogeneity [64]. Although producing graphene on SiC substrates is attractive, several hurdles prevent the real application. For example, control the thickness of graphene layers in the routine production of large area graphene is very challenging. Another uncertainty involves the different epitaxial growth patterns on different SiC polar face (i.e. Si-face or C-face). Unusual rotational graphene stacking were observed in multilayers graphene grown on the C-face surface but not on Si-face surface. Such mismatch of graphene growth process has profound effects on the physical and electronic properties of epitaxial graphene. On the C-face, the “twisted” interface leads to the decoupling between different layers of graphene, each of which behaves as a single layer [65]. However, the electronic properties of graphene multilayers on Si-face remains controversial [59]. Future investigation is required to understand the mechanisms of the growth processes. The third issue is to understand the relationship between the structure and electronic properties of the interface layer between graphene and substrate [61].

The similar approach was applied to other metallic substrates to grow graphene layers. The (0001) faces of ruthenium (Ru) crystals were used under UHV to produce epitaxial graphene layers where a very sparse graphene nucleation at high temperatures allowed a linear dimensions growth of macroscopic single-crystalline domains [66,67]. It was found that the first graphene layer coupled strongly to the Ru substrate, while the second layer was free of the substrate interaction and had the similar electronic structure to free-standing graphene. Other metal substrates including Ir, Ni, Co, and Pt have been employed to produce graphene layers and was nicely reviewed by Wintterlin and Bocquet [68].

3.3. Chemically derived graphene

3.3.1. Synthesis of graphene oxide and the reduction

At present, chemical conversion of graphite to graphene oxide has emerged to be a viable route to afford graphene-based single sheets in considerable quantities [69–73]. Graphite oxide (GO) is usually
synthesized through the oxidation of graphite using oxidants including concentrated sulfuric acid, nitric acid and potassium permanganate based on Hummers method [74]. Compared to pristine graphite, GO is heavily oxygenated bearing hydroxyl and epoxy groups on sp$^3$ hybridized carbon on the basal plane, in addition to carbyl and carboxyl groups located at the sheet edges on sp$^2$ hybridized carbon. Hence, GO is highly hydrophilic and readily exfoliated in water, yielding stable dispersion consisting mostly of single layered sheets (graphene oxide). It is important to note that although graphene oxide and graphene oxide share similar chemical properties (i.e. surface functional group), their structures are different. Graphene oxide is a monolayer material produced by the exfoliation of GO. Sufficiently dilute colloidal suspension of graphene oxide prepared by sonication are clear, homogeneous and stable indefinitely. AFM images of GO exfoliated by the ultrasonic treatment at concentrations of 1 mg/ml in water always revealed the presence of sheets with uniform thickness (≈1 nm). The pristine graphene sheet is atomically flat with the Van der Waals thickness of ≈0.34 nm, graphene oxide sheets are thicker due to the displacement of sp$^3$ hybridized carbon atoms slightly above and below the original graphene plane and presence of covalently bound oxygen atoms. A similar degree of exfoliation of GO was also attained for N,N-dimethylformamide (DMF), tetrahydrofuran (THF), N-methyl-2-pyrrolidone (NMP) and ethylene glycol [75]. Li et al. showed that the surface charges on graphene oxide are highly negative when dispersed in water by measuring the zeta potential due to the ionization of the carboxylic acid and the phenolic hydroxyl groups [76]. Therefore, the formation of stable graphene oxide colloids in water was attributed to not only its hydrophilicity but also the electrostatic repulsion.

The chemical structure of graphene oxide such as the type and distribution of oxygen-containing functional groups have been studied using NMR $^{13}$C-labelled graphene oxide [77,78] suggesting that the basal plane of the sheet is decorated with hydroxyl and epoxy (1,2-ether) functional groups with small amount of lactol, ester, acid and ketone carbyl groups at the edge. These results are in good agreement with the model proposed by Lerf–Klinowski [79,80] and Dékány Models with small modification [81]. These functional groups provide reactive sites for a variety of surface-modification reactions to develop functionalized graphene oxide- and graphene-based materials. On the other hand, due to the disruption of the conjugated electronic structure by these functional groups, graphene oxide was electrically insulating and contained irreversible defects and disorders [26,82], but chemical reduction of graphene oxide could partially restore its conductivity [26,82,83] at values orders of magnitude below that of pristine graphene.

Chemical reduction of graphene oxide sheets has been performed with several reducing agents including hydrazine [27,28,73,84], and sodium borohydride [83,85]. Hydrazine hydrate, unlike other strong reductants, does not react with water and was found to be the best one in producing very thin and fine graphite-like sheets. During the reduction process, the brown colored dispersion of graphene oxide in water turned black and the reduced sheets aggregated and precipitated [26,82]. The reduced graphene oxide became less hydrophilic due to the removal of oxygen atoms and thus precipitated. The reason of re-establishment of the conjugated graphene network could be attributed to the attraction pathway proposed by Stankovich et al. (Fig. 3.5) [26]. Hydrazine takes part in ring-opening reaction with epoxides and forms hydrazino alcohols [86]. This initial derivative reacts further via the formation of an aminoaziridine moiety which undergoes thermal elimination of dimide to form a double bond. Li and coworkers demonstrated the preparation of stable aqueous suspension of reduced graphene oxide nanosheets by adjusting the pH (with ammonia solution) of the aqueous solution during reduction with hydrazine [76]. The carboxylic acid groups were unlikely to be reduced by hydrazine and thus remained intact after hydroxyl reduction. The adjustment of pH with ammonia solution deprotonated the carboxylic acid groups and thus the electrostatic repulsion among the charged groups on reduced graphene oxide enabled the formation of well-dispersed graphene colloids in water without any stabilizers. But, unless stabilized by selected surfactants, reduced graphene in organic solvent tend to agglomerate due to their hydrophobic nature [26,82]. Another possible route to reduce GO was using sodium borohydride (NaBH$_4$) [83] in aqueous solution where sodium borohydride is more effective than hydrazine as a reductant of graphene oxide although it can be slowly hydrolyzed by water. Such reduction produced reduced graphene oxide with sheet resistances as low as 59 kΩ/square (compared to 780 kΩ/square for a hydrazine reduced sample, measured in the same study), and C:O ratios were as high as 13.4:1 (compared to 6.2:1 for hydrazine). The NaBH$_4$ treatment
eliminated all the parent oxygen containing groups and the resultant solid became IR inactive like pure graphite. Carbon elemental analysis revealed the evidence for the complete reduction of graphene oxide in this process [83,85]. Other chemical reduction routes including using hydroquinone [87], gaseous hydrogen (after thermal expansion) [88], and strongly alkaline solutions [89] have also been investigated. While the reduction by hydrogen proved to be effective (C:O ratio of 10.8–14.9:1), hydroquinone and alkaline solutions were not as effective as hydrazine and sodium borohydride based on semi-quantitative results.

Thermal reduction is another approach to reduce GO to reduced graphene oxide that utilizes the heat treatment to remove the oxide functional groups from graphene oxide surfaces. Aksay’s group have exfoliate and reduce stacked GO by heating GO to 1050 °C where oxide functional groups were extruded as carbon dioxide [71,90]. The authors reported that the exfoliation took place when the decomposition rate of the epoxy and hydroxyl sites of graphite oxide exceeded the diffusion rate of the evolved gases, thus yielding pressures that exceeded the Van der Waals forces holding the graphene sheets together. It was calculated that the pressure of 2.5 MPa was required to separate GO sheets by numerically evaluating the Hamaker constant while the pressure generated during the exfoliation was 1–2 orders of magnitude higher. Although the thermal reduction/exfoliation can produce 80% single layer reduced graphene oxide according to the AFM studies, the removal of the oxide groups caused about 30% mass loss and left behind vacancies and structural defects which may affect the mechanical and electrical properties of reduced graphene oxide. Nevertheless, the bulk conductivities

![Figure 3.5](image-url)
of the products was measured to be 1000–2300 S/m, suggesting the effective reduction and restoration of electronic structures from GO [71]. Recently, Dubin et al. reported a simple one-step, solvothermal reduction method to produce reduced graphene oxide dispersion in organic solvent [91]. The deoxygenation of GO resulted from both thermal deoxygenation at 200 °C when refluxing GO in N-methyl-2-pyrrolidinone (NMP) along with a concomitant reaction of GO with NMP molecules. The solvothermally reduced graphene oxide layers remained in a stable dispersion after the reaction.

This approach provides a simple, low-temperature method to produce reduced graphene oxide.

3.3.2. Surface functionalization of graphene oxide (GO)

The surface functionalization of graphene oxide not only plays an important role in controlling exfoliation behavior of graphene oxide and reduced graphene oxide but also holds the key to the gate leads to various applications. The surface functionalization has taken two approaches: covalent functionalization and non-covalent functionalization. In covalent functionalization, oxygen functional groups on graphene oxide surfaces, including carboxylic acid groups at the edge and epoxy/hydroxyl groups on the basal plane can be utilized to change the surface functionality of graphene oxide. Graphene oxide had been treated with organic isocyanates to give a number of chemically modified GO. Treatment of isocyanates reduced the hydrophilicity of graphene oxide by forming amide and carbamate esters from the carboxyl and hydroxyl groups of graphene oxide, respectively. Consequently, isocyanate modified graphene oxide readily formed stable dispersion in polar aprotic solvents giving completely exfoliated single graphene sheets with thickness of ~1 nm (Fig. 3.6). This dispersion also facilitated the intimate mixing of the graphene oxide sheets with matrix polymers, providing a novel synthesis route to make graphene–polymer nanocomposites. Moreover, modified graphene oxide in the suspension could be chemically reduced in presence of the host polymer to render electrical conductivity in the nanocomposites [92].

In order to use carboxylic acid groups on graphene oxide to anchor other molecules, the carboxylic acid groups have been activated by thionyl chloride (SOCl₂) [93–96], 1-ethyl-3-(3-dimethylaminopropyl)- carbodiimide (EDC) [97], N,N-dicyclohexylcarbodiimide (DCC) [98], or 2-(7-aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU) [99]. The subsequent addition of nucleophilic species, such as amines or alcohols, produced covalently attached functional groups

![Fig. 3.6. Isocyanate treatment of GO where organic isocyanate reacts with the hydroxyl and carboxyl groups of the graphene oxide sheets.](image-url)
on graphene oxide via the formation of amides or esters. The resultant amine functionalized graphene oxide has demonstrated various applications in optoelectronics [93,95,96], drug-delivery materials [97], biodevices [99], and polymer composites [98,100]. The attachment of hydrophobic long, aliphatic amine groups on hydrophilic graphene oxide improved the dispersability of modified graphene oxide in organic solvents [94], while porphyrin-functionalized primary amines and fullerene-functionalized secondary amines introduced interesting nonlinear optical properties [95,96]. The amine groups and hydroxyl groups on the basal plane of graphene oxide have also been used to attach polymers through either grafting-onto or grafting-from approaches. To grow a polymer from graphene oxide, an atom transfer radical polymerization (ATRP) initiator (i.e. \( \text{a-bromoibutyrylbromide} \)) was attached to graphene surfaces [101,102]. The following living polymerization produced graphene oxide with polymers that enhanced the compatibility of solvents and other polymer matrices. Besides the carboxylic acid groups, the epoxy groups on graphene oxide can be used to attach different functional groups through a ring-opening reaction. Various amine ending chemicals such as octadecylamine [87], an ionic liquid 1-(3-aminopropyl)-3-methylimidazolium bromide [96] with an amine end group and 3-amino propyltriethoxysilane (APTS) have reacted with epoxy groups.

The non-covalent functionalization of graphene oxide utilizes the weak interactions (i.e. \( \pi-\pi \) interaction, Van der Waals interactions and electrostatic interaction) between the graphene oxide and target molecules. The sp\(^2\) network on graphene oxide provides \( \pi-\pi \) interactions with conjugated polymers and aromatic compounds that can stabilize reduced graphene oxide resulted from chemical reduction and produce functional composite materials. The conjugated polymers and aromatic compounds include poly(sodium 4-styrenesulfonate) (PSS) [82], sulfonated polyaniline [103], poly(3-hexylthiophene) (P3HT) [104], conjugated polyelectrolyte [105], 7,7,8,8-tetracyanoquinodimethane anion [106], tetrasulfonate salt of copper phthalocyanine (TSCuPc) [107], porphyrin [108,109], pyrene and perylenediimide decorated with water-soluble moieties [110], and cellulose derivatives [111]. During the chemical reduction of graphene oxide, reduced graphene oxide nanosheets are stabilized via the \( \pi-\pi \) interaction between aromatic molecules and reduced graphene oxide nanosheets. Aromatic molecules have large aromatic plane and can anchor onto the reduced graphene oxide surface without disturbing its electronic conjugation, providing stability for reduced graphene oxide. For example, the sulfonate groups on TSCuPc introduce negative charges on reduced graphene oxide sheets and stabilize the RGO dispersion, providing single sheets of TSCuPc functionalized RGO for device fabrication. In contrast, irreversible aggregation and precipitation of graphitic sheets occurred upon the reduction of graphene oxide without TSCuPc (Fig. 3.7B inset). Atomic force microscopy (AFM) study (Fig. 3.7) of reduced graphene oxide/TSCuPc composites provides detailed information about the individual layer of the reduced graphene oxide/TSCuPc composite sheets. The cross section analysis in the AFM height image indicates the thickness of the TSCuPc attached RGO sheet to be \( \sim 1.9 \) nm whereas the thickness of a single layer RGO was found to be approximately \( 1 \) nm. Therefore, the AFM height image confirmed the non-covalent attachment of the aromatic molecules on the RGO basal plane through \( \pi-\pi \) interaction. The small dots in the AFM images are aggregates of TSCuPc [107]. Dye-labeled DNA have also been used to functionalize graphene oxide to detect proteins and DNA [112]. The fluorescence of the dye on the reduced graphene oxide was quenched by the substrate. In the presence of a target, the binding between the dye-labeled DNA and target molecule will alter the conformation of dye-labeled DNA, and disturb the interaction between the dye-labeled DNA and graphene oxide. Such interactions will release the dye-labeled DNA from the GO, restoring of dye fluorescence.

### 3.3.3. Structural and physical properties of reduced graphene oxide (RGO)

The optical and electrical properties of reduced graphene oxide depend on the spatial distribution of the functional groups and structural defects. For example, the electron mean free path is limited by the distance between two defective sites represented either by C\(-\text{O}\) or a vacancy [113]. A giant-infrared-absorption band was observed in reduced graphene oxide attributed to the coupling of electronic states to the asymmetric stretch mode of a structure consisting of oxygen atoms aggregated at the edges of defects [114]. Therefore, understanding the molecular structure evolution of the GO structure during reduction is the key to obtain reduced graphene oxide with desired optical and electrical properties. The structures of RGO have been studied both theoretically [115] and experimentally [78,114–118].
Bagri and coworkers used molecular dynamics (MD) simulation to study the atomic structure evolution from graphene oxide to RGO during the thermal annealing process [115]. As the author summarized in the paper, the carbonyl and ether groups on RGO formed from the hydroxyl and epoxy groups on graphene oxide during thermal annealing. Hydroxyl groups desorb at low temperature without altering the graphene basal plane. In contrast, isolated epoxy groups are relatively more stable, and substantially distort the graphene lattice on desorption. The removal of carbon from the graphene plane (generating structural defects) is more likely to occur when the initial hydroxyl and epoxy groups are close to each other. The reaction pathway during thermal annealing between two nearby functional groups leads to the formation of carbonyl and ether groups, which are thermodynamically very stable. These theoretical results are corroborated by FTIR spectroscopy and X-ray photoelectron spectroscopy (XPS) experiments.

A systematic investigation of the electrical and chemical structure evolution was performed on the reduction process via thermal treatment in UHV and in an Ar/H₂ reducing atmosphere on pristine GO thin films and those that were previously treated with hydrazine vapor [116]. The progressive loss of oxygen functional groups after each step of the reduction process was investigated by in situ XPS to reveal the change of carbon and oxygen bonds. It was found that the amount of carbon sp² bonding increased with the loss of oxygen during the annealing process, reaching a maximum value of ~80% at an oxygen content of ~8% (C:O ratio 12.5:1). This suggests that the remaining oxygen is
responsible for ~20% sp\(^3\) bonding and annealing up to 1100 °C is not sufficient to completely remove the oxygen from GO. Raman spectroscopy was also employed to reveal the structural evolution where the oxygen ratio of the D and G bands was used as measure of the size of sp\(^3\) ring clusters in a network of sp\(^3\) and sp\(^2\) bonded carbon. Using the empirical Tuinstra–Koenig relation [119] to obtain the lateral dimension of sp\(^3\) ring clusters, an average graphitic domain size of ~2.5 nm in pristine GO was calculated. After chemical (with hydrazine vapor) reduction and thermal annealing up to 500 °C, the change in the D/G peak area ratio was found to be negligible. A slight decrease in the full width half maxima (FWHM) of the D peak was observed only after annealing at 1100 °C, resulting in an increase in the size of the sp\(^3\) cluster to ~2.8 nm. This observation suggests that even when the sp\(^2\) carbon–carbon bonds are restored by de-oxidation, their spatial distribution in the honeycomb graphene lattice does not generate an expansion of a continuous sp\(^2\) phase. This may be due to the fact that the sp\(^2\) sites are isolated by disordered domains, which is indicated by the TEM studies [117,118]. The conductivity was also measured vs. the sp\(^2\) fraction. The data indicated that the presence of residual oxygen (~8%) significantly hampered the carrier transport among the graphitic domains, and transport at the initial stages of reduction was dominated by hopping or tunneling amongst the sp\(^2\) clusters. At latter stages of reduction, newly formed smaller sp\(^2\) domains connected the original sp\(^2\) clusters so that charge could transport through percolation network. However, carrier transport above the percolation threshold was limited by those clusters that are not perfect graphene crystals.

Erickson et al. have investigated the local chemical structures on graphene oxide and reduced graphene oxide using the TEAM 0.5 TEM (a monochromated aberration-corrected instrument operated at 80 keV) [117]. GO was produced via a modified Hummers method and drop cast onto lacy carbon TEM grids. For RGO specimens, GO-containing grids were reduced in a hydrazine atmosphere and then slowly heated to 550 °C under flowing N\(_2\). The TEM image of graphene oxide (Fig. 3.8) clearly shows the oxidized area (A and B) and unoxidized graphene crystal area (Fig. 3.8c). As explained in the figure caption, hydroxyl groups and epoxy were presented on the graphene oxide basal plane, in good agreement with Lerf–Klinowski [79,80] and Dékány Models [81].

On the other hand, the TEM image of RGO shows the disordered regions (Fig. 3.9A) that are believed to result from the oxidized area being reduced by hydrazine and thermal annealing, and the unoxidized graphene regions.

Similarly, Gomez-Navarro and coworkers have used high resolution transmission electron microscopy (HRTEM) to investigate the structure of reduced graphene oxide monolayers produced from chemical oxidation/reduction of graphite in atomic scale. Defect free graphene domains with sizes of a few nanometers were mixed with defect areas dominated by clustered pentagons and heptagons [120]. The atomic structure of the RGO layers obtained from HRTEM is shown Fig. 3.10 with different regions of the image marked by colors in Fig. 3.10b. The largest portion of the RGO layer is comprised of clean well crystallized graphene areas where the hexagonal lattice is clearly observed (light gray color in Fig. 3.10b). The average size of the visible well-crystallized areas is from 3 to 6 nm, covering ~60% of the surface. The formation of larger holes is caused by electron irradiation, similar to the TEM images of mechanically exfoliated graphene. In contrast to mechanically exfoliated graphene, RGO has a large amount of topological defects within the clean areas. These defects was classified into isolated topological defects, induce strain as well as in-plane and out-of-plane deformations in the surrounding RGO. Isolated topological defects, mostly dislocations, are also present and may have formed as a result of strain. The effects of these defects will have to be taken into account for any comprehensive study of the properties of RGO [120].

Gao et al. have investigated the structural change from graphene oxide to RGO using \(^{13}\)C NMR [78]. In their studies, RGO was produced from graphene oxide through a two-step reduction process—deoxygenation with NaBH\(_4\) (chemically converted graphene, CCG1), followed by dehydration with concentrated...
sulfuric acid (CCG2) and annealing of CCG2 in Ar/H\textsubscript{2} at 1100 °C for 15 min (CCG3). The authors suggested that this process produced graphene with a very low number of remaining functional groups, high conductivity, larger crystallite size and good solubility. The \textsuperscript{13}C NMR studies of graphene oxide illustrated the functional groups, as discussed in previous section while the \textsuperscript{13}C NMR of different reduced materials, indicated that NaBH\textsubscript{4} reduction removed the epoxy groups on the basal plane with the regeneration of C=C bonds, the concentrated sulfuric acid treatment dehydrate hydroxyl groups to C=C bonds and the thermal annealing extrudes the carboxylic acid groups at the edge with the regeneration of C=C. By measuring the electric conductivity of the materials, the authors demonstrated the increased electrical conductivity (GO: 4.08 \times 10^{-1} S/m, CCG1: 8.23 \times 10^{1} S/m, CCG2: 1.66 \times 10^{3} S/m, CCG3: 2.20 \times 10^{4} S/m) attributed to the restoration of conjugated electronic structures on RGO.

3.4. Other synthesis approaches

3.4.1. Total organic synthesis

Total synthesis of graphene-like polyacyclic hydrocarbons (PAHs), explored decades ago, has caught much attention as a possible alternative route to synthesize graphene. Although PAHs have some advantages including synthesis versatility and the capability of grafting aliphatic chains at the edge to modify solubility, the major challenge lies in preserving dispersibility and a planar geometry for large PAHs. While different PAHs synthesis routes are nicely reviewed by Mullen et al. [121], it is
important to note that Mullen’s group has made a major break-through in synthesizing two-dimension graphene ribbons with the size of 12 nm through the Suzuki–Miyaura coupling of 1,4-diiodo-2,3,5,6-tetraphenylbenzene with 4-bromophenylboronic acid [122]. The same group recently reported a bottom-up method to fabricate graphene nanoribbons (GNR) on gold surfaces from 10,10'-dibromo-9,9'-bianthryl precursor monomers [123]. In the fabrication process, thermal deposition of the monomers onto a gold surface removes the halogen substituents from the precursors, and provides the molecular building blocks for the targeted graphene ribbons (with a width of seven benzene molecules) in the form of surface-stabilized biradical species. During a first thermal activation step, the biradical species diffuse across the surface and undergo radical addition reactions to form linear polymer chains as imprinted by the specific chemical functionality pattern of the monomers. In a second thermal activation step, a surface-assisted cyclodehydrogenation establishes an extended fully aromatic system (Fig. 3.11).

![Figure 3.9](image-url)

**Fig. 3.9.** Aberration-corrected TEM image of a monolayer of RGO. The scale bar is 1 nm. Expansion (A) shows, from left to right, an enlarged region of the micrograph, then a proposed possible structure for the region where oxygen (indicated in red) and nitrogen (blue) remain as functionalities on the sheets, and finally a simulated TEM image for this proposed structure. Expansion (B) shows the structure of a graphitic region. (Reproduced with permission from [117].)
Fig. 3.10. Atomic resolution, aberration-corrected TEM image of a single layer reduced graphene oxide membrane. (a) Original image and (b) with color added to highlight the different features. The defect free crystalline graphene area is displayed in the original light gray color. Contaminated regions are shaded in dark gray. Blue regions are the disordered single-layer carbon networks, or extended topological defects, identified as remnants of the oxidation reduction process. Red areas highlight individual ad-atoms or substitutions. Green areas indicate isolated topological defects, that is, single bond rotations or dislocation cores. Holes and their edge reconstructions are colored in yellow. Scale bar 1 nm. (Reproduced with permission from [120].)

Fig. 3.11. Bottom-up fabrication of atomically precise GNRs. Basic steps for surface-supported GNR synthesis, illustrated with a ball-and-stick model of the example of 10,10'-dibromo-9,9'-bianthryl monomers (1). Grey, carbon; white, hydrogen; red, halogens; underlying surface atoms shown by large spheres. Top, dehalogenation during adsorption of the di-halogen functionalized precursor monomers. Middle, formation of linear polymers by covalent interlinking of the dehalogenated intermediates. Bottom, formation of fully aromatic GNRs by cyclodehydrogenation. (Reproduced with permission from [123].)
The product of each reaction was monitored by scanning tunneling microscopy (STM) and the graphene nanoribbon was characterized by Raman spectroscopy (Fig. 3.12). The STM image taken after surface assisted C–C coupling at 200 °C but before the final cyclodehydrogenation step shows a poly-anthrylene chain (Fig. 3.12b left) with a periodicity of 0.86 nm which is in good agreement with the periodicity of the bianthry core of 0.85 nm. Fig. 3.12b, right shows a DFT-based simulation of the STM image with partially overlaid model of the polymer (blue, carbon; white, hydrogen). The fully aromatic system has an \( N = 7 \) armchair ribbon (Fig. 3.12c) with half the periodicity of the polymeric chain (0.42 nm) and a markedly reduced apparent height of 0.18 nm. STM simulations are in perfect agreement with experimental images (Fig. 3.12e), confirming that the reaction products are atomically precise \( N = 7 \) GNRs with fully hydrogen-terminated armchair edges. The peak at 396 cm\(^{-1}\) in Raman spectrum is characteristic for the 0.74 nm width of the \( N = 7 \) ribbons. The inset in Fig. 3.12d shows the atomic displacements characteristic for the radial-breathing like mode at 396 cm\(^{-1}\). In addition, the authors also demonstrated the fabrication of the straight \( N = 7 \) GNRs and the chevron-type \( N = 6/9 \) GNRs having been grown sequentially on a Ag(111) surface. These achievements suggest that total synthesis is a versatile approach to make GNR with precise control of the composition and structure. Studies on the electrical, optical and mechanical properties of these GNR are expected to direct interesting applications.

3.4.2. Un-zipping carbon nanotubes (CNTs)

One of the graphene research goals is to introduce an energy band gap to realize the application in semiconductor devices since pristine graphene is a zero-gap material. The graphene materials with an energy gap can be produced through two approaches: controlled oxidation of a few layers of graphene and fabrication GNR. Currently, it is very difficult to oxide a few layers of graphene in a controlled
manner. GNRs with narrow widths (< 10 nm) and atomically smooth edges, are predicted to have band gaps useful for room temperature transistor operations with excellent switching speed and high carrier mobility (potentially even ballistic transport) [124–127]. Yan et al. predicted that field effect transistors (FETs) made from intrinsic semiconductor zigzag ribbons can exhibit very high levels of performance, with ON/OFF ratio up to $10^4$, subthreshold swing as low as 60 meV per decade, and transconductance of $9.5 \times 10^3$ S/m [127]. The most straightforward method to produce GNRs is through e-beam lithography which can generate wide GRNs with a width of 20 nm from graphene sheet. However, such approach is limited by poor scale resolution and large edge roughness [128]. A chemical sonication route developed by Dai group produced sub-10 nm GNR semiconductors from intercalated and exfoliated graphite but with low GNR yield and broad width distribution [8].

Dai and coworker recently have taken a unique approach to fabricate GNRs with well controlled dimension. Based on concept that carbon nanotubes (CNTs) are considered to be GNRs rolled up into seamless tubes and the fact that the size of CNTs have been well controlled, Dai's group developed a method to produce GNRs through controlled unzipping of CNTs using by an Ar plasma etching method [129]. In their approach, dispersed multiwalled carbon nanotubes (MWCNTs) were embedded in a poly (methyl methacrylate) (PMMA) layer (an etch mask) on a Si substrate. After baking, the PMMA–MWCNT film was peel off in a KOH solution, leaving a narrow strip of MWCNT sidewall exposed to a 10 W Ar plasma treatment. The exposed MWCNT area was etched faster than the other area covered by PMMA, leading to unzipped CNTs–graphene nanoribbons. This approach could produce single-, bi- and multilayer GNRs and GNRs with inner CNT cores, depending on the diameter and number of layers of the starting MWCNT and the etching time. The PMMA film was removed using acetone vapor followed by calcination at 300 °C for 10 min to remove polymer residue to produce GNRs on the substrate. The AFM images of the obtained GNRs show smooth edges and uniform width of 10–20 nm corresponding to half of the circumference of the starting MWCNTs (diameter ~8 nm) (Fig. 3.13). The Raman spectroscopic studies provided the ratio of D band and G band ($I_D/I_G = 0.38, 0.30$ and $0.28$ for single-, bi- and trilayer GNRs with 10–20 nm widths). Because defect density on the pristine MWCNTs was low, the D-band Raman signal of the GNRs was mainly due to the open edges. The $I_D/I_G$ values

![Fig. 3.13. Images of GNRs converted from MWCNTs.](image-url)
were lower than those for GNRs obtained by lithographic etching of pristine graphene sheets \( \frac{I_D}{I_G} \sim 2 \) for a bilayer GNR of 28 nm width obtained by lithographic patterning), indicating the high quality of the GNRs obtained through this approach.

On the other hand, the electrical properties of the fabricated FET devices using these GNRs were not as good as the predicted value. A 7 nm-wide GNR device had an \( \frac{I_{on}}{I_{off}} \) ratio of >10 and a 6 nm-wide GNR device had \( \frac{I_{on}}{I_{off}} > 100 \). These GNRs had quantum-confined semiconducting characteristics, rather than those of bulk graphene, with much weaker gate modulation of conductance. The mobility of the GNRs was similar to those fabricated by lithography with values 10 times lower than those of large two-dimensional graphene sheets, most likely because of the edge scattering in the GNRs.

Shimizu and coworkers produced GNRs through the oxidation and longitudinal unzipping of MWCNTs in concentrated sulphuric acid, followed by treatment with KMnO\(_4\) (Fig. 3.14) [130]. The oxidative unzipping generated the graphene nanoribbons that are initially oxidized. The authors used a three-step annealing treatment to completely remove the oxygen from the bulk and edges of the nanoribbons and also effectively dope charge carriers. The first step annealed freshly deposited nanoribbons on substrates at 800 °C to remove the bulk of the oxygenation. The second step was carried out at 750 °C in a H\(_2\) atmosphere to produce edge termination and charge carrier doping before the fabrication of the FET electrodes using electron-beam lithography (EBL). The third step, annealing was performed at 300 °C to clean the surface immediately before the formation of the electrodes. The obtained GNRs were examined by AFM, HRTEM and Raman Spectroscopy. The AFM height analysis of monolayer GNRs showed a thickness of 0.8 nm while the HRTEM studies indicated the presence of small amount of structural defects associated with the oxidation and uncompleted removal of oxidized groups which was supported by the investigation of electrical properties. The ratio of D band and G band \( \frac{I_D}{I_G} \) was found to be \( \sim 0.45 \), suggesting a good quality of the obtained GNRs.

Although the GNRs, obtained by various new unzipping methods [130–136], have inferior electronic properties compared to those of wide, mechanically peeled sheets of graphene, these pioneer work has paved a way leading to a large-scale production of GNRs with controlled structure and quality and tunable properties. The future research will focus on understanding the mechanism of the process and optimizing the experimental parameters to prepare highly ordered sub-10 nm GNRs for potential applications in room temperature transistors.

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**Fig. 3.14.** (A) Field-emission SEM image of an ensemble of the as-grown nanoribbons, which were dispersed on a SiO\(_2\) substrate in a water droplet containing a suspension of nanoribbons. The nanoribbons are entangled and not sufficiently exfoliated. Inset (right): AFM images of individual nanoribbons spread by applying a strong air flow to the droplet. Inset (left): height of the nanoribbon measured along the longitudinal direction. The thickness of \( \sim 0.8 \) nm indicates a single-layer nanoribbon. (B) FET fabricated using a nanoribbon end-bonded by two metal electrodes, which eliminates single-electron charging effects. The thickness of the SiO\(_2\) layer on the gold/titanium backgate electrode was 300 nm, and the spacing of source and drain electrodes was 500 nm in all samples. (Reproduced with permission from [130].)
4. Graphene: characterization and properties

4.1. Characterization

4.1.1. Optical imaging of graphene layers

Various techniques are being used to image single layers, bi-layers and few layers of graphene such as optical microscope, atomic force microscopy (AFM), scanning electron microscopy (SEM) and high resolution transmission electron microscopy (TEM). Often, a combination of two or more techniques completes imaging of different layers of graphene. After the discovery of graphene, the optical microscope was primarily used to image various layers since it is the cheapest, non-destructive, and readily available in laboratories. However, this requires graphene layers mounting on silicon dioxide substrate for good contrast imaging. Over the past few years, the substrate designing has been given a considerable attention to enhance the visibility of thin sheets [137–139]. The mechanism behind such contrast is explained in terms of Fabry–Perot interference in the dielectric surface layer that governs the fluorescence intensity that allows contrast between graphene layers and substrate. The visibility of sheets can be defined by the Michelson contrast (C) relation [140]:

\[ C = \frac{R_{\text{material}} - R_{\text{dielectric}}}{R_{\text{material}} + R_{\text{dielectric}}} \]

where \( R_{\text{material}} \) is the reflected intensity from the material and \( R_{\text{dielectric}} \) is the intensity without the material. If \( C = 0 \), the material is not detectable, \( C = 0 \) to +1 material is brighter than the substrate, and \( C = 0 \) to −1 the sample will be darker than the substrate.

\( \text{SiO}_2 \) and \( \text{Si}_3\text{N}_4 \) are the most commonly overlay materials on silicon for enhancing the contrast of graphene layers which are dielectric in nature [141]. Another governing factor that modulates contrast is the wavelength of the incident light. Blake et al. [141] demonstrated the contact variation using different narrow band filters to detect sheets for any thickness of \( \text{SiO}_2 \) support. They found that under normal white light illumination sheets were invisible on 200 nm \( \text{SiO}_2 \), while thick and thin sheets were visible on 300 nm \( \text{SiO}_2 \) when green light was used, whereas sheets were visible on 200 nm \( \text{SiO}_2 \) by blue light.

Fig. 4.1 shows the optical image of the different layers of the micromechanically exfoliated graphene on silicon substrate with 300 nm \( \text{SiO}_2 \) over-layer. The number of layers was identified by color contrast and AFM [142]. So far the detection technique demonstrated is dependent on the substrate thickness and incident light wavelength. More research is needed to facilitate graphene-based sheets visualization independent of support material without any modification of the graphene.

4.1.2. Fluorescence quenching technique

Recently, a fluorescence quenching microscopy (FQM) technique was used to image graphene, RGO and GO for immediate sample evaluation and manipulation so that the synthesis process can be improved [143]. They have demonstrated the low cost and time saving method of visualizing GO and RGO using substrate independent fluorescence quenching microscopy (FQM). The imaging mechanism involves quenching the emission from a dye coated GO and RGO; the dye can be removed by rinsing without disrupting the sheets. The contrast arises due to the chemical interaction between the GO and the dye molecule on the molecular scale because of the charge transfer from dye molecule to GO that causes quenching of fluorescence [144]. The contrast measured in the fluorescence images was achieved 0.78 for 300 nm \( \text{SiO}_2 \) layer. Furthermore, higher contrast was achieved when GO sheets were deposited on 100 nm \( \text{SiO}_2 \), quartz and glass substrates which gave the contrast \( \sim 0.52, 0.2 \) and \( 0.07 \) respectively. These values were sufficient for a clear visualization [144]. The image obtained by FQM is shown in Fig. 4.2 and compared to the AFM image of the same area. The technique has the capability to see the microstructures of the GO/RGO film even on plastic substrate. However, this technique is limited to the micron sized layers because it is based on light, and the lateral resolution of FQM is diffraction limited. This technique relies on dye addition on graphene surface, which prohibits further use of the same sample due to the attachment of unwanted functional groups.
Fig. 4.1. Optical microscopy image of single-, double- and triple-layer graphene on Si with a 300 nm SiO$_2$ over-layer, labeled in the paper as 1L, 2L and 3L, respectively. (Reproduced with permission from [142].)

Fig. 4.2. (A) AFM image showing G-O single layers deposited on a SiO$_2$/Si wafer before applying a 30 nm thick fluorescein/PVP layer for FQM. (B) A FQM image of the same area of the wafer, showing good correlation to the AFM view. (C) After washing off the dye coating, no residues can be detected by AFM. (D) Line scan data on a folded sheet show no significant deviation in thickness before and after FQM imaging (all scale bars ~10 μm). (Reproduced with permission from [143].)
4.1.3. Atomic force microscopy (AFM)

This technique of imaging can successfully determine the layer thickness at the nanometer scale. However, this is cumbersome for imaging large area graphene. Moreover, AFM imaging gives only topographic contrast, which cannot distinguish between the graphene oxide and the graphene layers in normal operation. However, phase imaging is one of the attractive features of tapping-mode AFM; this facilitates to distinguish between a defect free pristine graphene and its functionalized version. One of the reasons behind is the difference in the interaction forces between the AFM tip and the attached functional group. Paredes et al. [145] demonstrated the influence of attractive mode of AFM to determine the thickness of the sheet. They found that the repulsive mode induces deformation causing error in the height measurement. They observed thickness $\sim 1.0$ nm for the unreduced graphene oxide and 0.6 nm for the chemically reduced GO. The difference in the thickness and the phase contrast was reported due to hydrophilicity difference resulting from distinct oxygen functional group in the reduction process as shown in Fig. 4.3. Besides imaging and thickness detection, AFM has been explored for mechanical characterization of graphene as it can resolve the small forces involved in the deformation.

**Fig. 4.3.** Height (a and c) and corresponding phase (b and d) tapping-mode AFM images of unreduced (a and b) and chemically reduced (c and d) graphene oxide nanosheets deposited from aqueous dispersions onto freshly cleaved HOPG. The images were recorded in the attractive regime of tip sample interaction. Superimposed onto each image is a line profile taken along the marked red line. (Reproduced with permission from [145].)
process. Different AFM modes allowed the study of mechanical [7], frictional, electrical, magnetic and even elastic properties of graphene flakes.

4.1.4. Transmission electron microscopy (TEM)

In general, TEM is frequently used to image nano size materials to the atomic scale resolution where a transmitted electron beam passes through the ultra thin sample and reaches to the imaging lenses and detector. As graphene and reduced graphene oxide (RGO) are an atom thick layer, it seems that the TEM is the only tool which can resolve atomic features of the graphene. However, the use of traditional TEMs is limited by their resolution at low operating voltage, whereas the operation at high voltage damages the monolayer. Recently, few researches have used a new class of TEM which is an aberration corrected in combination with monochromator that can provide 1 Å resolution at an acceleration voltage of only 80 kV [120,146]. For the first time Mayer's group has shown direct high resolution images of the graphene lattice depicting every single carbon atom arranged in hexagonal fashion [147]. This clearly reveals the ball-and-stick model where bright and dark contrast in the image corresponds to the atoms and the gaps respectively shown in Fig. 4.4. Researchers have also

![Fig. 4.4.](image)

(A) Direct image of a single layer graphene membrane. (B) Contrast profile along the dotted line in panel a (solid) along with a simulated profile (dashed). The experimental contrast is a factor of 2 smaller: Panel (C) shows the same experimental profile with the simulated contrast scaled down by a factor of 2. (D and E) Step from a monolayer (upper part) to a bilayer (lower part of the image), showing the unique appearance of the monolayer. Panel (E) shows the same image with an overlay of the graphene lattice (red) and the second layer (blue), offset in the Bernal (AB) stacking of graphite. (F) Numerical diffractogram, calculated from an image of the bilayer region. The outermost peaks, one of them indicated by the arrow, correspond to a resolution of 1.06 Å. The scale bars are 2 Å. (Reproduced with permission from [147].)
demonstrated that the imperfection and topological peculiarities in graphene affected the electronic and mechanical properties, which can be determined using such aberration corrected low voltage TEM.

In another imaging technique, Gass et al. have shown atomic lattice, defects and surface contamination in high angle annular dark-field (HAADF) images using scanning transmission electron microscopy (STEM). The technique involves focusing an electron beam onto monoatomic region and further scanning. This technique easily detects the arrangement of atomic scale defects and contaminant atoms using Z contrast. Fig. 4.5 shows the HRTEM bright field and HAADF image of mono layer, revealing a clean graphene monolayer surrounded by the contaminants, and a mono- and di-vacancy defect due to missing C-atoms. It is also worth mentioning here that due to the transparent nature of the graphene and its oxide, these are used as a support for imaging and dynamics of light atoms and molecules under TEM [149–151]. They have demonstrated that even conventional TEM can be utilized to observe the smallest atom and molecule using graphene as a membrane to support other sample in TEM. As graphene is one atom thick; this provides the thinnest possible continuous support unlike other amorphous TEM support. Its crystallinity and high conductivity facilitate back ground subtraction and charging reduction.

Fig. 4.5. High-resolution images of monolayer graphene. Bright-field (a) and HAADF (b) images of the monolayer, showing a clean patch of graphene surrounded by a mono-atomic surface layer; individual contaminant atoms of higher atomic number can be seen in (b). The inset FFT shows the lattice in the HAADF image and, by applying a band pass filter, the atomic structure is apparent. HAADF lattice images of defects: showing a mono-vacancy (c) and a di-vacancy (d). Inset showing the FFT of the raw image. (Reproduced with permission from [148].)
As mentioned in the previous section, RGO has superior conductivity than GO but inferior to the pristine graphene. It is supposed that during the reduction process, many defects generate in the carbon 2D lattice (point defect or incomplete removal of epoxy/oxygenated functional groups). These defects and foreign functional groups remarkably affect the electronic and thermal conductivity. So it is important to identify the most dominant defects in graphene before incorporating in the technologically important electronic devices. In combination of other spectroscopy techniques HRTEM has unraveled the atomic structure of GO and RGO. Recently, the local chemical structure and defect structure of RGO and GO have been given more attention at atomic level [117,120]. It has been found that after reduction, layers consisted of the defect free nano size graphene region inter dispersed with defect areas dominated by clustered pentagons and heptagons as shown in Fig. 3.10 in Section 3.

4.1.5. Raman spectroscopy

Carbon allotropes show their fingerprints under Raman spectroscopy mostly by D, G, and 2D peaks around 1350 cm\(^{-1}\), 1580 cm\(^{-1}\) and 2700 cm\(^{-1}\) respectively due to the change in electron bands. Identification of these features allows characterization of graphene layers in terms of number of layers present, and their effect of strain, doping concentration, and effect of temperature and presence of defects. The G band is associated to the doubly degenerated \(E_{2g}\) phonon mode at the Brillouin zone center. This band (near 1580) arises due to the in plane vibration of the \(sp^2\) carbon atoms, whereas the 2D band is at almost double the frequency of the D band and originates from second order Raman scattering process. The D band appears due to the presence of disorder in atomic arrangement or edge effect of graphene, ripples and charge puddles. Comparison of Raman spectra between graphite, single and few layer graphene are shown in Fig. 4.6 [152]. The Raman spectra at the center of the graphene

![Fig. 4.6](image-url)
layers do not show D peak that confirms the absence of defects. Instead, the significant change in shape and intensity was observed for 2D band of graphene and graphite. Ferrari el al. [152] have shown that the 2D band splits into two components for bulk graphite and in four components for bi-layer graphene (Fig. 4.6 c and d). An increase in the number of layers reduces the relative intensity of 2D and increases its FWHM and makes it blue shifted [142,152,153]. The single sharp 2D peak was reported for mono layer that is four times more intense than the G peak. Effect of various factors on Raman spectra are summarized in Table 4.1. As the properties of graphene crucially depend on the number of layers and purity thus various researchers have used Raman spectra as a non-destructive tool to characterize and quality control of mono and few layers of graphene. Various effects on graphene have also been studied by following trends in Raman spectra including thickness determination, strain in graphene layers, defects and doping.

4.2. Properties

In the past few years many fascinating properties were discovered through the investigation of pristine graphene including extremely high charge (electrons and holes) mobility (230,000 cm²/Vs) with 2.3% absorption of visible light [159,160], thermal conductivity (3000 W/mK), and the highest strength (130 GPa), and the highest theoretical specific surface area (2600 m²/g), and half integer quantum Hall effect even at ambient temperature (minimum Hall conductivity $\sim 4e^2/h$, even at carrier concentration is zero), which has filled the research community with great enthusiasm. This section will focus on the graphene properties that lay foundation for their wider scope of applications. The elaborate discussion on graphene properties is beyond the scope of this article that can be found in some of the recent review articles. However, it is worth mentioning the important properties of graphene with single layer, bi-layers and few layers.

4.2.1. Electrical transport property

Pristine graphene, a two-dimensional honeycomb carbon lattice is a zero gap semiconductor. The sp² hybridized carbon atoms are arranged in hexagonal fashion in 2-dimensional layer. A single hexagonal ring comprises of three strong in-plane sigma bonds $P_z$ orbitals perpendicular to the planes. Different graphene layers are bonded by weak $p_z$ interaction while strong in-plane bonds keep hexagonal structure stable and facilitate de-lamination of 3D structure (graphite) into individual graphene sheet just by applying mechanical stress. As described earlier, the scotch tape method micromechanically creates single layer of defect free graphene and provides a 2-D platform, to investigate many fundamental properties of this 2-D crystal.

One of the most interesting aspects of the graphene is its highly unusual nature of charge carriers, which behave as massless relativistic particles (Dirac fermions). Dirac fermions behavior is very abnormal compared to electrons when subjected to magnetic fields for example, the anomalous integer quantum Hall effect (QHE) [2,161]. This effect was even observed at room temperature [3]. Graphene has distinctive nature of its charge carriers, which mimic relativistic particles, considered as electrons those have lost their rest mass, can be better described with (2 + 1) dimensional Dirac equation [162]. The band structure of single layer graphene exhibits two bands intersecting at two in

<table>
<thead>
<tr>
<th>Table 4.1</th>
<th>Effect on various factors on Raman peak position, shape and splitting.</th>
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<tr>
<td>Factors</td>
<td>Peak “G”</td>
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<tr>
<td>Graphene layers</td>
<td>–</td>
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<tr>
<td>Tensile strain</td>
<td>Red shift</td>
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<tr>
<td>Compressive strain (micromechanically Cleaved graphene)</td>
<td>Red shift with strain and splitting at higher strain</td>
</tr>
<tr>
<td>Compressive strain (epitaxial graphene on SiC)</td>
<td>Blue shift, no splitting</td>
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<tr>
<td>Temperature</td>
<td>Red shift with temperature</td>
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<tr>
<td>Doping</td>
<td>Blue shift with doping</td>
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equivalent point $K$ and $K'$ in the reciprocal space. Near these points electronic dispersion resembles that of the relativistic Dirac electrons. $K$ and $K'$ are referred as Dirac points where valence and conduction bands are degenerated, making graphene a zero band gap semiconductor (Fig. 4.7).

The high electronic conductivity in single layer is due to very high quality, i.e. low defect density of its crystal lattice. Defects in general act as scattering sites and inhibit charge transport by limiting the electron mean free path. There are evidences that pristine graphene is defect free, thus its conductivity must be affected by some extrinsic source. Various factors have been proposed which affect the conductivity such as, interaction with the under lying substrate while measurement, surface charge traps [164,165], interfacial phonons [166] and substrate ripples [167]. Kim and coworkers [159] reported the mobilities in excess of 200,000 cm$^2$/Vs at carrier density of $2 \times 10^{11}$ cm$^{-2}$ for mechanically exfoliated suspended layer of graphene above a Si/SiO$_2$ gate electrode (Fig. 4.8). Substrate induced

![Fig. 4.7. Bandgap in graphene. Schematic diagrams of the lattice structure of (A) monolayer and (B) bilayer graphene. The green and red colored lattice sites indicate the A (A1/A2) and B (B1/B2) atoms of monolayer (bilayer) graphene, respectively. The diagrams represent the calculated energy dispersion relations in the low-energy regime, and show that monolayer and bilayer graphene are zero-gap semiconductors. (C) When an electric field ($E$) is applied perpendicular to the bilayer, a band gap is opened in bilayer graphene, whose size ($2\Delta$) is tunable by the electric field. (Reproduced with permission from [163].)](image1)

![Fig. 4.8. (A) Measured four-probe resistivity $\rho_{xx}$ as a function of gate voltage $V_g$ before (blue) and after (red) current annealing; data from traditional high-mobility device on the substrate (gray dotted line) shown for comparison. The gate voltage is limited to $\pm 5$ V range to avoid mechanical collapse. (B) Mobility, $\mu = 1/en\rho_{xx}$ as a function of carrier density $n$ for the same devices. (C) AFM image of the suspended before the measurements. (Reproduced with permission from [159].)](image2)
scattering was minimized by using single layer graphene (SLG) in completely suspended condition. Importantly, study showed how absorbed impurities on graphene surface, and trapped in between the graphene and substrate, even in the suspended situation affected the electron mobility. Electric current induced annealing improved mobility up to 230,000 cm$^2$/Vs.

Another important characteristic of SLG is its ambipolar electric field effect at room temperature, that is charge carriers can be tuned between electrons and holes by applying a required gate voltage [5,162]. In positive gate bias the Fermi level rise above the Dirac point which promote electrons populating into conduction band, whereas, in negative gate bias the Fermi level drop below the Dirac point promoting the holes in valence band in concentrations of $n = \alpha V_g$ (where $\alpha$, coefficient depending on the SiO$_2$ layer used as a dielectric in the field effect devices, $V_g \sim$ gate voltage).

Graphene is a potential material for the future generation electronic devices suffers from zero energy band gap even at the charge neutrality point, which is one of the hurdle for graphene to be useful as an electronic material, for example, in graphene-based FET. The zero band gap does not allow its use in logic applications, which require frequent on/off switching. However, band structure of the graphene can be modified by lateral quantum confinement by constraining the graphene in nanoribbons [124,128,168] and in graphene quantum dots [169], and by biasing bi-layer [21,170,171] graphene. Bandgap opening in both zigzag and armchair nanoribbons was observed and proven experimentally and theoretically which vary with the width of the ribbons and disorderness in the edges [172]. Dop-ing and edge functionalization also change the band gap in nanoribbons [173].

It is important to note that the most of the primary work on graphene has been related to FET. A schematic of the graphene-based FET is shown in Fig. 4.9 consisting of the gate, a graphene channel connecting source and drain electrodes, and a dielectric barrier layer (SiO$_2$) separating the gate from the channel. In most of the studies ~300 nm SiO$_2$ layer is used, under the graphene acted as a dielectric layer and silicon acted as a back gate. Due to large parasitic capacitance of the 300 nm SiO$_2$ layer, it finds difficulty in integration with other electronic components. Thus, top gated graphene-based device have been developed in 2007 [174]. Top gated graphene-based MOSFETs have been prepared using exfoliated graphene [174–177], CVD grown graphene on Ni and Cu substrate [44] and epitaxial graphene [178,179], whereas, Al$_2$O$_3$, SiO$_2$ and HfO$_2$ dielectric materials have been used for top gate [171].

Recently, large area epitaxial graphene has attracted much interest due to its scalability for electronics, and even few layer graphene films grown on SiC show electronic properties similar to the isolated graphene sheet. However, the charge transport properties are lower than the pristine graphene by an order of one. Mixed opinion exists on band gap opening in large area epitaxial graphene. Some reports suggest a zero band gap in graphene layer just above the carbon buffer layer [180] and the other found around 0.26 eV [181,182].

De Heer group has developed a method of epitaxially growing graphene on SiC substrate. It was found that the mobility of the graphene grown on carbon terminated face was greater than the graphene grown on Si terminated face [183] due to the difference in the structure, and this can be gated. They have demonstrated the energy gap of ~0.26 eV which decreases with increasing thickness and approaches zero when number of layers exceeds four [181]. The energy gap, in single layer (0.26 eV), bilayer and triple layer (0.14 eV) was induced as a result of symmetry breaking due to the interaction with substrate.

Fig. 4.9. (a) Schematic diagram of back gated and (b) top gated graphene field effect devices. The perpendicular electric field is controllable by applied back-gate voltage ($V_g$) and the top gate voltage ($V_{top}$).
Seyller and coworkers [64] have achieved high electronic mobilities in wafer size graphene layers prepared in ex situ atmospheric pressure graphitization of SiC in Ar atmosphere which reached up to 2000 cm²/Vs at 27 K and to 930 cm²/Vs at 300 K for Si terminated face.

Whereas, other study showed the mobility variation for multilayer epitaxial graphene films from 600 to 1200 cm²/Vs for Si-face measured in ambient condition and could reached up to 5000 cm²/Vs for the carbon terminated face with on/off ratio up to seven, the difference was attributed to the different crystallographic domain size of graphene on the two faces [178]. The significantly larger single crystalline domain size was reported for C face graphene than Si-face [184] which provides structural coherency for longer mean free path to charges, and thus, provides high mobility.

Chemical vapor deposition is another method envisioned for large scale synthesis of graphene layers. Growth of monolayer and few layers on various substrates have been demonstrated in earlier sections. Reina et al. [48], showed single and few layer graphene (20 µm lateral size) growth at ambient pressure on Ni substrate using CVD. A large variation in field effect mobility ~100–2000 cm²/Vs for both electrons and holes was reported due to ineffective gate modulation caused by the inhomogeneous thickness of graphene films and grain boundary scattering inside the films. Recently, the charge mobility of large area graphene film grown on Ni by CVD and transferred to SiO₂ substrate was measured greater than 3700 cm²/Vs which exhibited the half-integer quantum Hall effect similar to micro-mechanically cleaved layer, confirming the monolayer characteristic of graphene [185]. It is worth to notice that nickel is the most commonly used metal substrate and studied well for large area, high quality mono and few layer of the graphene [41,43,48,186,187]. However, graphene grown on this substrate suffers from the small grain size, multilayer deposition at grain boundaries, and carbon solubility in nickel. Ruoff and coworkers [44] have used a copper foil, as carbon has low solubility in copper and grown predominantly single layer graphene with less than 5% area of few layer graphene. The films have achieved mobility as high as 4050 cm²/Vs. Another study [41] has also revealed the potential of CVD technique of depositing graphene film on large wafer (up to 3 in.) of copper substrate at ambient pressure. This study has shown the ambipolar field effect mobilities up to ~3000 cm²/Vs with on/off ratio ~4 and half integer QHE of the films.

Difficulties of graphene single layer scale up for applications, have led researchers to extend graphene study to bi-layer and few layers (<10).

Bilayer graphene also exhibits an anomalous QHE, different from that of the single layer. The charge carriers in bi-layer graphene have parabolic energy spectrum near the K point, which indicates bilayer graphene is also gapless (Fig. 4.7) [188]. Bilayer graphene remains metallic at the neutrality points [188]. In the case of bi-layer, the charge particles are chiral, similar to massless Dirac fermions, but have a finite mass (0.05 mₑ) called massive Dirac fermions.

Though, the bi-layer graphene is gapless, its electronic band gap can be controlled by an electric field perpendicular to the plane [163]. The double gated approach was used to demonstrate the controlled induction of an insulating state with large suppression of the conductivity in bi-layer graphene. The size of the gap is proportional to the voltage drop between the two graphene planes and value can be as high as 0.1–0.3 eV. In contrast, group at IBM Thomas J. Watson research center [189] has shown bi-layer graphene FET with high on/off current ratio of around 100 and 2000 at room temperature and 20 K respectively in dual-gated bi-layer graphene FETs. The measured band gap was more than 0.13 eV. In another study [190], it was reported that the electronic band gap of the bi-layer graphene can be tuned by applying electric field, which provide an opportunity to use graphene bi-layer as a tunable energy band gap semiconductor for many electronic applications like photodetectors, terahertz technology [191], infrared nanophotonics [192], pseudospintronics [193], and laser. They have also shown the band gap can be tuned to values larger than 0.2 eV.

Finally, processable graphene sheets in large quantities are also desirable for applications like graphene reinforced composites, transparent electrical conductive films, energy storage, etc. [194]. A promising approach including chemical and thermal reduction of graphene oxide can provide graphene in scalable amount [26,76]. Researchers have been making continuous effort to improve electrical transport properties of RGO in order to use in electrical applications. Graphene oxide has very high electrical resistance (4 MΩ/square) due to presence of oxygenated functional groups. Removal of attached functional group from 2-D carbon lattice by chemical and thermal reduction partially restores
the electronic conductivity however; these processes introduce structural imperfections in carbon lattice and degrade the electrical properties compared to the pristine graphene.

The conductivity and mobility of RGO were reported to be lesser by 3 and 2 orders of magnitude respectively than pure graphene. The reduced conductivity is due to lattice vacancies which cannot heal during reduction process. Presence of intact nano meter size domain in RGO results in hopping conduction has been suggested. The field effect mobilities of 2–200 cm²/Vs and conductivity of 0.05–2 S/cm were measured for RGO [195]. Moreover, graphene sheets obtained from hydrazine reduction behave as a P-type semiconductor [196]. In contrast, Chhowalla and coworkers's [197] study exhibited the ambipolar characteristics of RGO films when measured at low temperature, which is comparable to graphene. The scattering at the junction of the overlapping sheets caused lower mobility (1 cm²/Vs for holes and 0.2 cm²/Vs for electrons). They have observed the RGO sheet resistance as low as 43 KΩ/square prepared by chemical reduction. Whereas, the lower resistance of 10²–10³ Ω/square and electrical conductivity 0.05–2 S/cm were observed for thermally reduced GO (RGO) [28] in comparison to GO (~4 M Ω/square) [72] which was due to high temperature deoxygenation. Recently, a graphene paper of chemically converted graphene was prepared with electrical conductivity of 72 S/cm at room temperature [76]. This can have potential applications in membranes, anisotropic conductors, transparent electrodes, and super capacitors.

Furthermore, interested readers can refer article by Neto et al. [198] and Nilsson et al. [170] for more information on electronic properties of single, bilayer and few layer graphene.

4.2.2. Quantum Hall effect

The charge particles behave as massless Dirac fermion in a 2D lattice which exhibit interesting effect on energy spectrum of the landau levels produced in the presence of magnetic field perpendicular to the graphene sheets.

The Landau level energies are given by

\[ E_j = \frac{(j + \frac{1}{2}) \hbar e B}{m_e} \]  

where \( j = 0, 1, 2, 3, \ldots \) are the indices for the Landau index and \( \hbar = \hbar/2\pi \).

Due to disorder, the Hall conductivity \( \sigma_{xy} \) of the two-dimensional electron gas (2DEG) shows the plateaus at \( jh/2eB \) and is quantized, can be expressed by \( \sigma_{xy} = \pm j (2e^2/h) \) which leads to integer quantum Hall effect (IQHE).

In contrast to 2DEG, the energy of Landau levels for graphene is expressed by \( E_j = \pm \sqrt{2eB|j|} \), \( |j| = 0, 1, 2, 3, \ldots \) is the Landau index and \( B \) is the magnetic field applied perpendicular to the graphene plane. Since, the Landau levels are doubly degenerated for the K and K' points at \( j = 0 \), these levels are shared equally between electrons and holes. This leads to the anomalous IQHE, where the Hall conductivity is given by

\[ \sigma_{xy} = \pm \frac{4(j + \frac{1}{2}) e^2}{h} \]  

The Hall conductivity for the single layer graphene shows a plateau when plotted as a function of carrier concentration, \( n \), at a fixed magnetic field. Novoselov et al., have first observed anomalous IQHE (shown in Fig. 4.10), measured at \( B = 14 T \) and temperature of 4 K [161]. It is interesting to note that at the zero energy level \( (j = 0) \) a finite value \( (\sigma_{xy} = 2e^2/h) \) of conductivity is observed. The QHE plateaus occur at the half integer for high energy level. This gives a ladder of equidistant steps in the Hall conductivity. This QHE, in monolayer of graphene, is the distinctively different for both the holes and electrons than the conventional QHE as quantization condition is shifted by a half integer. This abnormal quantization was attributed to the topologically exceptional electronic structure of graphene [2].

In general QHE is observed at low temperatures typically below the boiling point of the liquid helium. Novoselov et al. [3] observed QHE in graphene at room temperature caused by very high concentration of carriers (up to 10¹³/cm²), with single 2D subband, important to occupy the lowest Landau
level even in ultra high magnetic field. Moreover, high mobility ($\mu \sim 10,000 \text{ cm}^2/\text{Vs}$) allows the movement of massless Dirac fermions with minimal scattering under ambient conditions.

In the case of bilayer graphene, charge carriers have parabolic energy spectrum which are chiral with finite mass [188]. The Landau quantization of these massive Dirac fermions results in plateaus in Hall conductivity which appears at standard integer positions. The Hall conductivity is given by $\sigma_{xy} = j4e^2/h$, where $j$ is an integer other than zero. The first plateau occurs at $j = 1$ however, the plateau at zero $\sigma_{xy}$ is absent unlike the conventional QHE (Fig. 4.11). Moreover, the Hall conductivity undergoes a double-sized step across this region.

### 4.2.3. Optical properties

Many reports confirmed that single layer graphene absorbs 2.3% of incident light over a broad wavelength range in spite of being just a monolayer (Fig. 4.12) [50,160]. Graphene transmittance can be well described in terms of fine structure constants [160,199]. The absorption of light was found to be increasing with the addition of a number of layers linearly, each layer absorption $A = 1 - T = \pi x = 2.3\%$, where $x \sim 1/37$ is the fine structure constant. The graphene can be imaged by optical image contrast on Si/SiO$_2$ substrate due to interference, and the contrast increases with the number of layers. The absorption for monolayer graphene is flat from 300 to 2500 nm, the peak at ~250 nm in UV region is attributed to the inter band electronic transition from the unoccupied $p$ states (Fig. 4.12) [199].

In addition, their optical transition can be modified by changing the Fermi energy considerably through the electrical gating [192,200]. The tunability, provided by the electrical gating and charge injection in graphene-based optoelectronics devices, have been predicted to develop tunable IR detectors, modulators, and emitters [192]. The exceptional electrical transport properties in conjunction with optical properties have fueled lot of interests in novel photonic devices. It has also been suggested that the zero band gap, large area monolayer and few layer graphene FET can be used as ultra-fast photodetectors [201]. The absorption of light on the surface generates electron–hole pairs in graphene which would recombine very quickly (Picoseconds) depending upon the temperature as well as electrons and holes density [202]. When an external field is applied these holes and electrons can be separated and photo current is generated. Similar behavior occurred in the presence of internal field. This field has formed near the electrode and graphene interface [201,203,204]. Xia et al. [201],

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**Fig. 4.10.** QHE for massless Dirac fermions in single layer graphene. Hall conductivity ($\sigma_{xy}$) and longitudinal resistivity ($\rho_{xx}$) of graphene as a function of their concentration at $B = 14T$ and $T = 4K$. The plateau occur half integer for high energy level results in a ladder of equidistant steps in Hall conductivity. Inset shows the $\sigma_{xy}$ in two-layer graphene where the quantization sequence is normal and occurs at integer $j$. (Reproduced with permission from [4].)
showed that the unique properties of graphene enabled very high bandwidth (>500 GHz) light detection, very wide wavelength detection range, zero current operation and good quantum efficiency.

Another property of graphene is photo luminescence (PL). It is possible to make graphene luminescent by inducing a suitable band gap. Two routes have been proposed, the first method involves cutting graphene in nanoribbons and quantum dots. The second one is the physical or chemical treatment with different gases to reduce the connectivity of the $p$ electron network \[205–207\]. For example it is shown that PL can be induced by oxygen plasma treatment of graphene single layer on substrate \[208\]. This gives an opportunity of making hybrid structures by etching just the top layer, while keeping the underlying layer unaffected. Broad PL from solid GO and liquid GO suspension was also observed and the progressive chemical reduction quenched the PL of GO. Whereas, oxidation produced a disruption of the $\pi$ network and open a direct electronic band gap \[209\].

Fluorescent organic compounds are very important for the development of low cost optoelectronic devices \[210\]. Particularly blue fluorescence from aromatic or olefinic molecules and their derivatives are important for display and lighting applications \[211\]. The blue PL was observed for GO thin films deposited from thoroughly exfoliated suspensions \[212\]. The PL characteristic and its dependence on the reduction of GO originate from the recombination of electron–hole pairs, localized within small $sp^2$ carbon clusters embedded within the GO $sp^3$ matrix \[212\].

Fig. 4.11. Quantum Hall effect in bilayer graphene. (a) Hall conductivity ($\sigma_{xy}$) and (b) Longitudinalin ($\rho_{xx}$) are plotted as functions of $n$ at a fixed $B$ and temperature $T = 4$ K. $\sigma_{xy}$ allows the underlying sequences of QHE plateaus to be seen more clearly. $\sigma_{xy}$ crosses zero without any sign of the zero-level plateau as expected in conventional 2D system. The inset shows the calculated energy spectrum for bilayer graphene, which is parabolic at low $\epsilon$. (Reproduced with permission from \[188\].)
Moreover, the combined optical and electrical properties of graphene have opened new avenues for various applications in photonics and optoelectronics. Numerous applications using graphene as a promising candidate have been suggested, which includes photodetectors, touch screens, light emitting devices, photovoltaics, transparent conductors, terahertz devices and optical limiters.

4.2.4. Mechanical properties

Unwanted strain can affect the performance and life of the electronic devices. Generally, application of external stress on crystalline material can alter inter atomic distances, resulting in the redistribution, in local electronic charge. This may introduce a band gap in electronic structure and modify the electron transport property significantly. After carbon nanotubes, graphene has been reported to have the highest elastic modulus and strength. Several researchers have determined the intrinsic mechanical properties of the single, bilayer and multiples layer of graphene are summarized in Table 4.2.

A single defect free graphene layer is predicted to show the highest intrinsic tensile strength with stiffness similar to graphite. One method to determine the intrinsic mechanical properties is to probe the variation of the phonon frequencies upon the application of tensile and compressive stress [154,157,215]. The Raman spectroscopy is one of the techniques which can monitor phonons

<table>
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<tr>
<th>Method</th>
<th>Material</th>
<th>Mechanical properties</th>
<th>References</th>
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| AFM    | Mono layer graphene | $E = 1 \pm 0.1$ TPa  
$\sigma_{int} = 130 \pm 10$ GPa at $\epsilon_{int} = 0.25$ | [7]         |
| Raman  | Graphene     | Strain $\sim 1.3\%$ in tension  
Strain $\sim 0.7\%$ in compression | [213]      |
| AFM    | Mono layer graphene | $E = 1.02$ TPa; $\sigma = 130$ GPa | [214]      |
|        | Bilayer      | $E = 1.04$ TPa; $\sigma = 126$ GPa                          |            |
|        | Tri-layer    | $E = 0.98$ TPa; $\sigma = 101$ GPa                          |            |
|        | Graphene     |                                                            |            |
frequency under uniaxial tensile and hydrostatic stress [155]. It has been observed that the tensile stress results in the phonon softening due to decreased vibrational frequency mode whereas compressive stress (hydrostatic) causes the phonon hardening due to increased vibrational frequency mode. Thus in graphene, studying the vibration of phonon frequency as a function of strain can provide useful information on stress transfer to individual bonds (for suspended graphene) and atomic level interaction of graphene to the underlying substrate (for supported graphene).

Compressive and tensile strain in graphene layer was estimated using Raman spectroscopy by monitoring change in the G and 2D peaks with applied stress. The splitting of the G peak and red shift was observed with increase in strain whereas the 2D peak also red shift without splitting for small strains ~0.8% [156]. Ni et al. have observed the opposite behavior for epitaxial graphene on SiC substrate [157]. They found, the blue shift in all the Raman bands for the epitaxial graphene, in comparison to that of the micromechanically cleaved graphene due to the compressive stress in grown graphene. Besides, the strain on graphene may change electronic band structure which indicates that the energy band gap can be tuned by introduction of the controlled strain. Recently, the band gap tuning was reported under uniaxial strain [155]. A layer of graphene was deposited on flexible polyethylene terephthalate (PET) so that uniaxial tensile strain (up to ~0.8%) can be applied on the single/three-layer graphene by stretching the PET in one direction. The band gap of 0.25 eV was detected under the highest strain (0.78%) for the single layer graphene. It was also suggested that the uniaxial strain affected the electronic properties of graphene much more significantly as it breaks the bonds of C—C lattice.

4.2.5. Thermal properties

Application of the graphene has been envisioned for electronic devices. Where, thermal management is one of the key factors for better performance and reliability of the electronic components. Considerable amount of heat generates during the device operation needs to be dissipated. Carbon allotropes such as graphite, diamond, and carbon nano tubes have shown higher thermal conductivity due to strong C—C covalent bonds and phonon scattering. Earlier carbon nanotubes are known for the highest thermal conductivity with room temperature value ~3000 W/mK for MWCNT [216] and 3500 W/mK for single wall CNT [217]. However, a large thermal contact resistance is the main issue with CNTs based semiconductor. Recently the highest room temperature thermal conductivity ~ up to 5000 W/mK for the single layer graphene has been reported (pure defect free graphene) [6] whereas for supported graphene conductivity is ~600 W/mK. Conductivity of the graphene on various supports are not studied much but their effect was predicted by Klemens [218]. Table 4.3 shows the comparative thermal conductivity values for graphene determined by various methods. A new approach of determining thermal conductivity of a thin atomic layer of graphene is shown in Fig. 4.13 [219]. In this method a suspended graphene layer is heated by laser light (488 nm), the heat propagated laterally towards the sinks on side of the corner of the flakes. The temperature change was determined by measuring the shift in the graphene G peak using confocal micro-Raman spectroscopy which acts as a thermometer. The thermal conductivity is affected by factors such as defects edge scattering [220] and isotopic doping [221]. In general, all these factors are detrimental to the conductivity due to phonon scattering at defect and phonons modes localization due to the doping.

<table>
<thead>
<tr>
<th>Method</th>
<th>Material</th>
<th>Thermal conductivity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Confocal micro-Raman</td>
<td>Single layer graphene</td>
<td>4840–5300 W/mK at RT</td>
<td>[6]</td>
</tr>
<tr>
<td>spectroscopy</td>
<td>Suspended graphene flake</td>
<td>4100–4800 W/mK at RT</td>
<td>[219]</td>
</tr>
<tr>
<td>Thermal measurement method</td>
<td>Single layer (suspended)</td>
<td>3000–5000 W/mK at RT (suspended)</td>
<td>[222]</td>
</tr>
<tr>
<td>Thermal measurement method</td>
<td>Single layer (on SiO₂ support)</td>
<td>600 W/mK at RT (on a silicon dioxide support)</td>
<td>[222]</td>
</tr>
<tr>
<td>Electrical four-point</td>
<td>Reduced graphene oxide</td>
<td>0.14–0.87 W/mK</td>
<td>[223]</td>
</tr>
<tr>
<td>measurement</td>
<td>flake</td>
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5. Chemically derived graphene: properties and applications

The pristine graphene has attracted a great deal of attention due to its unique electronic properties, making them model systems for the observation of novel quantum phenomenon and building blocks for future nano electronic devices. However, in practical point of view it is necessary, (i) to create graphene nanostructures in large quantities and (ii) to integrate them at selected positions of the circuits with high yield. The solution processing provides an attractive approach to produce GO/RGO sheets in large quantities at low cost. The easy processibility of GO/RGO and compatibility with various substrates make them an attractive candidate for high yield manufacturing of graphene based electronic and optoelectronic devices such as field effect transistors, chemical/bio sensors, organic solar cells, and transparent electrodes in photovoltaic devices. This chapter summarizes the recent progress of GO/RGO in device applications and their properties.

5.1. Assembly of GO/RGO for device applications

It has been discussed in previous sections that GO and RGO can be synthesized in large quantities through solution routes. Several approaches have been demonstrated in this regard which involve drop cast \cite{71,195}, dip coating \cite{224}, spraying \cite{196}, spin coating \cite{28,225–228}, Langmuir–Blodgett (LB) film \cite{36,229}, and vacuum filtrations deposition \cite{116,197,230}. The GO/RGO can be deposited either on prefabricated electrode patterns or the electrodes can be defined after deposition of GO/RGO. Using these processes, the devices using single layer, few layers (<10 nm) and thin film have been fabricated. For single layer and few layer devices, the throughput can be low since the processes involve random placement of GO/RGO sheets. On the other hand, thin film deposition can improve the throughput. The drop cast, dip coating, and spray depositions on the substrate are convenient ways to build GO/RGO devices, however, these techniques often result in non-uniform film thickness on substrate, due to aggregation of GO/RGO sheets. In spin coating, the thickness of layer can be tuned by varying the concentration of the graphene dispersion and can result in minimal wrinkling. LB assembly exploits the electrostatic repulsive forces between the individual GO sheets \cite{36,229}. In brief, a suspension of GO in a mixture of water and methanol carefully spreads over the water surface to obtain the floating GO sheets trapped at the water/air interface. The floating GO film is then deposited onto a substrate as it is slowly raised from the solution. The aggregation of RGO sheets is prevented by repulsive negative charge between the ionized edge functional groups of the sheets leading to a uniform monolayer thick film. This process can be repeated to make layer by layer deposition of RGO film of desired thickness. The filtration technique involves filtration of the suspension containing the GO sheets through porous membrane \cite{116,197,230}. The as-filtered GO sheets are then transferred from the filter membrane to the substrate surface. The thickness of each graphene oxide paper sample can be controlled by adjusting the volume of the colloidal GO suspension. This technique allows good

*Fig. 4.13. (a) High-resolution scanning electron microscopy image of the suspended graphene flakes. (b) Schematic of the experimental setup for measuring the thermal conductivity of graphene. (Reproduced with permission from \cite{219}.*
control of uniform film thickness on the substrate, however sometimes it can produce wrinkling of the sheets. All the above mentioned assembly techniques can provide a convenient route to produce large quantity RGO thin film devices. However, in these techniques, if many circuits need to be made on the wafer, additional materials outside of the electrode area need to be etched away, which increases the processing steps.

Techniques that promote directed assembly at the selected position of the circuit can be advantageous in this regard. Several studies have been shown for large scale assembly of GO/RGO devices at selected positions of the circuit. Molecular template is one of the method for producing the directed assembly of RGO based devices [231] using single layer as well as few layers. The concept of this technique is to transfer individual GO sheets from solution on to the predefined patterned areas (often referred as templates). The molecular templates are generated using micro-contact printing on mica-peeled gold substrates as shown in Fig. 5.1a. Then such templates are immersed into GO solution. The electrostatic interactions between the template and GO sheets make the sheets to assemble onto the template. The distribution of the GO sheets depends on the surface functionalization, background passivation, pH, immersion time, and the concentration of the GO dispersion. The longer immersion time generates more GO sheets on the templates (Fig. 5.1b). After GO sheets attaching to the template, they can be treated either by hydrazine vapor or high temperature thermal annealing to produce conducting RGO devices. Another convenient route to assemble large scale GO/RGO device between prefabricated electrodes is via dielectrophoresis (DEP) [232–240]. In this technique, an AC voltage gives rise to a time averaged DEP force given by

\[
F_{\text{DEP}} = (p \cdot \nabla)E
\] (5.1)

Fig. 5.1. (A) A scheme of the templating process that shows the formation of the amino-terminated template on mica-peeled gold, followed by immersion in a dispersion of graphite oxide to the reduction of the captured GO to form reduced graphite oxide. (B) (1–4) Friction images of an 11-amino-1-undecanethiol (AUT)-patterned Au following 5 s (1), 30 s (2), 10 min (3), and 17 h (4) immersion times in GO dispersions, respectively. All images are 10 µm wide and show the bright (high friction) AUT being covered with the lower friction GO [231]. (C) A cartoon of DEP setup. (D) Demonstration of high yield assembly Top: SEM of an active area of a chip containing after DEP assembly of the RGO sheets. The chip contained 18 pairs of electrodes numbered as E1–E18. The gap size between each electrode pairs is 500 nm. Bottom: Magnified SEM images of all 18 electrode pairs for a clearer picture. (Reproduced with permission from [235].)
where $p$ is the induced dipole moment of the polarizable object and $E$ is the non-uniform electric field. The strong electric field gradient causes the GO/RGO sheets to align along the field direction and to assemble between the pre-fabricated sources and drain electrodes as shown in schematic of the setup in Fig. 5.1c. DEP assembly of GO and RGO has been demonstrated by several groups which shows the device yield is almost 100% [232–240]. Fig. 5.1d shows the actual assembly of RGO sheets prepared by Joung et al. [235].

5.2. Electrical characterization of GO/RGO sheet

The electrical characterization of the as-synthesized GO and RGO, both in chemical and thermal route has been conducted using two-probe current ($I$)–voltage ($V$) measurement as well as three terminal field effect transistor (FET) devices. As-fabricated GO is found to be insulating due to the presence of oxidized functional group. The controlled reduction (thermal or chemical) process results in the removal of oxidized group causing GO to be electrically conducting. Although many of the oxidized groups were removed during reduction process, remaining oxidized groups still limits electron transport properties of the RGO sheets. The transport properties can be characterized by comparing the conductivity values and field effect mobility values for various reduction techniques.

The conductivity values can be calculated using the following expression:

$$\sigma = (Rt)^{-1}$$

where $R$ is the total resistance and $t$ is the sheets thickness. It has been shown that the conductivity of RGO can vary from 0.05 to 500 S/cm depending on the degree of reduction which is related to the ratio of the graphitic regions ($sp^2$) to oxidized regions ($sp^3$). Single or few layered RGO sheets (<5 nm) has been studied in this regard. For example, Jung et al. compared conductivity with different reduction processes including thermal, chemical, and a combined chemical/thermal approach [241]. The samples treated by a combined chemical/thermal reduction displays five times higher conductivity (~300 S/m) compared to the chemical or thermal reduction (Fig. 5.2a). In another work, Mattevi et al. investigated the role of graphitic domain ($sp^2$) fraction on the conductivity of RGO sheets using thermal reduction process (Fig. 5.2b) [116]. It can be concluded that the conductivity can be tuned

![Fig. 5.2. (a) Conductivity of single sheets of graphene oxide reduced by three different reduction methods: red, thermal reduction; blue, chemical reduction; purple, combined chemical/thermal reduction [241]. (b) Conductivity of thermally reduced GO as a function of the $sp^2$ carbon fraction. The vertical dashed line indicates the percolation threshold at $sp^2$ fraction of ~0.6. Fitting of the experimental data reveals two different regimes for electrical transport with $sp^2$ fraction. Tunneling and/or hopping (straight dashed line) mechanisms dominate at $sp^2$ fractions below 0.6 while percolation amongst the $sp^2$ clusters dominates above the percolation threshold. The 100% $sp^2$ materials are polycrystalline (PC) graphite and graphene. The two conductivity values are for doped by gating (upper triangle) and intrinsic graphene (lower triangle). (Reproduced with permission from [116].)
over 12 orders of magnitude by tuning the $sp^2$ fraction through oxidation and reduction process. It can be also seen from here that if $sp^2$ fraction can be increased to more than 0.9, the conductivity of RGO sheets can be close to that of pristine graphene [116]. For RGO thin film (>5 nm), the thermal reduction is effective for only top few layers of GO film [197]. This indicates that chemical reduction process may be more effective for achieving high electrical conductivity of RGO thin film followed by thermal treatments.

Another important characteristic of a semiconductor device is its field effect mobility ($\mu$). The $\mu$ can be calculated from $I$–$V_g$ curve with constant bias voltage using the formula:

$$\mu = (L/WC_{ox}V)/(\Delta I/\Delta V_g)$$

where $L$ is channel length, $W$ is channel width and $C_{ox}$ is capacitance per unit area of the gate insulator. Gomez-Navarro et al. first reported the ambipolar field effect transistor (FET) device using single layer RGO with hole and electron mobilities of 2 and 0.5 cm$^2$/Vs [195]. Eda et al. also reported hole and electron mobilities of 1 cm$^2$/Vs and 0.2 cm$^2$/Vs respectively in their single layer RGO FET [197]. In both of these cases, the measurements were done at room temperature at ambient condition and the device showed prominent p-type behavior. However, when measured at low temperature in vacuum, the device showed more symmetric “V” shape ambipolar characteristics. This suggests that dominant p-type behavior in air was due to $O_2$ and moisture. Indeed, Jung et al. demonstrated high sensitiveness of the GO to air by measuring FET properties [242]. When the sample was exposed to air, there was a large hysteresis effect on p-type FET. However, when the measurement was performed in vacuum, the hysteresis disappeared and FET showed more “V” shape ambipolar behavior as shown in Fig. 5.3a. The moisture effect can also be mitigated by annealing in Ar and H$_2$ atmosphere [235]. The large scale assembled chemically reduced GO FET via DEP showed high yield FETs with holes and electrons mobility of 4 and 1.5 cm$^2$/Vs respectively [235]. This study also found that the dominant p-type behavior can be removed upon mild thermal annealing (~1000 °C) in presence of hydrazine is also a common technique used by several groups which shows electrical conductivity of ~100 S/cm and mobilities ~1.2 for holes and 0.6 cm$^2$/Vs for electrons [87]. However, the high temperature is often results in a larger amount of topological defects [241,243]. Some recent reports on larger sized RGO sheets claimed to have higher mobilities (100–4000 cm$^2$/Vs) than discussed above. Although, such high mobility was claimed due to larger sheet size, however, a closer examination revealed $sp^2$/$sp^3$ ratio and domain size (calculated from Raman) to be of the same order as reported by other authors [244,245]. In addition to pure RGO, Eda et al. showed that RGO-polystyrene (PS) composite can also show ambipolar FET device with hole and electron mobilities of 0.7 and 0.2 cm$^2$/Vs respectively [246]. The solution of GO in an organic

![Fig. 5.3.](image-url) (a) Resistance-gate voltage dependence representative RGO device in vacuum and after exposure to air (Reproduced with permission from [242]). (b) Normalized channel conductance as a function of gate voltage for ~1.5, ~2.5, and ~4 layer RGO film at $T = 4.2$ K. The channel conductance ($G(V_g)$) is normalized to its minimum value ($G_{min}$), which occurs at the charge neutrality point. (Reproduced with permission from [247].)
solvent paved the way to produce good dispersion in the PS matrix. The chemical reduction of the GO using hydrazine in the presence of the PS avoids aggregation of the GO sheets in solution. The thin film (>5 nm) of RGO sheets showed slightly different FET properties compared to single layer devices. Fig. 5.3b shows $G_{\text{max}}/G_{\text{min}}$ for FET with different layers of RGO, where $G_{\text{max}}/G_{\text{min}}$ is the ratio between maximum and minimum conductivities respectively. The single layer RGO shows higher $G_{\text{max}}/G_{\text{min}}$ compared to multilayered devices consistent with what has been reported for single layer and multilayered graphene [247].

It is clear from the above discussions that the conductivity and mobility values of RGO are low compared to that of pristine graphene (200,000 cm$^2$/Vs). There are several reasons for poor performance in RGO sheets: (1) the charge percolation is limited by disconnected network of $\pi$ delocalized tracks in the sheets due to remaining oxidized functional groups and (2) defects in the sheets, mainly produced during reduction process. The trapped state retards charge carrier dissociation on defect sites. Therefore, controlling the initial stages of reduction and oxidation of RGO sheets are very important to move forward in producing high quality RGO devices.

5.3. Defect density in chemically derived graphene

As discussed above, the electrical conductivity and field effect mobility of RGO based device is not as good as pristine graphene. Structural characterization and theoretical calculation show that this is due to the large number of defects present in the RGO sheet. Typically 60% of the area contains graphitic domains with size varying from 3 to 10 nm. The rest lies in the structural disorder of oxygen groups and topological defects. The systematic studies indicate that increased charge percolation occurs with increasing $sp^2$ (graphitic regime) fraction which leads to the increase in the conductivity of the materials [116].

The degree of orderness in the materials can be identified by Raman spectroscopy where the G band ($sp^2$) corresponds to the ordered structure and the D band to the disordered structure ($sp^3$) of the material. All RGO films exhibit the D-band peak at $\sim 1346$ cm$^{-1}$ and the G-band peak at $\sim 1604$ cm$^{-1}$ (Fig. 5.4a) [248]. The broader D-band with higher relative intensity compared to that of G-band indicates the higher disorderliness in the RGO sheets. This relatively higher intensity of the D peak in RGO shows 2–3 orders of magnitude higher than that of pristine graphene. In addition, the ratio of $I_{2D}/I_G$ is correlated with the hole mobility of the RGO devices. The labels M0.4, M1.0, M4.6, M6.9, and M12 represent the devices with mobility ratio ($I_{2D}/I_G$, cm$^2$/Vs) of 0.4/0.13, 1.0/0.22, 4.6/0.26, 6.9/0.25, and 12/0.34, respectively in Fig. 5.4a. This shows that when the $I_{2D}/I_G$ ratio increases, the mobility also increases. The average domain size of graphene ($sp^2$) was estimated by the intensity of D and G bands of the RGO sheets using empirical Tunistra-Koening relation [119] and was found

![Fig. 5.4](image-url)
to be about 2.5–6 nm [116,195,238,239]. This calculated domain sizes of graphitic domain size are in good agreement with the domain size obtained from the TEM study (see Fig. 3.10 in Section 3).

The XPS also characterizes the defects in RGO/GO and provides the qualitative information of the defects. Ruoff’s group reported that the nonconjugated sp³ carbon in RGO sheets mostly consists of defects. Therefore, in XPS the ratio of C₁₆ to O₁₆ peak related to the estimation of the defect density in RGO sheets. The higher ratio values corresponds to better reduction with lower defects [116].

Quantitative information about the defects can be obtained from electron transport measurements. It has been shown by Joung et al. that the defects in RGO sheets leads to the space charge limited conduction (SCLC) [238]. SCLC occurs in low mobility semiconductor, when injected charge density exceeds the intrinsic free carrier density of the material. Analysis of the current density (J)–voltage (V) characteristics using the SCLC model is one of the experimental methods for the detection of charge trap states in disordered semiconductors. In the absence of any trap states or when trap states do not dominate the transport, the J–V characteristics can be described by

\[ J = \frac{9\varepsilon_0\varepsilon_r \mu V^2}{8d^3} \] (5.4)

where \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_r \) the dielectric constant of the RGO, \( \mu \) is the charge carrier mobility, \( d \) is the spacing between electrodes. Whereas, in presence of trap states those are exponentially distributed in energy, the J–V relationship is given by

\[ J = \left( \frac{\mu N_r}{q^2} \right) \left( \frac{2l}{l+1} \right) \left( \frac{l+1}{l(l+1)} \right) \left( \varepsilon_0 / N_l \right) \left( l / (l+1) \right) \left( V^{l+1} / d^{2l+1} \right) \] (5.5)

where \( l \) is an exponent and should be greater than 1, \( q \) is the electronic charge, \( N_r \) is effective density of states, and \( N_l \) is the trap density. By plotting \( J \) and \( V \) in log–log scale one can determine the value of exponent \( m \). For trap free (TF-SCLC) regime, \( m = 2 \) while for exponentially distributed trap (EDT-SCLC) regime \( m = l+1 > 2 \). Fig. 5.4b shows temperature dependent current density (J)–voltage (V) characteristics curve of a DEP assembled RGO device. The solid lines are fit to \( J \propto V^m \) [249,250]. At low bias, the conduction is Ohmic with \( m = 1 \), while at higher bias voltages \( m \) increases from 2 to 3 with reducing temperature, signifies space charge limited conduction (SCLC) with a transition from trap free SCLC regime at room temperature to exponentially distributed trap SCLC regime at low temperatures. An exponential distribution of trap in energies is expected from the originated surface defects and structural disorders. Defect density can be calculated by extrapolating J–V curve to find a temperature independent critical voltage \( V_c \) which is related to the defect density through \( V_c = q N_r d^2 / 2 \varepsilon_r \varepsilon_0 \), where \( N_r \) is defect density, \( d \) is the spacing between electrodes, \( \varepsilon_r \) dielectric constant of RGO, and \( \varepsilon_0 \) is permittivity. The \( V_c \) for RGO device was about 10 V as shown in Fig. 5.4c, from which one obtain an average trap density of \( \sim 1.75 \times 10^{16} \) cm⁻³. The large trap density indicates the presence of large number of defects and structural disorder, which cause lower transport properties.

5.4. RGO as graphene quantum dot array: Coulomb blockade effect

The structural characterization through TEM, XPS, scanning tunneling Microscopy (STM) and Raman spectra show that the RGO consists of ordered graphitic (nanocrystalline) regions surrounded by areas of oxidized carbon atoms, point defects, and topological defects [116,117,120,195,251]. The graphitic regions were estimated to be of 3–10 nm from the TEM, STM and Raman studies [116,117,120,195,251]. Optical studies of RGO also showed blue light emission [212] and infrared absorption [114,252], determined by the size, shape and edge configuration sp³ graphitic domain. All these studies suggest that RGO can be modeled as a two-dimensional array of graphene quantum dots (GQD) [239], where graphitic domains act like QDs while oxidized domain behave like tunnel barriers. This has been verified by Joung et al., in the low temperature electrical conduction in few layers RGO. Fig. 5.5a shows current–voltage (I–V) characteristics of one of their device. As the temperature is lowered to less than 15 K, a complete suppression of the current below a threshold voltage \( V_t \) was observed. Such current suppression was explained due to Coulomb blockade (CB) of charges, as at low temperatures there is not enough energy for the charges to overcome Coulomb charging energies of the QD array formed by graphitic domains. It is expected from theory that for a QD array, the I–V curves should follow a relation \( I \propto (V - V_t) / V_t^{\alpha} \) for \( V > V_t \), where \( \alpha \) is the scaling exponent that
depends on the dimensionality of the arrays. This is also shown to be the case in RGO (Fig. 5.5b) where \(a\) was estimated to be \(3.4\). For a two-dimensional array of nanoparticles, the theoretical value of \(a\) was predicted as 1.6 while numerical simulations yielded as 2.0 [253]. However, experimental studies of two dimensional metal nanocrystal arrays, the exponent \(a\) was reported to vary from 2 to 2.5 which depends on size distribution, while for quasi 2D system with multilayered nanoparticles the value was 2.6–3.0 [254–258]. Therefore, the experimental results in RGO which showed \(a \approx 3.4\) is higher than 2D array system. However, recent experimental and computer simulations involve gold nanoparticles array with strong topological inhomogeneity show large scaling exponents \(a \approx 4.0\) [259,260]. Since RGO has a lot of topological defects which came from oxidation and reduction process, the high value of \(a\) is in agreement with charge transport in an inhomogeneous quasi 2D QD array network. Fig. 5.5c shows a schematic of RGO as a QD array with strong topological heterogeneity. The light gray areas represent GQDs, the white regions represent oxidized carbon groups and topological defects. This shows that the GQDs are isolated (or localized) by oxidized carbon atoms and topological defects and there is strong size distribution of GQDs. The lines between GQDs indicate tunnel barriers.

5.5. Hopping conduction in RGO

Since RGO contains a lot of disorder consisting of localized graphene domains along with oxidized areas, the low temperature resistance measurements show hopping transport phenomenon. Both Mott variable range hopping (VRH) [261,262] and Efros–shklovskii VRH [239] have been reported in RGO.

5.5.1. Mott variable range hopping

Mott described that at very low temperatures, when there is not enough thermal energy for the charge to go from valance band to conduction band, the charge conduction occurs via hopping among
the localized states [263]. When the energy is low, the carrier will hop longer distance. This is called variable range hopping. According to Mott, the conductivity of such a system can be described as,

$$\sigma = A \exp \left(-\frac{T_0}{T^{1/(d+1)}}\right)$$

(5.6)

where $A$ is a constant, $T_0$ is critical temperature and $d$ is the dimensionality of the system. So for a 2D system, the relation became $\sigma \sim T^{-1/3}$. However, it should be noted that in Mott VRH, the Coulomb interaction among localized states is neglected and there is no minimum energy needed for the carriers to hop. Since, RGO has a lot of defects which localizes charge carriers, it is expected that low temperature transport properties of the RGO can be explained using VRH model.

Kern and coworkers, first applied Mott VRH model to describe the temperature dependence of current for various back-gate voltages [261]. They showed that $\ln I$ followed linear relation with $T^{1/3}$ as shown in Fig. 5.6a. From the slope of these curves, the obtained values for $T_0$ which in 2D is given by

$$T_0 = \left(\frac{3}{N(E_F)k_B L_i^3}\right)^{1/3}$$

(5.7)

where $L_i$ is the localized length and $N(E_F)$ is the density of state near the Fermi level.

Applying negative $V_g$ leads to the lower value of $T_0$ (same as B) indicate higher localization length (Fig. 5.6b). However, the values of $T_0$ for positive gate voltages are considerably larger than those for the negative gate voltages, indicating shorter localization lengths ($L_i$). Eda et al. also reported Mott VRH model for their study of transport properties of RGO with various reduction process with temperature ranging from 78 to 300 K (Fig. 5.6c) [262]. Lightly reduced GO device (10 min and 30 min reduction) showed linear trend in whole temperature ranges, while well reduced GO devices (16 h, HG-A, and HG-B) showed transition from Mott VRH ($T^{-1/3}$) to Arrhenius-type ($T^{-1}$) hopping above 240 K.

Fig. 5.6. (a) Natural logarithm of the measured current $I$ vs. $T^{-1/3}$ fitted to representing 2D variable range hopping in parallel with a temperature-independent term, for different values of the gate voltage $V_g$ as indicated, for bias voltages. (b) Parameters for the fits in figure (a), plotted as a function of gate voltage $V_g$ for different values of bias voltage $V_{ds}$ (Hopping parameter $B$) [261]. (c) Temperature and electric field dependence of the RGO device properties. Minimum conductivity $\sigma_{\text{min}}$ of RGO as a function of $T^{-1/3}$. The linear fits show agreement with the VRH transport. For samples 16 h, HG-A, and HG-B, deviation to thermally activated transport is observed at temperatures indicated by the arrows. (Reproduced with permission from [262].)
5.5.2. Efros–Shklovskii (ES) VRH

Efros and Shklovskii [264–266] pointed out that for certain systems, the Coulomb energy between localized states near the Fermi level must be overcome for a carrier to hop from one site to another. In other words, there is a Coulomb gap near the Fermi level where the density of states vanishes. Under such circumstance, the conductivity is independent of dimension and should follow, ES VRH

\[ R = A \exp \left( -\frac{T_0}{T} \right)^\frac{1}{2} \]  

(5.8)

where \( T_0 \) is a constant related to the disorderness of the material. And the \( T_0 \) is described as

\[ T_0 = \left( \frac{2.8e^2}{4\pi\varepsilon_0 k}\right) \] 

(5.9)

for a 2D system, where \( \varepsilon \) dielectric constant of RGO and \( \xi \) is localized length [264–266]. ES VRH model was successfully applied for granular metals and QD array systems with significant size and structural disorders.

Joung et al. noted that the structural information strongly suggests that RGO can be modeled as an array of QDs with significant size and structural disorder (polydispersed QD array), which has been verified in low temperature \( I-V \) curve [239]. In addition, recent study of individual 10 nm sized graphene quantum dots show room temperature Coulomb blockade (CB) [162,267]. This suggests that Coulomb interaction should be important in the transport study of RGO. Moreover, it was also noted that for a polydisperesed QD array, the temperature dependent resistance data should follow ES VRH. This was experimentally verified by obtaining resistance data (calculated from the linear part of the \( I-V \) curve), which vary by three orders of magnitude for temperature ranges of 30–295 K. Since, fitting the resistance data with different behavior can be tricky and the same data can often fit with several behaviors (such as \( T^{-1} \), \( T^{-1/2} \), and \( T^{-1/3} \)), the behavior was determined by considering a generalized formula \( R(T) = R_0 \exp(T_0/T)\) and then calculating the value of \( p \) from \( \ln W = A - p \ln T \), where \( W = -\frac{\partial}{\partial \ln R(T)} \ln T = p(T_0/T)^p \) is the reduced activation energy and A is a constant [268,269].

Fig. 5.7a shows \( \ln W \) plot vs. \( \ln T \). From the slope (indicated by red line) of this curve, \( p = 0.48 \pm 0.05 \) was obtained over the whole temperature range which is consistent with ES VRH. From the plot of \( R \) versus \( T^{-1/2} \) in a semi-log scale (Fig. 5.7b) the value of \( T_0 = 4200 \) K was calculated. The localization length \( \xi \) was calculated to be 3.5 nm which is comparable to the graphitic domain size suggesting strong localization of wave functions inside each GQDs.

5.6. Application of RGO for photodetector, phototransistor and emitter

It is clear from different characterization and transport studies that RGO contains a lot of defects and they do not have the same extraordinary electrical properties as pristine graphene. However,
considering their high throughput processing ability, they may find many useful applications where extraordinary electrical characteristics are not required including sensors, transparent electrodes, solar cells, field emitters, etc. In addition, their graphitic domain nature may also be of great use for optoelectronic applications.

Photoconductivity of bulk RGO thin film has been studied using various intensities of light, external field, and photon energies [270]. The study showed higher photocurrent under same photon energy with the increase of incident light intensity and external electric field. This indicates that the charge carrier generation is influenced by the number of photons and the external field intensity in RGO sheets. Higher photoconductivity has also been observed with higher photon energy under same intensity and electric field. The time dependent photocurrent decay results show extra time required to recombine charge carriers upon increase of external field and light intensity. It can be concluded that the RGO film generates more charge carriers per unit volume upon irradiation of higher photon energy. In comparison with SWNT, the RGO film shows high photocurrent generation efficiency [270].

Position dependent RGO thin film photo-detector has been reported by using near-infrared (wave length of ~800 nm) light [252]. Fig. 5.8a shows a schematic diagram of the device and electron transport measurements setup. L corresponds to illumination on the left electrode/film interface, R corresponds to illumination on the right electrode/film interface, and M corresponds to the middle position of the film. Fig. 5.8b shows the photocurrent with different laser spot positions. The photocurrent either increases and decreases or remains almost zero depending on the position of the laser spot with respect to the electrodes. In detail, the I–V curves for position M and in dark lie on top of the one another and pass directly through the origin. Whereas, when the light illuminated at position L and R, the I–V curve is shifted above or below the origin respectively. A large enhancement of photocurrent as well as a finite photo-voltage at the interface indicates that there is an existence of locally generated electric field at the metal-RGO film interface. This mechanism of the local electric field generation was explained using Schottky barrier (SB) model. In schematic diagram (Fig. 5.8c), the black filled and open circles inside the dotted oval region represent the photogenerated excitons (bound electron–hole pair) due to absorption of NIR source (curved red arrow). Solid line is the potential variation within the graphene channel and dashed lines are the Fermi levels ($E_F$) of the two electrodes. When NIR is illuminated on the left electrode/RGO film interface, excitons are generated and dissociated into free charge carriers at the interface. Since RGO thin film has a lot of defects, it will also help in dissociation of excitons into free carriers. Some of the free carriers (holes) might have sufficient energy to overcome the SB and enter into the metal electrode leaving the electron in the film. This causes a hole–electron separation at the interface creating a positive photo-voltage. In addition, the time constant of the dynamic photo response was ~2.5 s which is much larger compared to the single sheets of pristine graphene, possibly due to the disorder from the chemical synthesis and interconnection of sheets.

RGO FET phototransistor also has been studied based on their energy band gap values [271]. In this case, RGO FET, in which few layer RGO sheets serves as the semiconducting channel and is designed to conduct positive and negative charge carriers (holes and electrons, respectively). The band gap, which

![Fig. 5.8.](image-url)
ranges from 2.2 eV to 0.5 eV, can be made tunable by reduction treatments. These results also indicate that the photosensitivity is strongly related to the number of oxidized functional group. The rough estimation of the photosensitivity of RGO FET was calculated to be around 0.85 A W, three orders lower than that of the pristine graphene [272].

In addition to RGO thin film, the optical properties of individual GO/RGO sheet was also studied. Semiconducting GO/RGO shows absorption from ultraviolet (UV) to infrared (IR), wavelength of from 10 to 2500 nm [97,114,209,212,273]. Acik et al. reported that the single layer GO and RGO have different response of infrared absorption band due to their different functional groups on the edge region (Fig. 5.9a and b) [114]. If the GO is well reduced, oxygen-containing functionalized groups get removed and the infrared spectra of RGO become strong due to the in-phase electron band population with mobile electrons localized at the edge resulting in stronger absorption. In another study, Eda et al. [212] demonstrated that RGO thin films emitted near-UV blue light, when excited with UV radiation. The blue photoluminescence (PL) was observed for the RGO sheets. By appropriately controlling the reduction process, the PL intensity increased by a factor of 10 compared to the as-synthesized GO sheets. The results indicated that RGO offers tunable optoelectronic device via controlling the reduction process through chemical and/or thermal route.

5.7. Graphene thin film as transparent electrodes

It has been demonstrated that thin film (<30 nm) of RGO is semi-transparent to visible and NIR region while thick films are opaque. The transmittance and conductivity of the GO/RGO film can be tuned by tuning the thickness of the film and the degree of reduction [28]. Fig. 5.10 shows how the transparency of RGO varies with film thickness. The leftmost film is 9 nm thick GO while rest of the films are RGO (annealed in 1100 °C for 3 h) with thickness 6, 8, 27 and 41 nm (from left to right). As it can be seen that, as the film gets thicker, the transmittance gets reduced. While the conductivity of the RGO thin film increases with the degree of reduction and transmittance decrease. Therefore, the optimization of film thickness and reduction parameters is the key in achieving high performance transparent and conducting RGO thin film. Table 5.1 summarizes the recent progress on optoelectronic properties of graphene-based thin films in terms of their reduction and fabrication methods.

Optical and mechanical properties of RGO thin film were also studied on flexible substrates. For example, Yin et al. [278] studied the effect bending on the properties of RGO for film thickness of 4–21 nm. After applying tensile stress (tensile strain of 2.9%) on the device, the performance was monitored by resistance change with the number of bending cycles. The device showed an excellence stability of resistance, even when bending cycles reached about 1000 times.

Fig. 5.9. (a) Transmission infrared-absorbance spectrum of GO-1L. (b) Transmission infrared absorption spectra of thermally reduced GO-1L after annealing at 850 °C. (Reproduced with permission from [114].)
Due to their transparency, conducting and flexible nature, RGO thin film is considered to be a promising electrode material for organic electronic and optoelectronic applications. Presently, indium doped tin oxide (ITO) is widely used as transparent and conducting electrodes in optoelectronic application. However, the ITO based materials are expensive and their limitation of mechanical flexibilities makes them un-attractive for flexible display and solar cell applications. In this respect, RGO electrodes provide several advantages; (i) possibilities on one phase reaction without additional surfactant due to water soluble properties, (ii) the homogeneity and composition of the films are simply determined by the composition of the parent suspension and surface modification of the substrate, (iii) relatively inexpensive starting materials, and (iv) low temperature and high throughput processing. In addition, the work function of RGO (4.2–4.6 eV) matches with the HOMO level of most of the organic materials, and $\pi$–$\pi$ interaction exists between RGO and organic material.

Several research groups successfully used RGO electrode for the fabrication of organic light emitting diodes (OLED) and solar cells. Efficient RGO-based OLEDs have been first demonstrated by Wu

Table 5.1
Progress in graphene-based transparent electrodes and their properties.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reduction</th>
<th>Fabrication method</th>
<th>Film thickness</th>
<th>Sheet resistance (Ω/square)</th>
<th>Wave length (nm)</th>
<th>Transmittance (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO</td>
<td>Hydrazine solution/annealing</td>
<td>Spray coating</td>
<td>~1 nm</td>
<td>20 M</td>
<td>600–1000</td>
<td>96</td>
<td>[194]</td>
</tr>
<tr>
<td>RGO</td>
<td>Hydrazine vapor/annealing</td>
<td>Vacuum filtration</td>
<td>~3 nm</td>
<td>0.16 M</td>
<td>550</td>
<td>90</td>
<td>[197]</td>
</tr>
<tr>
<td>RGO</td>
<td>Hydrazine vapor/annealing</td>
<td>LB</td>
<td>1–3 nm</td>
<td>8 K</td>
<td>1000</td>
<td>83</td>
<td>[36]</td>
</tr>
<tr>
<td>RGO</td>
<td>Hydrazine vapor/annealing</td>
<td>Spin coating</td>
<td>1</td>
<td>$10^2$–$10^3$</td>
<td>400–1800</td>
<td>80</td>
<td>[28]</td>
</tr>
<tr>
<td>RGO</td>
<td>Acetylene-assisted thermal</td>
<td>Spin coating</td>
<td>1.1</td>
<td>1425</td>
<td>500</td>
<td>70</td>
<td>[274]</td>
</tr>
<tr>
<td>RGO</td>
<td>SOCl$_2$ treatment</td>
<td>Vacuum filtration</td>
<td>~10 nm</td>
<td>40 K</td>
<td>300–900</td>
<td>64</td>
<td>[230]</td>
</tr>
<tr>
<td>RGO/SWNT</td>
<td>Hydrazine solution/annealing</td>
<td>Spin coating</td>
<td>5 nm</td>
<td>240</td>
<td>UV visible</td>
<td>86</td>
<td>[275]</td>
</tr>
<tr>
<td>RGO</td>
<td>Hydrazine solution/annealing</td>
<td>Spin coating</td>
<td>5–8</td>
<td>0.4–19 K</td>
<td>1000</td>
<td>60–80</td>
<td>[276]</td>
</tr>
<tr>
<td>RGO (OLED device)</td>
<td>Hydrazine solution/annealing</td>
<td>Spin coating</td>
<td>~7</td>
<td>0.8 K</td>
<td>550</td>
<td>82</td>
<td>[277]</td>
</tr>
</tbody>
</table>

Due to their transparency, conducting and flexible nature, RGO thin film is considered to be a promising electrode material for organic electronic and optoelectronic applications. Presently, indium doped tin oxide (ITO) is widely used as transparent and conducting electrodes in optoelectronic application. However, the ITO based materials are expensive and their limitation of mechanical flexibilities makes them un-attractive for flexible display and solar cell applications. In this respect, RGO electrodes provide several advantages; (i) possibilities on one phase reaction without additional surfactant due to water soluble properties, (ii) the homogeneity and composition of the films are simply determined by the composition of the parent suspension and surface modification of the substrate, (iii) relatively inexpensive starting materials, and (iv) low temperature and high throughput processing. In addition, the work function of RGO (4.2–4.6 eV) matches with the HOMO level of most of the organic materials, and $\pi$–$\pi$ interaction exists between RGO and organic material.

Several research groups successfully used RGO electrode for the fabrication of organic light emitting diodes (OLED) and solar cells. Efficient RGO-based OLEDs have been first demonstrated by Wu
et al. [277]. The RGO-based OLED performance nearly matches with that of the ITO based device, even though higher resistance (800Ω/square) and different work function of the RGO anodes. Wang et al. reported that RGO films can be employed for fabrication of dye-sensitized solar cells [224]. In this application, Spiro-OMeTAD was used as a hole transport material, and porous TiO$_2$ used for electron transport materials. The solar cell was fabricated using RGO as an anode and Au as cathode (Fig. 5.11a). Fig. 5.11b shows the energy level diagram of a RGO (4.42 eV)/TiO$_2$/dye/spiro-OMeTAD/Au (5.0 eV) device. The electrons are first injected from the excited state of the dye into the lowest unoccupied molecular orbital (LUMO) level of TiO$_2$ and then reached the RGO electrode via a percolation mechanism inside the porous TiO$_2$ structure. Meanwhile, the photo-oxidized dyes are regenerated by the spiro-OMeTAD hole conducting molecules (highest occupied molecular orbital (HOMO)) and then hole inject into Au cathode. Fig. 5.11c shows I–V curve of the solar cell using RGO (black curve) as anode and the comparison with fluorine tin oxide (FTO) (red curve) electrode. Lower short-circuit current in RGO electrode lead to low power conversion efficiency (0.26%) compared to FTO (0.84%). This may be due to the series of resistance of the device, lower transmittance of the materials (70.7%), and space charge limited conduction on contact between active materials and RGO electrodes.

To overcome the contact problem, Yin et al. [276] suggested the use of hole transport interlayer (ZnO nanorod) between RGO electrodes and active polymeric materials by electrochemical deposition. The structures of the device was RGO/ZnO/P3HT/PEDOT:PSS/Au. The observed higher power conversion efficiency of 0.31% was demonstrated, compared to ZnO-free interlayer. As can be seen, the solar cell fabricated with RGO electrode suffers from low efficiency and more work is needed to make RGO as an efficient electrode material.

5.8. Solar cell using GO/RGO

As mentioned in the previous section, RGO transparent electrodes can be used for solar cell electrode. Several studies suggest that GO/RGO can also be used as hole transport layer as well as a part of active material. In vertical bulk heterojunction (BHJ) devices, both the donor and acceptor phases are in the direct electrical contact with the cathode and anode electrodes. Most vertical organic solar cells are composed of ITO/P3HT:PCBM/Al configuration. The polymeric donor and acceptor materials often result in recombination of carriers and current leakage. To minimize such detrimental effects, electron blocking and hole transport layers (HTLs) are deposited on top of the transparent and conducting ITO anode (Fig. 5.12a) [281]. The most common HTL in polymer solar cells is PEDOT:PSS. However, PEDOT: PSS combination has been made from highly acidic aqueous suspensions that corrodes the ITO at high temperatures and contributes water/moisture into the active layer, which leads poor device performance [281]. To overcome this issue, ITO/GO/P3HT:PCBM/Al configuration was introduced for more efficient collection of holes and the band energies of the configuration are 4.4–4.5/4.9/4.9:4.2/4.2 eV respectively. Interestingly the power efficiency values are dependent on GO film thickness. GO thickness of 2 nm has shown best efficiency performance compared to higher thickness (>4 nm) due to the increase in serial resistance and the slightly lower transmittance of the films with thickness.

Fig. 5.11. (A) Illustration of dye-sensitized solar cell using graphene film as electrode, the four layers from bottom to top are Au, dye-sensitized heterojunction, compact TiO$_2$, and graphene film. (B) The energy level diagram of graphene/TiO$_2$/dye/spiro-OMeTAD/Au device. (C) I–V curve of graphene-based cell (black) and the FTO-based cell (red), illuminated under AM solar light (1 sun). (Reproduced with permission from [224].)
Other studies have shown the use of RGO as acceptor materials in the BHJ photovoltaic devices. For instance, Liu et al. reported the organic solution-processable RGO as an acceptor material in organic photovoltaic devices with P3HT as an electron-donor material. Fig. 5.12b shows a schematic diagram of a solar cell using RGO as an active material. The RGO was well dispersed in P3HT with 10 wt% doping. The properties of the materials induce quenching of the photoluminescence (PL) of the P3HT and lead to strong electron/energy transfer from the P3HT to the RGO. Power-conversion efficiency $\sim1.1\%$ was achieved by using RGO as an active material. Table 5.2 shows the role of graphene-based materials in solar cell and their photovoltaic properties including RGO as an active materials as well as an electrode.

**Table 5.2**

<table>
<thead>
<tr>
<th>Active material</th>
<th>Electrode material</th>
<th>Reduction</th>
<th>Deposition</th>
<th>Thickness (nm)</th>
<th>Fill factor (FF)</th>
<th>Power-conversion efficiency (%)</th>
<th>Role of GO/RGO</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PCBM</td>
<td>RGO/PET</td>
<td>Thermal</td>
<td>Spin coating</td>
<td>16</td>
<td>0.32</td>
<td>0.78</td>
<td>Electrode</td>
<td>[278]</td>
</tr>
<tr>
<td>TiO$_2$ film (RGO/TiO$_2$ composite interlayer)</td>
<td>FTO</td>
<td>Photocatalytically by UV irradiation</td>
<td>Spin coating</td>
<td>$\sim15$</td>
<td>N/A</td>
<td>5.26</td>
<td>Interfacial layer</td>
<td>[283,284]</td>
</tr>
<tr>
<td>P3HT:graphene/ PEDOT:PSS</td>
<td>Al:LiF/ITO</td>
<td>Thermal</td>
<td>Spin coating</td>
<td>100 with P3HT</td>
<td>0.3</td>
<td>1.1</td>
<td>Acceptor</td>
<td>[285]</td>
</tr>
<tr>
<td>PEDOT:PSS/P3HT/ ZnO nanorods</td>
<td>Au/RGO</td>
<td>Hydrazine vapor/ thermal</td>
<td>Spin coating</td>
<td>5–13</td>
<td>0.33</td>
<td>0.31</td>
<td>Electrode</td>
<td>[276]</td>
</tr>
<tr>
<td>TiO$_2$/dye/spiro-OMeTAD</td>
<td>Au/RGO</td>
<td>Thermal</td>
<td>Dip coating</td>
<td>10</td>
<td>0.36</td>
<td>0.84</td>
<td>Electrode</td>
<td>[224]</td>
</tr>
</tbody>
</table>

Fig. 5.12. (a) Schematic of the photovoltaic device structure consisting of the following: ITO/GO/P3HT:PCBM/Al. (b) Energy level diagrams of the bottom electrode ITO, interlayer materials (PEDOT:PSS, GO), P3HT (donor), and PCBM (acceptor), and the top electrode Al (Reproduced with permission from [281]). (c) The schematic chemical structure of SPF Graphene and P3HT. (d) Schematic structure of the devices with the P3HT/SPF graphene thin film as the active layer; ITO ($\sim17\,\Omega\,\text{sq}^{-1}$)/PEDOT:PSS (40 nm)/P3HT:SPFGraphene (100 nm)/LiF (1 nm)/Al (70 nm). (Reproduced with permission from [282].)
5.9. Electrochemical sensors and biosensors

RGO is highly promising for electrochemical and biological sensors due to their different functionalities on the edge [286–288] which are very sensitive to change in chemical and biological environment. The responses have been analyzed by changes in conductivities, capacitances, and doping effects on FETs made with RGO. Table 5.3 summarizes the sensors fabricated with RGO based-materials.

Table 5.3
Graphene based chemical/biosensors.

<table>
<thead>
<tr>
<th>Active material</th>
<th>Reduction method</th>
<th>Sensor type</th>
<th>Analyte</th>
<th>Measurement</th>
<th>Detection limits</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO</td>
<td>Thermal</td>
<td>Gas</td>
<td>NO₂, NH₃</td>
<td>I vs. t</td>
<td>~100 ppm</td>
<td>[289]</td>
</tr>
<tr>
<td>RGO + Pd</td>
<td>Chemical</td>
<td>Gas</td>
<td>H₂</td>
<td>R vs. t</td>
<td>N/A</td>
<td>[290]</td>
</tr>
<tr>
<td>RGO</td>
<td>Thermal</td>
<td>Molecular</td>
<td>HCN, CEES DMMP, DDT</td>
<td>G vs. t</td>
<td>~ppb</td>
<td>[226]</td>
</tr>
<tr>
<td>RGO</td>
<td>Chemical</td>
<td>Gas</td>
<td>NO₂, NH₃, DNT</td>
<td>R vs. T</td>
<td>~ppm</td>
<td>[287]</td>
</tr>
<tr>
<td>RGO</td>
<td>Chemical</td>
<td>Electrochemical/chemical</td>
<td>Electroactive compound (potassium ferricyanide, free bases of DNA), neurotransmitter (dopamine), biological molecule (ascorbic acid, uric acid, acetaminophen)</td>
<td>I vs. E/V</td>
<td>~μM</td>
<td>[291]</td>
</tr>
<tr>
<td>RGO + DNA</td>
<td>Chemical</td>
<td>Bio</td>
<td>DNA, bacterium</td>
<td>G</td>
<td>~single-stranded DNA, molecule ~single bacterium</td>
<td>[99]</td>
</tr>
<tr>
<td>RGO + Au</td>
<td>Electrochemical</td>
<td>Bio</td>
<td>DNA</td>
<td>I vs. E/V</td>
<td>~μM/L</td>
<td>[292]</td>
</tr>
<tr>
<td>SDBS functionalized graphene (RGO + HRP)</td>
<td>Chemical</td>
<td>Bio</td>
<td>H₂O₂</td>
<td>I vs. t</td>
<td>~30 μM</td>
<td>[293]</td>
</tr>
<tr>
<td>RGO + Au antibody</td>
<td>Thermal</td>
<td>Bio</td>
<td>DNA, Protein</td>
<td>R vs. t</td>
<td>~ng/ml</td>
<td>[294]</td>
</tr>
<tr>
<td>GO</td>
<td>N/A</td>
<td>Bio</td>
<td>H₂O₂</td>
<td>I vs. E/V and I vs. t</td>
<td>~μM</td>
<td>[295]</td>
</tr>
<tr>
<td>GO/MNO₂</td>
<td>N/A</td>
<td>Bio</td>
<td>NO₂</td>
<td>I vs. t</td>
<td>~ppm</td>
<td>[296]</td>
</tr>
<tr>
<td>RGO</td>
<td>Thermal, chemical</td>
<td>Gas</td>
<td>Water vapor</td>
<td>R vs. t</td>
<td>N/A</td>
<td>[241]</td>
</tr>
<tr>
<td>RGO, RGO/Nafion, Fatigued-RGON</td>
<td>Chemical</td>
<td>Bio</td>
<td>Organo Phosphate (OPH)</td>
<td>I vs. E/V and I vs. t</td>
<td>1.39 μM, 0.137 μM, 0.360 μM</td>
<td>[298]</td>
</tr>
<tr>
<td>RGO (inkjet printer)</td>
<td>Chemical</td>
<td>Gas (Vapor)</td>
<td>NO₂, Cl₂</td>
<td>R vs. t</td>
<td>~ppm</td>
<td>[299]</td>
</tr>
<tr>
<td>RGO</td>
<td>Chemical</td>
<td>Molecule (Redox species)</td>
<td>Ru(NH₃)₆³⁺/²⁺, Fe(CN)₃⁻/²⁻, FeCl₂³⁻/²⁻</td>
<td>I vs. E/V</td>
<td>~mM</td>
<td>[300]</td>
</tr>
<tr>
<td>GO-CdTe (NPs or QDs)</td>
<td>N/A</td>
<td>Molecule</td>
<td>Thiole-containing compound</td>
<td>I vs. E/V</td>
<td>~μM</td>
<td>[301]</td>
</tr>
<tr>
<td>Pt/(RGO)/SiC</td>
<td>Thermal</td>
<td>Gas</td>
<td>H₂</td>
<td>I vs. t</td>
<td>N/A</td>
<td>[302]</td>
</tr>
</tbody>
</table>

* HRP: Horseradish peroxide a type of enzyme, current (I), conductivity (G), resistance (R), potential E/V, time (t), ppm: part per million, ppb: part per billion, SDBS: sodium dodecyl benzene sulphonate.
The sensitivity of the gas (or vapor phase) sensor depends on the charge carrier transfer on GO/RGO surfaces caused by the adsorption of gases and vapors such as NO$_2$, NH$_3$, H$_2$O, CO, dinitrotoluene (DNT), iodine, and ethanol and hydrazine hydrate [226,286–288,303,304]. For example, the as-synthesized GO transistor showed little response to chemical gases such as NO$_2$ [287]. In contrast, the RGO was highly responsive to NO$_2$ and showed a typical p-type transistor behavior most likely due to the recovery of many graphitic carbon atoms as active sites for NO$_2$ adsorption, which leads to enhancing charge concentration. This leads to a decrease in resistance as a function of time (Fig. 5.13a). The NH$_3$ makes n-type RGO transistor behaviors [289,297] since oxygen groups in RGO were responsible for reactions with NH$_3$ and C=–N bond [243]. This reaction decreases device conductivity (Fig. 5.13b) as a function of time [287].

High temperature (∼1000 °C) reduced GO shows faster chemoresistive (or resistance changes in time) response than the hydrazine and low temperature reduction upon exposure to water vapor. This is attributed to the presence of larger number of defects during the high temperature reduction process [241]. These results indicate that the gaseous vapor may respond with both structural defects, such as vacancies and/or small holes generated during reduction treatments, and functionalized groups. Therefore, the sensitivity of RGO based sensors can be modified by controlling of reduction treatment process [226,241].

Besides chemical (by hydrazine) and thermal reduction, the ascorbic acid (vitamin C) has also been used as a mild and green reduction agent for RGO based chemical sensors [299]. The flexible RGO chemical sensor, using inkjet-printed films of poly-(ethylene terephthalate) (PET) decorated RGO sheets reversibly detect NO$_2$ and Cl$_2$ vapors at parts per billion level. This demonstrates the use of ascorbic acid as an effective alternative to hydrazine to reduce GO into RGO.

Graphene based composite materials have been studied for gas sensor. For example, Pt/RGO/SiC based devices for hydrogen gas sensing [302]. The electrical characteristics and hydrogen gas sensing mechanism of the device were described by analyzing the effect of hydrogen interaction at the graphene/SiC and Pt/graphene interfaces. High work function of Pt leads to a weak interaction energy at the interface and preserves the electronic structure of RGO and electrons transfer from RGO to Pt to equilibrate the Fermi level. Upon exposure of hydrogen gas, the carrier concentration is increased due to dissociation of hydrogen molecules, which occurs on the Pt surface.

Several studies have been demonstrated RGO based biosensors as well. Mohanty and Berry [99] reported on the fabrication and functioning of a novel RGO-based (i) single-bacterium device, (ii) label-free DNA sensor, and (iii) bacterial DNA/protein and polyelectrolyte transistor. The bacteria/RGO bio-device was highly sensitive with a single bacterium with a p-type FET property. The presence of DNA on RGO increased both the conductivity and the mobility (Fig. 5.14 a and b) due to the interaction between the charged amine group and the RGO. Similarly, single-stranded DNA when tethered on graphene, hybridizes with its complementary DNA strand which reversibly increases the hole density by $5.61 \times 10^{12}$ cm$^{-2}$. Also the bending-insensitive RGO FETs were able to detect the presence and

**Fig. 5.13.** (a) NO$_2$ detection and (b) NH$_3$ detection using a graphene film. The sensor has gold electrodes and measurement used a four wire method with 500 µA driving current. The NO$_2$ concentration is 5 ppm in dry nitrogen. (Reproduced with permission from [287].)
dynamic cellular secretion of biomolecules. The specificity of the demonstrated detection is realized in the defined biological context. The RGO FETs can also specifically detect biomolecules with high sensitivity using specific antibodies [305].

The fabrication and characterization of a highly sensitive and selective FET biosensor using Au NP-antibody conjugates decorated with GO sheets have been reported [294]. The study demonstrates a GO-based immuno-biosensor for detecting a rotavirus as a pathogen model. The sensor showed high sensitivity and selectivity by using GO. CdTe/RGO composite also exhibited the chemical–biological sensing where graphene worked as an amplified electrogenerated chemiluminescence (ECL) platform [301]. The study opens avenues for glutathione drug detection with graphene-based electronics glutathione drug detector or sensor.

6. Graphene based composites

Various polymers and nano particles (metal, metal oxide, semiconductor) composites have been developed based on the unique properties of the graphene. Graphene possesses similar mechanical properties as CNTs but has superior electrical and thermal properties, and larger surface area (2620 m²/g) [306] because of its 2-dimensional crystal structure. The mechanical exfoliation of graphite is not suitable for large scale production, while chemical oxidation of graphite into graphite oxide offered an easy path to obtain graphene oxide in a large quantity that can be reduced chemically, electrochemically [290] or thermally into graphene. The bulk production of GO and RGO has given opportunities to explore this flat structure of carbon with polymer and nano particles in composites.

6.1. Graphene–polymer composites

Graphene and its derivatives as fillers for polymer matrix composites have shown a great potential for various important applications. In the past few years, researches have made successful attempts for GO and graphene–polymer composites similar to CNT-based polymer composites. 2-D graphene has better electrical, thermal and mechanical properties as well as higher aspect ratio and larger surface area than other reinforced materials such as CNTs, fibers of carbon and Kevlar. Its reinforcement can offer exceptional properties in composites and applications in the field of electronics, aerospace,
automotive and green energy. The recent advancement in bulk synthesis processes of graphene and RGO has generated great interest to incorporate such unique material into various polymer matrices. Several challenges need to be overcome to realize graphene or graphene oxide based polymer composites,

1. Functionalization of graphene sheets
2. Homogeneous dispersion of materials with minimal restacking
3. Effective mixing of graphene oxide and graphene with polymer
4. Understanding of the interfacial structure and properties
5. Controlling the folding, crumpling and bending of graphene materials

This section is devoted to only graphene and graphene oxide–polymer composites and highlights their properties and applications.

Two potential approaches are commonly used to produce a single layer of graphene with high yield: (1) chemical and (2) thermal reduction of exfoliated sheets of graphene oxide, as explained in earlier sections. Both the methods disrupt the conjugated electrical structure of graphene and reduce the electrical conductivity. On the other hand, the functional groups introduced by these invasive approaches can be used to achieve good dispersion of derived graphene in different solvents. Numerous efforts have been made to improve the dispersion of GO and RGO by functionalizing the use of organic molecules compatible with the polymer matrix to enhance interfacial interaction with matrix. For example, GO has carboxylic, hydroxyl and epoxy groups on the surface which improve its dispersion in water and keep individual layers separated from each other [26,307]. However, these functional groups and defects on GO make it electrically insulating and thermally unstable, and the removal of these functional groups during reduction makes RGO hydrophobic and increases tendency to agglomerate irreversibly in an aqueous medium unless stabilized by polymers and surfactants [82].

The dispersion behavior of GO in different organic solvents has been demonstrated in Fig. 6.1, which can guide the selection of compatible polymer matrix for bulk synthesis [75].

The dispersion of graphene oxide and reduced graphene against their agglomeration in organic solvents, after complete exfoliation of graphitic layers, has been achieved by surface functionalization through non-covalent and covalent bonding [75,308,309]. Various organic functional groups such as polystyrene [69,308], 1-pyrenebutyrate [310], dopamine [311], 7,7,8,8-tetracyanoquinodimethane [312], coronene carboxylate [313] have been used to produce stable aqueous and organic solvent dispersion and facilitated nanocomposite synthesis to induce desirable properties.

Non-covalent functional groups including 1-pyrenebutyrate [310] and 7,7,8,8-tetracyanoquinodimethane [312] have strong affinity with the basal plane of graphite through π–π interactions, while covalent functional groups attach to the surface through the reaction between the functional groups (–OH, –COOH, –CO) present on the GO and RGO surfaces and edges. For example, Xu et al. have demonstrated the covalently functionalized GO through the coupling amine-functionalized prophyrin (TPP-NH₂) and carboxylate groups [93]. The covalent polymer functionalization of graphene

Fig. 6.1. Digital pictures of as-prepared graphite oxide dispersed in water and 13 organic solvents through bath ultrasonication (1 h). Top: dispersions immediately after sonication. Bottom: dispersions 3 weeks after sonication. The yellow color of the o-xylene sample is due to the solvent itself. (Reproduced with permission from [75].)
nanosheets via atom transfer radical polymerization (ATRP) initiator was recently reported \cite{100,101,314} to achieve the dispersion of graphene sheets in polymer matrix and precise interface control (Fig. 6.2). The ATRP initiator covalently immobilized on the surface of the graphene was subsequently used for grafting polymer brushes from the sheets surface. Such controlled polymerization allows the control of the molecular structure of the grafted polymer, providing an effective approach to tune the properties of the hybrids.

In this approach, the initiator molecules were covalently attached to the graphene surfaces via diazonium addition. The subsequent atom transfer radical polymerization linked ATRP compatible polymer chains (i.e. polystyrene, polymethyl methacrylate) to the graphene sheets. Another example of the covalent functionalization of graphene sheets with polymers is through grafting-to process by the esterification of carboxylic groups in GO. The covalent functionalization of sheets with polyvinyl alcohol (PVA) via the esterification provided a facile way of producing water and DMSO soluble, similar to PVA \cite{315}.

6.1.1. Synthesis of graphene reinforced polymer composite

The method of solution blending, melt mixing, and in situ polymerization are the most common synthesis strategies of the polymer matrix composites. These methods will be summarized in this section.

6.1.1.1. Solution blending. Solution blending is the most common technique to fabricate polymer-based composites provided the polymer is readily soluble in common aqueous and organic solvents, such as water, acetone, DMF, chloroform, DCM and toluene. This technique involves the solubilization of the polymer in suitable solvents and mixing with the solution of the dispersed graphene suspension. The polar polymers including PMMA, PAA, PAN and polyesters have been successfully mixed with GO in solution blending where the GO surface was usually functionalized by isocyanates, alkylamine, alkyl-chlorosilanes, etc., to improve its dispersability in organic solvents. For instance, esterificated GO was mixed with PVA dissolved in DMSO to fabricate the PVA–GO nano composite \cite{315}.

To homogenize the dispersion of graphene sheets, ultrasonic power can be used to produce metastable suspension. It is important to note that long time exposure to high power ultrasonication can induce defects in graphene sheets which are detrimental to the composite properties. Functionalization of graphene sheets may help in obtaining a higher loading of sheets and allow dispersion in water and other organic solvents. During the blending, the polymer coats the surface of the individual sheet and interconnects each sheet after the solvents are removed. Solution blending of GO and RGO sheets tend to agglomerate during slow solvent evaporation, resulting in inhomogeneous distribution of sheets in polymer matrix. The distribution can be controlled by controlling the evaporation time using spin coating or drop casting. Various polymer composites such as graphene–PVA \cite{316}, GO–PVA \cite{317},
graphene–PVC [318], PVA–GO layer by layer assembly [319], and PVDF-thermally reduced graphene [320] have been prepared using this technique.

6.1.1.2. Melt mixing. Melt mixing technique uses a high temperature and shear forces to disperse the reinforcement phase in the polymer matrix. The process avoids the use of toxic solvents. The high temperature liquefies the polymer phase and allows easy dispersion or intercalation of GO and reduced graphene sheets. The melt mixing is less effective in dispersing graphene sheets compared to solvent blending due to the higher viscosity of the composite at increased sheets loading. The process can be applicable to both polar and non-polar polymers. However, this technique is more practical for thermo plastic manufacturing composite in large scale. Varieties of graphene reinforced composites such as, exfoliated graphite–PMMA [321], graphene–polypropylene (PP), GO-poly (ethylene-2,6-naphthalate) (PEN) [322] and graphene–polycarbonate [323], are prepared by this method. Low throughput of chemically reduced graphene restricts the use of graphene in the melt mixing process. However, graphene production in bulk quantity in thermal reduction can be an appropriate choice for industrial scale production. The loss of the functional group in thermal reduction may be a hurdle in obtaining homogeneous dispersion in polymeric matrix melts especially in non-polar polymers. Kim and Macosko [323] have not observed significant improvement in mechanical properties due to the elimination of the oxygen functional groups, which affected the interfacial bonding in graphene composite with polycarbonate and PEN, and the defects caused by high temperature reduction.

6.1.1.3. In situ polymerization. This fabrication technique starts with the dispersion of GO or RGO in monomer followed by the polymerization of the monomers. Like solution blending, functionalized graphene and GO sheets can improve the initial dispersion in the monomer liquid and subsequently in the composites. The in situ polymerization technique enables the covalent bonding between functionalized sheets and polymer matrix through various condensation reactions. On the other hand, non-covalent bonded composites such as PMMA–GO [324], PP–GO [325] and PE-graphite [326] have also been prepared by this technique. Extensive research has been performed on producing epoxy-based nano composites using in situ polymerization where sheets are first dispersed into resin followed by curing by adding hardener [284]. Recently, graphene oxide sheets have been used for Mg/Ti catalysis support for in situ Ziegler–Natta polymerization of PP, process are shown in Fig. 6.3 [325].

The prepared composite showed a good exfoliation of GO and homogeneous dispersion in PP matrix (Fig. 6.4), leading to high electrical conductivity. In situ polymerization has also been explored

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**Fig. 6.3.** Fabrication of PP/GO nanocomposites by in situ Ziegler–Natta polymerization. (Reproduced with permission from [325].)
widely for the high level of dispersion of graphite-based layered structure in a polymer matrix, such as expanded graphite and graphite oxide [326–328]. The *in situ* polymerization increases interlayer spacing and exfoliates the layered structure of graphite into graphite nano plates by the intercalation of monomers that generate polymers after polymerization, producing well-dispersed graphene in a polymer matrix. This approach has produced a variety of composites, such as PANI–GO/PANI–graphene [329], graphene nanosheet/carbon nanotube/polyaniline [330], and PANI–GO [331].

6.1.2. Mechanical properties

Higher mechanical properties (elastic modulus and tensile strength) of graphene sheets have attracted the attention of researchers. The polymer reinforced with graphene has been employed to explore intrinsic strength (125 GPa) and elastic modulus (1.1 TPa) of nanosheets to bulk polymer composites. Similar to other composites, the mechanical properties are dependent on the reinforcement phase concentration and distribution in the host matrix, interface bonding, and reinforcement phase aspect ratio, etc. For example, an increase in tensile strength of the composite (graphene–PS) with reinforcement concentration is shown in Fig. 6.5, representing an increase in the mechanical properties of the composite attributed to effective load transfer between graphene and polymer [101].

![Fig. 6.4.](image)
(A) PP/GO nanocomposites powder as obtained after coagulation in ethanol (containing 0.1 M HCl). (B) SEM images obtained from fracture surface of neat PP without GO. (C–E) SEM images obtained from fracture surface of composite samples of 0.42, 1.52, and 4.90 wt%, respectively, GO loadings. (F) TEM image of sample PP1 with 0.96 wt% of GO (the inset showing the measured electron diffraction pattern). (G) TEM image of sample PP3 with 1.52 wt% of GO. (H) TEM image of sample PP4 with 4.90 wt% of GO. (Reproduced with permission from [325].)
Although the pristine graphene has the highest theoretical strength, the presence of functional groups on the GO surfaces has the additional benefits of its high level of dispersion in polar solvents and water. The improved GO/polymer interaction facilitates high molecular level dispersion and enhanced interfacial interaction, leading to high mechanical properties. For example, GO–PVA composite showed enhancement in mechanical properties by 76% and 62% in elastic modulus and strength, respectively, with 0.7 wt% GO sheets [317]. Xu et al. have also observed a similar trend for GO–PVA composite films with a layered structure prepared by vacuum filtration [332]. Whereas, situation with the chemically reduced graphene oxide (CRG) and thermally reduced graphene oxide (TRG) is different, the presence of defects arise in carbon lattice due to the reduction process certainly have an adverse effect on the mechanical properties [120,317,322]. High surface defects and wrinkles in TRG reinforced in poly (ethylene-2,6-naphthalate) (PEN) indicated a relatively small increase in tensile properties compared to the graphite reinforced PEN.

The interaction of graphene and polymer at the interface of effective load transfer has been extensively investigated. The tailoring of mechanical properties by a covalent and non-covalent bond configuration between the matrix and sheets reinforcement can provide exceptional features. The responsible Van der Waals forces and hydrogen-bond interactions were reported for improved mechanical properties [316,333]. A recent ATRP strategy has been shown to grow styrene, methyl methacrylate, or butyl acrylate polymer brushes directly from the GO surfaces without damaging the GO structure [102]. One study used a similar strategy and revealed that when pre modified GO with PMMA chain synthesized via ATRP and mixed with PMMA matrix have better dispersion and interfacial bonding. The results showed that the loading of 1% (w/w) GO grafted PMMA made tougher films than the pure PMMA films and unmodified GO–PMMA films. The elastic modulus and tensile strength values were slightly lower than that of the pure PMMA films [314].

Research in graphene-based composites has been concentrated on improving the stiffness and the mechanical strength using graphene as filler [317,334–337]. Other mechanical properties, fracture toughness, fatigue, and impact strength of the graphene reinforced composites were also studied [284,338–340]. Recent, investigation about graphene reinforced Nayon-12, has shown the significant improvement with 0.6 wt% addition of graphene filler in tensile strength and elongation at break by 35% and 200% respectively. While, the improvement in $K_{IC}$ and impact failure energy were by 72% and 175% respectively. It has also shown that the graphene filler suppressed the crack propagation in epoxy polymer matrix. The improvement in fracture and fatigue resistance was similar to CNT and nanoparticles reinforcement but only need one to two orders of magnitude lower weight fraction of graphene nanofiller to achieve the same degree of reinforcement [284]. The superior mechanical properties of composite made of graphene platelets over carbon nanotubes was related to their high specific surface area, enhanced nanofiller matrix adhesion/interlocking arising from their wrinkled (rough) surface and 2-D flat geometry [340].
6.1.3. Electrical properties

The most fascinating property of graphene is its very high electrical conductivity. When used as fillers with insulating polymer matrices, conductive graphene may greatly enhance the electrical conductivity of the composites. Various factors have been corroborated by experimental results that influence the electrical conductivity and the percolation threshold of the composite. These factors include the aggregation of filler, the presence of functional groups on graphene sheets, concentration of fillers, aspect ratio of the graphene sheets, inter-sheet junction, distribution in the matrix, wrinkles and folds, processing methods, etc. The pristine graphene has the highest conductivity, however difficulty in producing a large amount by mechanical exfoliation limits its use and compels to rely on CRG and TRG.

Although graphene oxide is electrically insulating, the thermal reduction eliminates the oxygen functional groups and partially restores the electrical conductivity, making reduced graphene oxide suitable filler for composite. Reduced graphene oxide sheets in composite provides a conductive path for the electron when the concentration of the conductive filler is above the percolation threshold. The lowest electrical percolation threshold (0.1 vol%) of graphene has been reported for the hydrazine reduced PS-isocyanate treated GO mixture [69]. It is reported that thermally reduced graphene has higher electrical conductivity than CRG due to absence of oxygenated functional groups. Thus, polymer composite with TRG might show better electrical conductivity than that with CRG. Various polymer matrices such as polyurethane, epoxy [341], polyamide, polyaniline [342], PVDF, PVA [343], polycarbonate [344] for CRG, TRG and GO reinforcement have been studied in the past few years. These composite materials can be used for electromagnetic shielding [345], photovoltaic devices, sensors and conducting paint. As explained earlier, that pristine graphene offers great electrical and transport properties, however the application is limited by its poor dispersion into individual sheet in matrix. Therefore, functionalized sheets may provide better opportunities for improved dispersion in polymer matrix, which can be helpful for improving the mechanical properties. The attachment of the foreign molecules may change the charge transport properties. Thus, sometimes it is important to trade off the properties.

Macosko and coworkers [346] studied the effect of exfoliation (thermal and chemical) processes and different dispersion methods including solvent blending, in situ polymerizations, and melt compounding on electrical property of graphene/thermoplastic polyurethane (TPU) composites. Increased electrical conductivity was observed for both graphite and TRG filled composites. However, the percolation threshold was lower for TRG (0.5 vol%) than that of graphite (2.7 vol%) due to the difference in aspect ratio. Among the TRG composites, the conductivity of solvent blended and in situ polymerized samples was higher than the melt blended for the same volume of TRG. The sheets reaggregation in melt blending reduced conductive surfaces and attrition during the melt extrusion reduced the lateral size of TRG. The effect of graphene sheet’s orientation and different processing methods (compression, injection molding, and long term annealing) was also demonstrated by studying polycarbonate/graphene composites [323]. Various useful properties of polycarbonate matrix make the composite an important engineering polymeric material for various applications. For electrical percolation reinforcement of TRG in polycarbonate required only 0.66 vol%, the composite was prepared by melt extrusion, and the TRG remained highly exfoliated throughout the matrix as compared to graphite [323]. Alignment of the TRG sheets has noticeable effect on electrical conductivity. For instance, the squeezed films or injection molded polycarbonate/TRG samples have shown lower conductivity than the annealed disks. A similar composite system (polycarbonate/graphene) was studied by emulsion mixing and solution blending followed by compression molding [344], which exhibited lower electrical percolation threshold of ~0.14 and ~0.38 vol%, respectively compared to injection molded composites [323]. The low percolation threshold and high electrical conductivity were due to the wrapping of single and few layer graphene sheets around the polycarbonate microsphere, which generated a high conductive path for electrons.

The effect of temperature on electrical conductivity of the graphene-based composite was studied using PVDF nano composite reinforced with TRG produced by solution processing followed by compression molding [320]. TRG–PVDF showed a decrease in electrical resistance with temperature (negative temperature coefficient) as compared to the increased resistance (positive temperature coefficient, PTC) of the expanded graphite–PVDF composite. This behavior of the TRG-based composite was attributed to the higher aspect ratio of graphene which leads to contact resistance predominating
over tunneling resistance. Whereas, tunable PTC of resistance was observed in graphene nanosheets/polyethylene composite when composite was isothermally treated at 180 °C for different time interval due to low viscosity of the polymer matrix which helped in migration of graphene sheets and weaken the overlapping conductive joints of graphene sheets [347].

6.1.4. Thermal conductivity

Thermal conductivity ($\kappa$) of the material is governed by the lattice vibrations (phonon). The 2D structure of graphene has shown highest thermal conductivity (~3000 W/mK) [6], making it excellent candidate in various polymer matrices to enhance heat transport. The polymer composites of good thermal conductivity have potential applications in electronic circuit boards, heat sink and light weight high performance thermal management systems. In spite of the highest thermal conductivity of the graphene sheets, the enhancement in thermal conductivity of nano composites was not like electrical conductivity because the contrast in thermal conductivity ($\kappa_{\text{graphene}}/\kappa_{\text{polymer}}$) is of the order of 4 in comparison to the contrast in electrical conductivity ($\sigma_{\text{graphene}}/\sigma_{\text{polymer}}$) which is the order of 15–19. The second important factor is high interfacial thermal resistance between graphene sheet and polymer matrix due to strong phonon scattering which affects heat transfer. Other factors such as aspect ratio, orientation and dispersion of graphene sheets will also affect thermal property similar to electrical and mechanical properties.

Improved thermal conductivity was demonstrated for various polymer matrices, reinforced with expanded graphite and multilayer graphene sheets, such as, epoxy [348–352], PVC [318], polypropylene (PP) [353], and polyethylene (PE). For thermal conductivity of the polymer composites, most of the studies are focused on the epoxy matrix and graphite nano platelets (GNPs). Haddon and coworkers [348] prepared graphite nano platelets from natural graphite by the acid intercalation followed with the exfoliation by rapid thermal shock. These GNP sheets were dispersed in epoxy matrix and showed thermal conductivity up to 6.44 W/mK at 25 vol% of GNP loading, which is higher than the neat epoxy. The effect of orientation of GNPs on thermal properties was noticed by Drzal and coworkers [353]. They measured coefficient of thermal expansion (CTE) along the longitudinal and the transverse direction of the flow of the melt during injection molding for GNP–PP composite. They found that the loading of 3 vol% GNPs reduced the CTE of PP by 20–25% in both transverse and longitudinal directions. The thermal conductivity ~1.2–1.5 W/mK was achieved at 25 vol% GNP, which is six times higher than that of PP. In an effort in keeping high aspect ratio and good dispersion of GNPs in matrix during processing, Veca et al. [354] used expanded graphite reinforcement in epoxy matrix where the expanded graphite was exfoliated in sheets using alcohol and oxidative acid treatment by simultaneous stir and vigorous sonication. This treatment facilitated the well dispersion of the sheets in epoxy matrix with a thickness of less than 10 nm. The thermal conductivity properties of the composite were highly anisotropic with a large ratio between the in-plane and cross-plane thermal conductivities. The 33 vol% loading of nanosheets showed thermal conductivity of 80 W/mK (based on diffusivity value) in plane, whereas cross-plane thermal conductivities were about one tenth to one fifth of the in-plane value. It was observed that the conductivity increased linearly with addition of nanosheets due to the reduced interfacial thermal resistance. However, the composite lost its flexibility above 33 vol% loading of graphene fillers.

To reduce interfacial phonon scattering, a hybrid of carbon nanotube and GNPs in polymer matrix was proposed by Yu et al. [355]. They have combined SWCNT and GNPs filler in epoxy and achieved a synergistic effect in the thermal conductivity enhancement of the composite. They proposed that the enhancement was originated from the bridging of planar nano platelets by the SWCNT, which decreased the thermal interface resistance due to the extended area of the SWNT–GNP junctions. The composite with the optimized loading of SWNT–GNP hybrid filler in the range of 10–20 wt% and the ratio of filler SWNT/GNP around 1:3 has shown the highest thermal conductivity (1.75 W/mK). Recently, Yang et al. [349] have also demonstrated the synergistic effect of graphene platelets and MWCNT in improving thermal conductivity of the epoxy composite. The stacking of GNP was inhibited by the MWCNT and their long tortuous feature bridge adjacent to GNP, resulting in high contact area between hybrid and polymer matrix. Thermal conductivity was increased by 147% by adding 1 wt% (MWCNT:GNP ratio of 1:9). As mentioned in earlier sections, the functionalization of graphene can enhance the interface bonding between graphene filler and polymer matrix, which can also minimize phonon scattering. In one study, functionalizing graphene with 4,4’diaminodiphenyl sulphone (DDS) to enhance bonding between sheets and
polymer matrix for improved interfacial heat transfer was also reported [351]. The thermal conductivity of the functionalized graphene composite (0.49 W/mK) shows 30% enhancement over that of functionalized MWCNT composite (0.38 W/mK) at 0.5 vol% loading.

6.1.5. Other properties

The reduced gas permeability and high thermal stability of the graphene reinforced polymer have also been demonstrated. The permeability of the gases is the gas channeling through the polymer. Various studies showed that the dispersion of impenetrable graphite nanoplatelets, graphene and GO sheets of the high aspect ratio and surface area, into polymer matrices provide a tortuous path for the diffusing gas molecules, enhancing the gas barrier properties as compared to neat polymer [356,357]. The recent study by Compton et al. [357] have shown that the incorporation of 0.02 vol% of crumpled graphene sheets in polystyrene matrix drastically inhibit the O₂ molecules permeation. The reduction of phenyl isocyanates functionalized GO in the presence of polystyrene have provided a fully dispersed polymer graphene nano composite leading to the densification of polystyrene film just by the addition of a small amount (0.02 vol%) of sheets. The transmittance was also reduced for 280 µm thick composite film by three times at 350 nm. Detailed studies by Macosko group on permeability of different gases through the graphene and graphite oxide reinforced polymer composites have concluded the significant improvement in gas barrier properties compared to that of the graphite reinforced composite [322,323,346]. For example, permeation of N₂ and helium was suppressed by 39% and 32% respectively by the addition of 1.6 vol% TRG in polycarbonate matrix [323]. The comparison of different processing techniques reinforced with various form of carbon (graphite, TRG, GO, and isocyanate treated GO) in thermoplastic polyurethane have shown a great difference in N₂ permeability (Fig. 6.6) [346]. The incorporation of isocyanate treated GO showed a 90% reduction in N₂ permeability at 1.6 vol% loading due to high aspect ratio of the exfoliated sheets. Among three commonly used techniques for composite production, the solvent-based blending technique has shown more effective distribution of sheets in polymer matrices. The oxygen permeability study by Drzal group on graphite nanoplatelets reinforcement on widely used and important thermoplastic, polypropylene indicated 20% improvement in gas barrier property at 3 vol% [356]. Whereas, higher oxygen permeability was observed for other additives of different shapes and aspect ratios such as carbon black, nano clay, and PAN-based carbon fiber for similar amount of loading.

Outstanding thermal stability of graphene makes it attractive filler for fabrication of thermally stable composites. The thermal degradation temperature measured by thermogravimetry method showed the improvement in thermal stability for graphene/GO composite with PVA [332,343], PMMA [358] and PS [359]. One study showed the improvement in thermal stability by 100 °C for
In addition of raising the thermal degradation temperature, graphene fillers reduce thermal decomposition kinetics due to strong interaction between sheet and polymer, which impedes the chain mobility.

Similar to SWCNTs, graphene sheets have negative in plane coefficient of thermal expansion (CTE) as compared to the host polymer matrix. Thus, it is reasonable to expect the improvement in CTE by graphene and GO reinforcement in polymer. Comparative studies show that the SWCNT and graphene have similar affect in decreasing CTE in epoxy matrix. The test results also demonstrate that the increasing graphene fraction reduces CTE more significantly. The 5 wt% GO/epoxy composite showed 31.7% reduction in CTE below the glass transition temperature.

6.1.6. Applications

The reinforcement of graphene and GO in polymer matrices has shown very exciting results in improving electrical conductivity at a very low percolation threshold, increase in strength and elastic modulus, high thermal conductivity and stability, and reduced permeation of gas molecules. All of these results open a new avenue for developing high strength light weight structural polymer composites for automobile, aerospace, and thermally conductive support in the electronic industry for thermal management. Graphene-based polymer composites can also find application in packaging for food, medicine, electronics and beverages due to low permeability of gas molecules such as N₂, O₂, moisture and CO₂. However, it is too early to commercialize the graphene-based polymer composites because of challenges in mass production of the low cost high quality graphene and the control dispersion in polymer matrix.

Few applications of graphene/polymer composites in energy storage, electrically conductive polymers, antistatic coatings and electromagnetic interference shielding have been demonstrated. Extensively studied graphene/polyaniline nano composites have shown high specific capacitance up to 1046 F/g and good cyclic stability, which can be used for flexible supercapacitor electrodes. Whereas, other carbon additives i.e. SWCNT, MWCNT to PANI have shown capacitance of 450–500 F/g. It is important to note that non-conductive polymer can be made electrically conductive/semi conductive by percolation of graphene network. This has shown the possibility of their use in electronic devices. Recently, a composite film of graphene/PS was prepared using solution blending, showed the semi conductive nature and exhibited the field effective ambipolar property. These films were electrically conducting with a conductivity of 1–24 S/m.

Other potential applications of graphene polymer composites have also been explored in making transparent conductive electrode for dye-sensitized solar cells with conducting polymer, and electrode for electrochromic devices. The graphene and poly(3,4-ethylidioxythiophene)(PEDOT) composite films exhibited excellent transparency, flexibility, conductivity and thermal stability may be a promising component for the future touch screens, video displays, and plastic solar cells.

6.2. Graphene–nanoparticles composites

The nano particle's synthesis is the well established, and explored for many applications, as extraordinary properties of graphene opened new frontiers for their composite with nano particles (NPs) to achieve the synergistic effects of individual components. Recently, various metals, metal oxides and semiconducting NPs have been incorporated to graphene 2-D structures aiming to realize exceptional properties in composite form. It is worthy to mention that the NPs are directly decorated on the graphene sheets, and no molecular linkers are needed to bridge the NPs and the graphene which may prevent additional trap states along the sheets. Therefore, many types of second phase can be deposited on graphene sheets in the form of nanoparticles to impart new functionality to graphene aiming at catalytic, energy storage, photocatalytic, sensor, and optoelectronics applications.

6.2.1. Synthesis

Few important issues need to be addressed for bulk graphene–NPs composite's synthesis. These issues include: (1) separation of individual pure graphene sheets (2) non-uniform dispersion of NPs on graphene sheets (3) the mechanism of NPs' attachment to two-dimensional structures (4) the role of intentional/unintentional functional groups on GO/RGO in hybrid structures formation (5) the
interaction between NPs and graphene, and its effect on intended property and (6) the effect of graphene size and presence of defect.

Many different types of synthesis methods have been developed for preparing graphene–NPs composites, includes three main strategies: pre-graphenization, post-graphenization and syn-graphenization (often called one-pot strategy).

- **Pre-graphenization:** In this method pre-synthesized RGO is mixed with the nano particles for composite manufacturing. The incorporation of second phase NPs and solubility of RGO in various solvents are important considerations for the composite preparation. The hydrophobic nature of RGO restricts the process to limited organic solvents, explained earlier in this article.

- **Post-graphenization:** This method consists of thorough mixing separately prepared NPs and/or salt precursors with GO suspension followed by reduction. Initial studies of composite preparation show mixing of GO aqueous suspension with water soluble metal precursors followed by the reduction to form RGO/NPs composite. This synthesis technique has been used to deposit metal NPs (e.g. Au, Pd, Pt, Ag), metal oxide NPs (Fe$_2$O$_3$, Fe$_3$O$_4$, Al$_2$O$_3$, SnO$_2$, NiO, MnO$_2$, TiO$_2$, ZnO, Cu$_2$O and Co$_3$O$_4$) and semiconducting NPs (CdSe, CdS, ZnS) on GO. The procedure consisted of mixing respective metal salts ([HAuCl$_4$, K$_2$PtCl$_4$, K$_2$PdCl$_4$, and AgNO$_3$]) to GO suspension followed by the reduction using hydrazine monohydrate or sodium borohydride [85]. Attachment of NPs prevents the aggregation and restacking of RGO in the reduction process. The incorporation of NPs could be through physical absorption, electrostatic interaction or covalent bonding with RGO. The possibilities of detachment of NPs, incorporated by physical absorption or electrostatic attraction, can be surmounted using functionalized NPs that can form covalent bonding.

- **Syn-graphenization strategies:** This is often called the one-pot approach. The second components of the composite act as a stabilizer for improving composite properties.

Based on these strategies, numerous composites have demonstrated an integration of NPs on the surfaces of graphene to achieve unique properties from individual components and from their interaction. Various composites based on functionalized graphene with metals, semiconductors and metal oxides are summarized in Table 6.1.

Various synthesis strategies have been proposed for NPs/RGO composites. In situ growing graphene/NPs have been adopted from the methods to produce CNT composites. The major advantage of the technique is direct contact between graphene sheets and NPs. The homogeneous distribution of NPs on 2D sheet occurs due to nucleation of NPs in situ. The functional groups and defects (due to synthesis) on GO surface can assist the nucleation and size control of NPs. The functional group on GO, including carboxylic, hydroxyl, and epoxy groups can be utilized as nucleating sites on GO to control the size, morphology and crystallinity of grown NPs [383]. Furthermore, lattice defects (missing atoms) in 2-D crystal are thermodynamically unstable high energy sites those favor the nucleation and trap nano particles.

Although the functional groups on GO and RGO can provide preferred reactive site for nucleation and anchoring sites for grown NPs [385] GO and RGO have different nucleation sites that generate different NP morphology. Wang et al. [383] demonstrated a different growth mechanism of Ni(OH)$_2$ nano crystal on GO and RGO sheets. The functional groups on GO provided strong interactions with the deposited species, providing pinning forces to restrict diffusional growth of small particles. In contrast, RGO has less functional groups than GO, which allows easy diffusion and re-crystallization to form large single crystals as shown in Fig. 6.7. The similar synthesis strategy was extended to Co$_3$O$_4$ and Mn$_2$O$_4$ graphene hybrids to fabricate anode material for lithium batteries, since graphene can act as a high conductive support, and its chemical stability can improve the electrochemical performance of the electrode [386].

The stable suspension of GO/RGO and reduced aggregation during composite formation is further improved by solvothermal synthesis. Solvothermal can be performed through one-pot reaction to synthesize NPs decorated graphene composites without any reducing agent (toxic hydrazine) [392,397,401]. High temperature and pressure during the solvothermal reaction reduces graphene oxide leading to composite formation. Fig. 6.8 (a,b) shows solvothermal scheme to produce RGO/CdS in dimethyl sulfoxide (DMSO) [397]. This approach overcomes low yield production of single layer graphene and prevents the aggregation of graphene layers. The electrical conductivity of the
Table 6.1
A summary of NP decorated RGO composite and their proposed application.

<table>
<thead>
<tr>
<th>Nano particles</th>
<th>Graphenization</th>
<th>Synthesis</th>
<th>Application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>Post-</td>
<td>GO + CdSe + TOPO ligands</td>
<td>Transparent film, photo switching</td>
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<tr>
<td>Au</td>
<td>Post-</td>
<td>LBL method, Au NPs formation by reduction of Au ions in a gold salt solution on the RGO films</td>
<td>–</td>
<td>[374]</td>
</tr>
<tr>
<td>Pt</td>
<td>Pre-</td>
<td>N doped RGO + DMF + NaOH + ethylene glycol + H₂PtCl₆ + 6H₂O (stirring at 160 °C)</td>
<td>Electrocatalytic activity (methanol fuel cell)</td>
<td>[375]</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>Post-</td>
<td>GO + Fe₃O₄ + doxorubicin hydrochloride (DXR)</td>
<td>Magnetic hybrid graphene (drug delivery)</td>
<td>[376]</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>Pre-</td>
<td>High temperature reaction of ferric triacetylacetonate with GO in 1-methyl-2-pyrrolidone</td>
<td>Magnetized RGO</td>
<td>[377]</td>
</tr>
<tr>
<td>Si, SnO₂, TiO₂, Co₃O₄</td>
<td>Post-</td>
<td>APS modified NPs + GO &gt; encapsulating GO/NPs</td>
<td>Lithium storage electrode (capacitor)</td>
<td>[378]</td>
</tr>
<tr>
<td>Pt, Au, Pd</td>
<td>Post-</td>
<td>GO + HCl + SnCl₂ + 60 °C for 6 h</td>
<td>Capacity behavior</td>
<td>[379]</td>
</tr>
<tr>
<td>Pt/Au, Au</td>
<td>Pre-</td>
<td>Ethylene glycol + metal precursor (K₂PtCl₆, K₂PtCl₄, H₂PtCl₄, H₂O) 100 °C heat in oil bath</td>
<td>Metal nano composite prevents restacking graphene</td>
<td>[380]</td>
</tr>
<tr>
<td>Au</td>
<td>Pre-</td>
<td>Nafion + glucose oxidase + chloroplatinic acid (H₂PtCl₆, 6H₂O) phosphate buffer (H₂PO₄, KH₂PO₄) + RGO</td>
<td>Biosensor (amperometric biosensor)</td>
<td>[381]</td>
</tr>
<tr>
<td>Ni(OH)₂</td>
<td>Pre-</td>
<td>Ni(CH₃COO)₂ + DMF + GO &gt; crystal growth on graphene Ni(OH)₂</td>
<td>–</td>
<td>[382]</td>
</tr>
<tr>
<td>Pd</td>
<td>Pre-</td>
<td>H₂ electrochemical plasma</td>
<td>Gas sensing</td>
<td>[290]</td>
</tr>
<tr>
<td>Ag</td>
<td>Syn-</td>
<td>Heating 75 °C GO on 3-amino propyltriethoxysilane (APTES) + Ag NPs</td>
<td>–</td>
<td>[384]</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>Post-</td>
<td>GO + Fe₃O₄ functionalizing with TEOS, APTES, EDC, NHS and magnetic separation</td>
<td>Magnetic hybrid graphene (heterogenous catalysts and drug delivery)</td>
<td>[284]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Post-</td>
<td>Direct growing, 2 step method (TiO₂ + GO) + antanase hydrothermal treatment</td>
<td>Photocatalytic activity (solar cell and lithium ion battery)</td>
<td>[385]</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>Post-</td>
<td>Mn₃O₄ on GO, 2 step method (Ni(OH)₂ + GO, TiO₂ + GO) + KMnO₄ = Mn(CH₃COO)₂ + DMF/H₂O</td>
<td>Lithium ion battery</td>
<td>[386]</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Pre</td>
<td>RGO + SnO₂ (obtained from hydrolysis of SnCl₄ + NaOH)</td>
<td>Lithium energy storage</td>
<td>[387]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Syn</td>
<td>GO + TiCl₃ + H₂O₂ in SDS solution &gt; self-assembly TiO₂</td>
<td>Investigation Li ion insertion properties</td>
<td>[388]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Post-</td>
<td>GO + TiCl₃ + Na₂SO₄ + H₂O₂ (self-assembly)</td>
<td>Photocatalytic activity, p/n heterojunction</td>
<td>[389]</td>
</tr>
<tr>
<td>CdS QDs</td>
<td>Post-</td>
<td>In situ growth</td>
<td>Photoelectrochemical cells</td>
<td>[390]</td>
</tr>
<tr>
<td>TSCuPc</td>
<td>Post-</td>
<td>Hydrothermal treat 200–300 °C 2 h in furnace with N₂</td>
<td>Blue luminescence (PL) (optoelectronics and biological labeling)</td>
<td>[273]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Post-</td>
<td>GO + Ti(OBu)₃ + DEA + NH₄OH + H₂O₂ (sol-gel process)</td>
<td>Photoconductor for ink print methods</td>
<td>[391]</td>
</tr>
<tr>
<td>CdSe</td>
<td>Pre-</td>
<td>Cd(SA₂)₂/HDA/TOP (in situ growing)</td>
<td>Optoelectronic device</td>
<td>[392]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Post-</td>
<td>TiO₂ colloidal solution + GO (UV light reaction)</td>
<td>Dye sensitized solar cell</td>
<td>[283]</td>
</tr>
<tr>
<td>TSCuPc</td>
<td>Post-</td>
<td>TSCuPc + GO (hydrate heat 1 h at 90 °C with stirring)</td>
<td>Optoelectronics devices</td>
<td>[107]</td>
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</table>

(continued on next page)
Table 6.1 (continued)

<table>
<thead>
<tr>
<th>Nano particles</th>
<th>Graphenization</th>
<th>Synthesis</th>
<th>Application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO nano wire</td>
<td>Post-</td>
<td>ZnO nano wire grown on RGO/PDMS substrate using hydrothermal method</td>
<td>Transparent and flexible optoelectronics</td>
<td>[393]</td>
</tr>
<tr>
<td>TiO$_2$/Ag</td>
<td>Post-</td>
<td>TiO$_2$ + UV $&gt;$ + GO (became RGO)$&gt;$ + Ag ion (photocatalytic methods)</td>
<td>Chem/biological sensor</td>
<td>[394]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Post-</td>
<td>TiO$_2$ + GO sheets (photocatalytic reduction) 100 mW/cm$^2$ mercury lamp at 275, 350, 660 nm</td>
<td>Photoinactivation of bacteria in solar light irradiation</td>
<td>[395]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Pre-</td>
<td>RGO + ultrasonic spray pyrolysis ZnO (LBL assembly)</td>
<td>Supercapacitor</td>
<td>[396]</td>
</tr>
<tr>
<td>CdS</td>
<td>Syn-</td>
<td>DMSO Reduction of GO an depositing CdS</td>
<td>Optoelectronic device</td>
<td>[397]</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>Post-</td>
<td>GO + CO$_3$O$_4$ Di water + H$_2$O centrifugation, HCl wash and vacuum oven 60 °C for 3 days</td>
<td>Catalytic effect for Al perchlorate decomposition</td>
<td>[398]</td>
</tr>
<tr>
<td>RuO$_2$</td>
<td>Post-</td>
<td>GO + RuCl$_3$ + NaOH (reduced at 150 °C)</td>
<td>Electrochemical capacitor and supercapacitor (energy storage)</td>
<td>[399]</td>
</tr>
<tr>
<td>CdTe</td>
<td>Post-</td>
<td>CdTe + GO + Molecular beacon + abtamer</td>
<td>Biomolecular sensor</td>
<td>[400]</td>
</tr>
<tr>
<td>CdS, ZnS</td>
<td>Syn-</td>
<td>Cd(CH$_3$COO)$_2$-2H$_2$O + GO</td>
<td>Photovoltaics</td>
<td>[401]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Post-</td>
<td>TiO$_2$ colloidal solution + GO (UV light reduction)</td>
<td>photoactive devices</td>
<td>[402]</td>
</tr>
<tr>
<td>Silica</td>
<td>Post-</td>
<td>TMOS + GO (sol–gel)</td>
<td>Transparent conductors</td>
<td>[403]</td>
</tr>
<tr>
<td>Au</td>
<td>Pre-</td>
<td>Au NPs deposited on top of RGO (micropatterning method)</td>
<td>Memory devices</td>
<td>[404]</td>
</tr>
</tbody>
</table>


Fig. 6.7. Schematic illustration of two-step Ni(OH)$_2$ nanocrystal growth on (A) graphene sheets (GS) and (B) graphite oxide (GO). Dark gray balls, Carbon atoms; blue balls, H atoms; red balls, O atoms; green plates, Ni(OH)$_2$. After the first step of the growth process (Ni precursor coating), the same coating of Ni(OH)$_2$, 0.75H$_2$O was obtained both on GS and GO. After the second step (hydrothermal transformation), however, the coating on GS diffused and recrystallized into large single-crystalline hexagonal Ni(OH)$_2$ nanoplates (C), while the coating on GO remained as densely packed nanoparticles pinned by the functional groups and defects on the GO surface (D). (Reproduced with permission from [383].)
The functional groups on GO and RGO have provided anchoring sites for NPs, leading to various applications. However, this approach is limited by several factors including the lack of control of the functional groups on GO and RGO surface, and the poor dispersity of GO in organic solvents and RGO in water. Future research is needed to control the functionalization of GO and RGO to achieve controlled deposition of NPs. Other methods such as sol–gel, UV assisted reduction and solution mixing have also been employed for graphene–NPs composites.

The Sol–gel method was initially employed to fabricate graphene/silica composite thin films for transparent conductors, consisted of hydrolysis of tetramethyl orthosilicate in presence of GO suspension in water. This film was subsequently reduced in presence of hydrazine vapors for RGO/SiO$_2$ conductive composite film. Recently, a modified sol–gel method was adopted for TiO$_2$/GO composite using blending of GO sheets with a titanium hydroxide-based ionic salt, which was further reduced photocatalytically.

UV-assisted photocatalytic reduction of GO was also observed and employed for composite formation. Kamat and coworkers, have shown photocatalytic reduction of GO under ultra violet light (UV) in presence of TiO$_2$ NPs. This strategy avoids the chemical reduction and maintains well dispersed TiO$_2$–RGO in suspension. Under UV radiation, TiO$_2$ NPs generate long life-time electron–hole pairs. The generated holes are scavenged, leaving electrons on TiO$_2$ surface and reduce the oxidized groups on GO surface. The UV assisted reduction is fast and straightforward but only applicable to those NPs system which are sensitive to external light irradiation such as TiO$_2$ and ZnO.

Another method consists of adding pre-synthesized NPs to GO suspension followed by chemical and/or thermal reduction for hybrid composite synthesis. The ex situ synthesis allows precise control of the size and surface properties of NPs as there is no interference from the GO/RGO and their reducing chemicals, as observed in the in situ case. However, synthesis process involves a chemical/thermal reduction to obtain NPs/RGO composite which may change the NPs surface properties and damage graphene lattice. Therefore, further investigation may require revealing the impact of the reduction processes on the composite properties.

### 6.2.2. Applications

#### 6.2.2.1. Optoelectronic devices

To extend the application of graphene-based electronics to the field of optoelectronics, it has been proposed to incorporate with excited states of semiconducting NPs (or
quantum dots), so that the optoelectronic properties of the composite materials can be tuned over a wider range of the spectrum.

Formation of the photogenerated excitons in semiconductor nanoparticles is the primary event for the photocurrent generation. To enhance the photocurrent, retardation of the recombination of the electron–hole species is essential. Due to high electronic conductivity of graphene, it can act as efficient electron–transport matrices that retard the recombination reactions. The photocurrent generation in graphene/semiconducting NP QDs composite shows potential for large area optoelectronic devices. Several semiconducting nanoparticles such as CdS [397], CdSe [373,392], ZnO [396], TiO$_2$ [283,378,385,388,389,391,395,407,408], TSCuPc [107] and Co$_3$O$_4$ [398] have been anchored on graphene for hybrid solar cell and optoelectronic device applications. For example, RGO/CdSe NPs composite showed a dramatically enhanced photo response with fast time response under visible light (Fig. 6.9) [373,392]. Such behavior can be interpreted by the efficient and separate transfer of the photo-induced carriers from the CdSe NPs to the RGO. The photosensitivity, a ratio of the current under the irradiation to that of dark, of the CdSe composites showed improvement of 1700 % [392]. The photosensitivity of the composites was also improved by three folds using composite with CdSe. The photocconductivity of the composite film can be up to 10 orders of magnitude higher than that of intrinsic CdSe QD films [373]. Another study detected a picoseconds ultrafast electron transfer from the excited CdS to graphene by time-resolved fluorescence spectroscopy, suggesting that CdS/graphene can also be a potential candidate for harvesting optoelectronic applications [397].

In addition, the number of photo generated free carrier and the photo response of the composite film can be tuned by changing wave length and intensity of light source [389]. This suggests that RGO/semiconducting NPs can be a potential candidate for tunable semiconductors. Until now, most of the optoelectronic applications of graphene/NPs composites are focused from UV to visible light range. If the ranges are extended to the wider regime, graphene composite devices could have potential for planar-integrable active optical sources, modulators, channel monitors and switches at telecommunication wavelengths.

6.2.2.2. Graphene composite for energy storage.
6.2.2.2.1. Lithium ion batteries. Increasing energy demands have motivated researchers to look for the alternative energy resources. Among various alternatives, a considerable attention has been given to the lithium ion batteries due to its rechargeable characteristics, higher specific energy and longer cycle life.

The unique properties of graphene including superior electrical conductivity, high surface to volume ratio, ultrathin flexible nature and chemical stability make it ideal candidate to build the composites with metal and metal oxide nanoparticle for energy storage applications. In such composites,
graphene provides support for nanoparticles and prevent the volume expansion-contraction of nanoparticles during charge and discharge process.

Various electrode materials based on transition metal oxides such as SnO$_2$, Co$_3$O$_4$, Fe$_3$O$_4$, TiO$_2$, Mn$_3$O$_4$ are proposed for lithium ion batteries (LIBs) to achieve higher specific capacities than currently being used graphite. These transition metal oxides have very high theoretical capacities but extremely low electrical conductivity that restricts their direct application in LIBs. For instance, Mn$_3$O$_4$ has electrical conductivity about $10^{-7}$–$10^{-8}$ S/cm that limits its specific capacity lower than 400 mA h/g. Whereas, a superior specific capacity of SnO$_2$ (an anode material with theoretical specific capacitance of 780 mA h/g) in LIBs is affected by its phase transformation and pulverization due to Li ion insertion and extraction during the charge–discharge cycles [387]. Furthermore, electrochemical stability of active materials at various current densities and decrease in cyclic performance are other issues with LIBs. Therefore, various conductive additives such as CNTs [409–411] and carbon particles [412] have been added to increase specific capacity. Currently used graphitize carbon anode material show low capacity (372 mA h/g) because of limited Li ion storage sites within sp$^2$ carbon hexahedrons. One possibility to increase the Li intercalation in the charge/discharge process is using the layered structure of graphene nanosheets. Yoo et al. [413], reported the enhanced specific capacity of these carbon-based electrodes through the interaction of graphene nanosheets with C60 and CNT, which facilitates the nano space size for lithium ion ($r \sim 0.06$ nm) intercalation. Higher reversible capacity (794–1054 mA h/g) and cyclic stability was also demonstrated in disordered graphene nanosheets, as the presence of edge and vacancies defects in graphene sheets provides additional reversible storage sites for Li ions (Fig. 6.10) [414].

Recent studies show the addition of the graphene-based material to transition metal oxide enhances the specific capacity of the electrodes at high discharge rare and improve the electrochemical stability for longer cycles. The improvement was attributed to the excellent electronic conductivity, high surface area, thermal and chemical stability and mechanical flexibility of monolayer graphene sheets. The flexible graphene sheets accommodate a large volume expansion of metal oxide during the charge–discharge process and prevent the pulverization of the electrodes leading to higher electrical conductivity of the electrode. Moreover, high surface area of graphene facilitates Li ions intercalation. Researchers have made a significant effort towards the development of high cyclic performance of the LIBs using nano metal oxide and graphene composite, summarized in Table 6.2. These metal oxide nano particles are grown on graphene oxide using solution chemistry followed by hydrothermal, thermal or chemical reduction to intimate contact between RGO and NPs.

Wang et al. [386], have demonstrated a simple two-step solution based method for Mn$_3$O$_4$–graphene hybrids using slow hydrolysis of their salts (Manganese acetate) in DMF and hydrothermal

![Fig. 6.10](image_url). Reversible (charge) capacity verse cycle numbers at a current density of 0.05 A/g, for natural graphite (i), pristine GO (ii), hydrazine reduced GO (iii) 300 °C pyrolytic GO (iv), 600 °C pyrolytic GO (v), and electron-beam-reduced GO (vi). (Reproduced with permission from [414].)
treatment for reduction of GO in to RGO. The slow hydrolysis has shown the uniform distribution of the nano particles on RGO sheets, resulting enhanced capacity at various current density (Fig. 6.11).

To avoid the aggregation of nanoparticles during the charge–discharge cycle, a new strategy consisting encapsulation of metal oxide particles by graphene sheets was developed (Fig. 6.12) [378] through the co-assembly of negatively charged graphene oxide with positively charged oxide nanoparticles using electrostatic attraction. The resultant composite has shown very high reversible capacity (1100 mA h/g in first 10 cycles) for graphene-encapsulated Co$_3$O$_4$ and 1000 mA h/g after 130 cycles.

The functionalization of hydrophobic graphene sheets before mixing with the hydrophilic oxide nanoparticles is another excellent approach to form a uniform metal oxide coating [385]. The use of anionic surfactant (i.e., sodium dodecyle sulfate) helps in dispersing individual graphene sheets and in situ crystallization of metal oxide particles. TiO$_2$/RGO composites were prepared for LIBs electrodes using surfactant assisted growth of nanoparticles of TiO$_2$ and showed the more than double specific capacity than control rutile TiO$_2$ at a high discharge rate of 30 C [388]. The ternary self-assembly approach has been used to prepare well controlled and ordered metal oxide (SnO$_2$, SiO$_2$, NiO, MnO$_2$)/graphene nanocomposites includes self-assembly of metal oxides, surfactants, and graphene for LIB electrodes. The high concentration of RGO (30–60 wt%) with anionic surfactant has been used to build layered metal oxide–graphene composite film electrolyte (Fig. 6.13) [417].

The controlled growth of TiO$_2$ on graphene oxide sheets was achieved by limiting the rate of hydrolysis during synthesis without surfactants [385]. The TiO$_2$-RGO composite showed superior photocatalytic activity than a variety of other TiO$_2$ materials. Furthermore, study is not limited to the inorganic oxide particles–graphene composite. Recently, nitrogen doped graphene was also tried for the LIBs anode fabrication [53].

### 6.2.2.2. Supercapacitors

Supercapacitors or ultra capacitors are passive and static electrical energy storage devices for short load cycle applications. Supercapacitors with very high power density, fast charge/discharge ability without degradation and burst release characterisitic makes them ideal candidates for applications in mobile electronic gadgets and hybrid electric automobiles.

Energy stored in supercapacitor is through the ion adsorption at the electrode interface which make electrical double layer (electrical double layer capacitors, EDLC) or due to electron transfer between the electrolyte and the electrode through fast Faradic redox reactions (psuedocapacitors). Several supercapacitor materials have been studied to enhance specific capacitance and power density.

**Table 6.2**

Graphene based lithium ion battery materials and properties.

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy density (mA h/g)</th>
<th>Current density (mA/g)</th>
<th>Cycles</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene encapsulated-Co$_3$O$_4$</td>
<td>1000–1100</td>
<td>74</td>
<td>~130</td>
<td>[378]</td>
</tr>
<tr>
<td>Graphene anchored Co$_3$O$_4$</td>
<td>935</td>
<td>50</td>
<td>~30</td>
<td>[415]</td>
</tr>
<tr>
<td>Graphene–Mn$_3$O$_4$</td>
<td>730–780</td>
<td>400</td>
<td>~50</td>
<td>[386]</td>
</tr>
<tr>
<td>Free Mn$_3$O$_4$</td>
<td>115–300</td>
<td>40</td>
<td>~10</td>
<td>[386]</td>
</tr>
<tr>
<td>Pure Co$_3$O$_4$</td>
<td>900</td>
<td></td>
<td></td>
<td>[416]</td>
</tr>
<tr>
<td>SnO$_2$–graphene</td>
<td>625</td>
<td>10</td>
<td>~10</td>
<td>[417]</td>
</tr>
<tr>
<td>Pure SnO$_2$</td>
<td>782</td>
<td></td>
<td></td>
<td>[418]</td>
</tr>
<tr>
<td>Graphene-wrapped Fe$_3$O$_4$</td>
<td>1026</td>
<td>35</td>
<td>~30</td>
<td>[419]</td>
</tr>
<tr>
<td></td>
<td>580</td>
<td>700</td>
<td>~100</td>
<td></td>
</tr>
<tr>
<td>Anatase TiO$_2$–FGS</td>
<td>160</td>
<td></td>
<td>~100 (at 1C charge/discharge rates)</td>
<td>[388]</td>
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<tr>
<td>Rutile TiO$_2$–FSG</td>
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<td>Graphene–Si</td>
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<td>–</td>
<td>~50</td>
<td>[420]</td>
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<tr>
<td></td>
<td>1500</td>
<td></td>
<td>~200</td>
<td></td>
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<tr>
<td>Graphene nanosheets (GNS) GNS + C60</td>
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<td>50</td>
<td>~20</td>
<td>[413]</td>
</tr>
<tr>
<td>GNS + CNT</td>
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<td>50</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Disordered graphene</td>
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<td>50</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Graphene–SnO$_2$ (nanoporous electrode)</td>
<td>794–1054</td>
<td>–</td>
<td>~30</td>
<td>[387]</td>
</tr>
<tr>
<td>Pure graphite</td>
<td>810</td>
<td>50</td>
<td>~30</td>
<td></td>
</tr>
<tr>
<td>Pure graphite</td>
<td>372</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Disordered graphene</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

6.2.2.2.2. Supercapacitors. Supercapacitors or ultra capacitors are passive and static electrical energy storage devices for short load cycle applications. Supercapacitors with very high power density, fast charge/discharge ability without degradation and burst release characteristic makes them ideal candidates for applications in mobile electronic gadgets and hybrid electric automobiles.
Among them carbon based materials such as activated carbons, carbon fibers and CNTs have been extensively investigated as an electrode material for EDL supercapacitors owing to their good electrical conductivity, chemical and mechanical stability, long cycle life, and highly modifiable nanostructures [421–424]. Whereas, materials such as,

\[ \text{Fig. 6.11.} \] Electrochemical characterizations of a half-cell composed of \( \text{Mn}_3\text{O}_4\)/RGO and Li. The specific capacities are based on the mass of \( \text{Mn}_3\text{O}_4 \) in the \( \text{Mn}_3\text{O}_4\)/RGO hybrid. (a) Charge (red) and discharge (blue) curves of \( \text{Mn}_3\text{O}_4\)/RGO for the first cycle at a current density of 40 mA/g. (b) Representative charge (red) and discharge (blue) curves of \( \text{Mn}_3\text{O}_4\)/RGO at various current densities. (c) Capacity retention of \( \text{Mn}_3\text{O}_4\)/RGO at various current densities. (d) Capacity retention of free \( \text{Mn}_3\text{O}_4 \) nanoparticles without graphene at a current density of 40 mA/g. (Reproduced with permission from [386].)

\[ \text{Fig. 6.12.} \] (A) SEM and, (B) TEM images of graphene-encapsulated silica spheres. (Reproduced with permission from [378].)
RuO$_2$ and MnO$_2$ and polymer are promising for pseudocapacitors. Various graphene-based super capacitor materials are summarized in Table 6.3.

Supercapacitors store charge electrostatically by the adsorption of ions onto electrodes that have high accessible specific surface area. Therefore, a high specific capacitance active electrode plays a vital role in efficient energy storage. Various forms of porous carbon, for instance CNT [433–436], mesoporous carbon [437], activate carbon [438] and carbide derived carbon [439] have been studied for electrodes in this respect. A new class of material e.g. graphene and RGO, have also been predicted as a potential candidate for supercapacitor electrodes due to very high specific surface area (2675 m$^2$/g), chemical stability, excellent electrical, thermal conductivity and capacitance and low cost [331,425,427,440]. Interestingly, graphene has demonstrated the intrinsic capacitance near 21 μF/cm$^2$, that set new upper limit for capacitance [441]. Ruoff and coworkers [425], pioneered the application of chemically reduced graphene in supercapacitor. They have shown CRG’s potential as an electrode for super capacitor, even though the used surface area was 707 m$^2$/g and graphene sheets were not fully accessible by the electrolyte. The supercapacitor had specific capacitances of 135 F/g and 99 F/g in aqueous KOH and organic electrolytes, respectively. Improved capacitance (191 F/g, in KOH) was obtained after using microwave power to expand GO layers and reduce the

Fig. 6.13. Schematic illustrations of the ternary self-assembly approach to ordered metal oxide–graphene nanocomposites. (a) Graphene or graphene stacks, which are used as the substrate instead of graphite. Adsorption of surfactant hemimicelles on the surfaces of the graphene or graphene stacks causes its dispersion in surfactant micelles in an aqueous solution. (b) The self-assembly of anionic sulfonate surfactant on the graphene surface with oppositely charged metal cation (e.g., Sn$^{2+}$) species and the transition into the lamella mesophase toward the formation of SnO$_2$ graphene nanocomposites, where hydrophobic graphenes are sandwiched in the hydrophobic domains of the anionic surfactant. (c) Metal oxide–graphene layered nanocomposites composed of alternating layers of metal oxide nanocrystals and graphene/graphene stacks after crystallization of metal oxide and removal of the surfactant. (d) Self-assembled hexagonal nanostructure of metal oxide precursor (e.g., silicate) with nonionic surfactants (e.g., Pluronic P123) on graphene stacks. (Reproduced with permission from [417].)
GO to RGO (surface area ~463 m²/g) [442]. Wang et al. [427] have achieved specific capacitance value ~205 F/g for hydrazine reduce GO of effective surface area ~320 m²/g. It is worth noting that the surface area of graphene sheets plays a significant role which directly affects the performance of the supercapacitors.

A main drawback of using graphene and RGO is the agglomeration and restacking due to Van der Waals attraction between the neighboring sheets. The aggregation reduces the effective surface area resulting loss of capacitance. Therefore, a few researchers have made effort to keep graphene sheets separated by addition of metal oxide nanoparticles [399]. Metal oxide RuO₂, MnO₂ and polyaniline (PANI), nano composite with graphene have also been explored for superior capacitance (Table 6.3). The approach utilizing nanoparticles to improve the electrochemical performance is an indication of a positive synergistic effect of graphene sheets and nanoparticles. For example, in RuO₂/graphene composite, graphene sheets were well separated by RuO₂ nanoparticles that were attached through the oxygen containing functional groups on graphene surfaces. The composite exhibited a high specific capacitance of 570 F/g for 38.3% Ru loading with excellent electrochemical stability (97.9% retention after 1000 cycles) and high energy density (20.1 W h/kg) at high power density (10 kW/kg). Similarly, MnO₂/GO composite electrode had a capacitance of 216 F/g that is much higher than that of individual GO (10.9 F/g) and bulk MnO₂ (6.8 F/g) [429]. Wu, et al. [432], demonstrated a MnO₂/graphene high voltage asymmetric capacitor based on graphene as a negative electrode and MnO₂/graphene composite a positive electrode, which exhibited a superior energy density of 30 kW/kg and power density (5 kW/kg at 7 W h/kg). Although the metal oxide–graphene nano composite have

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Capacitance (F/g)</th>
<th>Energy density</th>
<th>Electrolyte</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemically reduced GO</td>
<td>135</td>
<td>20.1 W h/kg at 100 mA/g</td>
<td>Aqueous KOH</td>
<td>[425]</td>
</tr>
<tr>
<td>Graphene–hydrous RuO₂ (38.3 wt%)</td>
<td>570</td>
<td>10 kW/kg at 4.3 W h/kg</td>
<td>Organic electrolyte 1 M H₂SO₄</td>
<td>[399]</td>
</tr>
<tr>
<td>Graphene (2675 m²/g)</td>
<td>550</td>
<td>150 mA/g discharge current</td>
<td>5M KOH electrolyte</td>
<td>[442]</td>
</tr>
<tr>
<td>Graphene (microwave assisted reduction of GO)</td>
<td>191</td>
<td>KOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal reduction in propylene carbonate</td>
<td>120</td>
<td>Organic electrolyte</td>
<td></td>
<td>[426]</td>
</tr>
<tr>
<td>Graphene (hydrazine reduced GO)</td>
<td>205</td>
<td>28 W h/kg</td>
<td>KOH</td>
<td>[427]</td>
</tr>
<tr>
<td>Graphene–PANI (50:50 wt%) (microwave-solvothermal)</td>
<td>408</td>
<td>1 M H₂SO₄</td>
<td></td>
<td>[428]</td>
</tr>
<tr>
<td>Graphene–PANI</td>
<td>1046</td>
<td>6 M KOH</td>
<td></td>
<td>[363]</td>
</tr>
<tr>
<td>Graphene–MnO₂</td>
<td>216</td>
<td>1 M Na₂SO₄</td>
<td></td>
<td>[429]</td>
</tr>
<tr>
<td>Polymer modified graphene sheet + MWCNT</td>
<td>120</td>
<td>–</td>
<td></td>
<td>[430]</td>
</tr>
<tr>
<td>Curved Graphene Sheets</td>
<td>100–250</td>
<td>85.6 W h/kg at 1 A/g</td>
<td>1-Ethyl-3-methylimidazolium tetrafluoroborate</td>
<td></td>
</tr>
<tr>
<td>Thermally reduced graphene</td>
<td>75 F/g</td>
<td>31.9 W h/kg</td>
<td>N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR14TFSI)</td>
<td></td>
</tr>
<tr>
<td>MnO₂ nanowire–graphene</td>
<td>117 F/g</td>
<td>–</td>
<td>Neutral aqueous Na₂SO₄</td>
<td></td>
</tr>
</tbody>
</table>
shown a great prominence for the supercapacitors and high energy density capacitor, the high energy density supercapacitors with high charge/discharge rates are still up to research stage. Recent study of Jang and coworkers [431] reveals the graphene-based supercapacitor that exhibits specific energy density of 85.6 W h/kg at room temperature and 136 W h/kg at 80 °C at very high current density of 1 A/g. These values are comparable to Ni metal hydride (40–100 W h/kg). They have reported that the mesoporous structure of the curved graphene sheet are responsible, the curved nature of graphene sheets prevent face to face restacking and maintain large pore size (2–25 nm) and capacitance (Fig. 6.14). Further quick charge–discharge ability in seconds and minimal loss of capacity or energy density make it prominent candidate better than existing batteries.

Recently, graphene–polymer composites have also received much attention owing to their flexibility, and superior capacitance than existing carbon-polymer based capacitor. Among various conductive polymers, PANI has been considered as a most promising conductive electrode material and studied considerably with CNT and carbon system [367,369,443–446]. A graphene nanosheets–PANI composite was synthesized by in situ polymerization [367]. The specific capacitance of 1046 F/g was obtained at a scan rate of 1 mV/s. Conductive graphene nanosheets provide more active sites for nucleation of PANI and is homogeneously coated by PANI nano particles on both sides, resulting in energy density of 39 kW h/g at a power density of 70 kW/kg. Graphene–PANI composite paper was also prepared by in situ anodic electropolymerization of polyaniline film on graphene paper (Fig. 6.15) [363]. The flexible as prepared composite paper combined the high conductivity and flexibility properties of graphene sheet with large capacitance polymer and showed the gravimetric capacitance of 233 F/g.

6.2.2.3. Other applications. Fuel cells are considered as one of the most promising power sources for the mobile and stationary applications due to their high energy conversion efficiency, low operating temperature and ease of handling. Pt and Pt based materials are widely used for the fuel cell, which renders them ineffective and prevents fuel oxidation. Recently, graphene based materials have been explored for fuel cell applications [447–449]. The proton exchange membrane (PEM) fuel cells prototype using graphene was developed by Serger et al. [448]. They constructed using a Toray paper modified with RGO/Pt composites as a cathode and Pt-dispersed on carbon black as an anode. The performance of the fuel cell was compared to unsupported Pt cathode PEM (Fig. 6.16).

The RGO/Pt-based fuel cell showed a maximum power of 161 mW/cm² compared to 96 mW/cm² for an unsupported Pt-based fuel cell. The role of graphene support not only maximized the availability of electrocatalyst surface area for electron transfer but also provided better mass transport of reactants to the electrocatalyst.

Fig. 6.14. Scanning electron microscopy image of curved graphene sheets (scale bar 10 μm). (Reproduced with permission from [431].)
For biological applications of GO/RGO, RGO-based single-bacterium biodevice, label-free DNA sensor, bacterial DNA/protein and polyelectrolyte chemical transistor have been reported [99]. Liu et al. observed that the GO sheets are biocompatible without obvious toxicity and employed GO for drug delivery [97]. One of the promising targeting methods is the use of magnetic particles loaded with drugs. Thus, magnetic NPs with graphene composites have been used in various areas of drug carrier and magnetic resonance imaging (MRI) [284,376,377,450]. The magnetization curve of GO–Fe₃O₄ composite was measured at room temperature (Fig. 6.17) showed a magnetic hysteresis loop of “S” line curve with nearly zero value of the magnetic remanence. This suggested that GO–Fe₃O₄ exhibited a superparamagnetic behavior.

Myung et al. reported the assembly of Au NPs fabricated on top of a reduced GO junction [404]. At the crossing point the forward bias from −10 to 10 V (or reverse bias from 10 to −10 V) sweep curves showed a positive (or negative) slope indicating an n-type (or p-type) FET behavior (Fig. 6.18a). It indicates that in the forward sweep, charges move along in n-type channels (right of Fig. 6.18a). While, in reverse sweep, charge transfer shows p-type characteristics left of Fig. 6.18b. These properties
suggested that the metal NPs based graphene device can be operated as a conventional conductive switching memory by adjusting the charge density on the metal NPs. Despite the rapid increase of research on chemically functionalized graphene-based NPs composite, there is lack of theoretical understanding of charge transport studies. Therefore, theory based transport studies with energy band are strongly encouraged in pristine graphene [451,452].

7. Toxicity of graphene/graphene oxide/reduced graphene oxide

Recent advancement in nanoscience opens a wide range of applications of nanoparticles towards industrial level as well as in medicine. Nanoparticles exhibit extraordinary physiochemical properties and reflect their unique electrical, thermal, and mechanical properties which further bring along a concern about their toxic behavior when exposed to the environment and living system. In the near, the future potential occupational and public exposure to the nanoparticles will be dramatically increased due to the versatile applications of nanomaterials [453]. In the recent years government and scientific
communities put forward more attention towards the bio-safety aspect of the nanomaterials. The main agenda in the field of nanotoxicology is to understand the exposure and assessment of nanoparticles, environmental and biological fate, transport, persistence, transformation, recyclability and overall stability of the nanoparticles [453]. For example, though carbon nanotubes (CNTs) were an exceptional scientific finding in the field of electronics; its wide use allows potential exposure to the environment and living systems. Several reports have revealed that the CNTs could induce genotoxicity via induction of reactive oxygen species (ROS) [454, 455]. Similarly, graphene and graphene oxide are now very much attractive due to their potential applications such as electrochemical devices, energy storage, and catalysis, adsorption of enzyme, cell imaging, drug delivery, and biosensors. However, information related to the long term fate, health, and environmental risk assessment of this newly discovered graphene is widely lacking [456].

RGO’s good conductive property has a potential for developing various bio-medical applications including biosensor, transplant devices, invasive instruments, and implants [457]. RGO and RGO-Tween 20 paper like composites have been studied for their toxicological aspects. In vitro experiments with mouse fibroblast cell shows no toxicity of RGO paper [458]. Though surface of the RGO-Tween 20 composite is electrically insulating, RGO-Tween 20 composite also reported to be non-toxic towards Vero cells, bovine embryonic cells and Crandell–Rees feline kidney cells [457]. In contrast to this report, GO-nanosheets reported to be toxic to the bacterial cell [459]. GO-nanosheets showed 60% and 70% cell viability decrease in Escherichia coli and Staphylococcus aureus, respectively. Toxicity of graphene nanosheets towards the E. coli has also been reported [460]. Metabolic activity of the E. coli decreased to 13% when incubated with 85 µg/ml GO nanosheets. Moreover, bacterial cell viability loss was almost 98.5% in the same concentration. A transmission electron microscope study revealed disruption of the bacterial cell membrane and a loss of membrane integrity. Therefore, it may be concluded that the toxicity of graphene oxide nanosheets mainly attributed to the mechanical damage of the cell membrane of the bacteria due to the sharp edges of the nanosheets. Moreover, hydrazine reduced GO nanosheets were reported to be more toxic to the bacterial cell, may be due to the better charge transfer efficiency in addition to their sharp edges [459].

In the in vitro mammalian cell line experiment, the cytotoxic effect of GO was found to be dose and time dependent, even at a concentration of less than 20 µg/ml. Above 50 µg/ml, GO severely affects the cell survival rate and induces apoptosis in human fibroblast cell line [456]. Alteration of cellular morphology by GO treated fibroblast cell is shown in Fig. 7.1.

Similar cytotoxic effects were also observed in other cell lines such as MGC803, MCF-7, MDA-MB-435, and HepG2. Experimental data also demonstrates that the GO enters into the cytoplasm of the cell and was found to be present in the sub cellular compartments such as lysosomes, mitochondrion, endoplasm, and even in the nucleus. It has been hypothesized that GO attaches to the cell membrane and induces down regulation of the adhesion associated gene which in turns affect the cell adhesion and causing cell to float in medium. Moreover, GO enters into the cell and can interfere with cellular metabolism and finally results in cell apoptosis and death [456]. In a recent report, the toxicological effect of CNTs and graphene nanomaterial towards neuronal PC12 cells are compared [454]. Relative toxicity of graphene nanostructure is less as compared to CNTs. The 100 µg/ml of the graphene significantly increases the ROS generation and lactate dehydrogenase release, which are markers of cell death via necrosis. The reports further document that the shape and size of graphene play a critical role in evaluating the toxicity caused by graphene. Concentrations and size of the GO used to evaluate in vitro cytotoxicity are summarized in Table 7.1.

Recently, the size effect of the GO towards cytotoxicity has been reported [461]. The cytotoxicity of smaller size GO (160 ± 90 nm) was found to have higher values compared to larger size GO nanosheets (430 ± 300 nm and 780 ± 410 nm). Smaller size GO also induced apoptosis to the A549 cell at a concentration of 200 µg/ml. Though apoptosis was not observed in the presence of larger GO nanosheets (780 ± 410 nm), a slight increase in necrosis was noticed. Medium size GO nanosheets neither showed apoptosis nor necrosis towards A549 cells. A similar effect was observed on the cell viability and the cell mortality was observed in the following order; 160 ± 90 nm size nanosheets >780 ± 410 nm nanosheets >430 ± 300 nm nanosheets. The nanosheets of size 430 ± 300 nm showed a significant decrease in cell viability only at 200 µg/ml concentration, whereas 160 ± 90 nm and 780 ± 410 nm size nano-
**Table 7.1**
Size, concentration, and cytotoxicity of GO nanosheet.

<table>
<thead>
<tr>
<th>Size range (nm)</th>
<th>Concentration (μg/ml)</th>
<th>Intra-cellular localization</th>
<th>Cell/cell line</th>
<th>Toxic concentration (μg/ml)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–2 μm</td>
<td>5–100</td>
<td>Lysosomes, mitochondrion, endoplasm, and nucleus</td>
<td>Human fibroblast cell, MGC803, MCF-7, MDA-MB-435, and HepG2 cell lines</td>
<td>50</td>
<td>[456]</td>
</tr>
<tr>
<td>3–5 nm</td>
<td>0.1–100</td>
<td>–</td>
<td>PC12 cells</td>
<td>100</td>
<td>[454]</td>
</tr>
<tr>
<td>70–250 nm</td>
<td>10–200</td>
<td>Hardly localized inside the cell</td>
<td>A549</td>
<td>50</td>
<td>[461]</td>
</tr>
<tr>
<td>130–730 nm</td>
<td>10–200</td>
<td>Hardly localized inside the cell</td>
<td>A549</td>
<td>200</td>
<td>[461]</td>
</tr>
<tr>
<td>370–1190 nm</td>
<td>10–200</td>
<td>Hardly localized inside the cell</td>
<td>A549</td>
<td>50</td>
<td>[461]</td>
</tr>
<tr>
<td>100–700 nm</td>
<td>20–85</td>
<td>Endosome</td>
<td>A549</td>
<td>85</td>
<td>[460]</td>
</tr>
<tr>
<td>100–700 nm</td>
<td>20–85</td>
<td>–</td>
<td>E. coli</td>
<td>85</td>
<td>[460]</td>
</tr>
</tbody>
</table>

**Fig. 7.1.** Morphology of human fibroblast cell line in GO treated and control cell; A-Control, B-100 μg/ml for 1 day; C-20 μg/ml for 3 days; D-5 μg/ml 5 days. (Reproduced with permission from [456].)
sheets showed a decrease at a concentration of 50 μg/ml. The reduction in cell viability has been correlated to oxidative stress which is generated by GO nanosheets. It has also been found that the GO nanosheets generate reactive oxygen species in cell free F-12 K medium, which is further supported by the oxidative stress, induced cell viability reduction. The extent of reactive oxygen species generation is 50% higher in 780 ± 410 nm size nanosheets as compared to 160 ± 90 nm and 430 ± 300 nm size nanosheets. However, cell proliferation in the GO film was found to be similar as control and no cellular internalization of graphene nanosheets was observed. Therefore it can be concluded that the oxidative stress induced to the cells by GO nanosheets is due to external generation of reactive oxygen species.

The in vivo study in mice model does not show any toxicity at a dose ≤0.25 mg per mouse. However, 0.4 mg per mouse was found to be lethal to the mouse, and all four mice died within 1–7 days of GO injection. Histopathology of the lung tissues showed a blocking of the major airways by the GO conglomeration. Moreover, a loss of 10% body weight was observed within the 1st week of the GO injection. Long term stay of the GO in kidney makes it a very poor agent for in vivo application, although GO has been investigated as a cellular imaging and drug delivery agent. It is a challenge to reduce the toxicity effect of the GO and successfully use GO for medical applications. Therefore, graphene has been tried to conjugate with biocompatible polymer such as polyethylene glycol (PEG) and chitosan, for safe bio-medical application. The graphene functionalized with PEG shows a better solubility and stability in physiological solution and has been studied for in vitro drug delivery, imaging, and in vivo photothermal therapy for tumor. In vitro experiments with PEG functionalized GO do not show any cytotoxicity towards HCT-116 cell line [97]. No toxic side effect was reported in the case of PEG functionalized GO in in vivo mice model at a dose of 20 mg/kg of the body weight, however an excellent passive targeting of the tumor was achieved. Moreover, haematoxylin and eosin stained organ slices did not reveal any organ damage. The tumor disappeared in the mice received PEG functionalized GO after 1 day of photothermal therapy and no tumor growth was noticed within 40 days time [462]. However, there is always a chance of quenching the fluorescence (Cy7) which may leads to an inaccurate conclusion regarding the bio-distribution. The same group has conducted a similar kind of study with 125I labeled PEG–GO for in vivo pharmacokinetics, bio-distribution and toxicological study. Stability of the 125I labeled PEG–GO was confirmed by incubating the 125I labeled PEG–GO in 0.9% NaCl solution, mouse plasma and serum at 37°C. 125I labeled PEG–GO was injected intravenously and radioactive levels in the blood were estimated over times. PEG–GO followed a two component blood circulation model with a half life of 0.39 ± 0.097 h for the first phase and 6.97 ± 0.62 h for the second phase. PEG–GO was found to be accumulated mainly in the liver, kidneys, and spleen, however, accumulation in bone marrow was also observed at the early in the experiments. Radioactivity level measurement and histology analysis of the organs revealed that with time, accumulated PEG–GO cleared out from the organs like the liver, kidneys and spleen. PEG–GO was excreted from the body though renal and fecal excretion which also reflectd the kidney and intestine uptake of PEG–GO. Body weight loss or toxic side effects were not observed within the 3 months after the introduction of PEG–GO. Moreover, blood biochemistry, hematological and histological analysis did not reveal any potential toxic effects [463]. Besides the PEG–graphene study, graphene–chitosan composites have also been studied for tissue engineering application; they are reported to be biocompatible [333]. Recently, few other polymers were tried to reduce graphene toxicity towards living cells and to make it more compatible for bio-medical use. The 3,4,9,10-perylene tetracarboxylic acid (PTCA) is one of them, PTCA functionalized graphene sheets did not show any significant toxicity towards HeLa cells. PTCA–graphene and aptamer AS1411 sensor have been successfully shown to differentiate cancer and normal cells [464]. Graphene–polyethyleneimine (PEI) composite also found to be less toxic towards HeLa cells as compared to graphene alone. Moreover, graphene–PEI nanocomposite has been demonstrated as an efficient gene transfection vehicle [465].

Controversial reports exist on cytotoxicity of the graphene/GO/RGO which restricts their potential bio-medical applications. This may be associated with the different preparation, size of the sheets and the functionalization. Therefore, thorough toxicology studies of functionalized and bare graphene/GO/RGO at different doses using different animal model is necessary before any potential bio-medical applications.
8. Future prospects

It has become evident that the exceptional properties of graphene (including electrical, thermal, mechanical, optical, and long electron mean free paths) made it compelling for various engineering applications. Much effort has been devoted to exploring the fundamental physics and chemistry of graphene. Novel properties such as room temperature quantum Hall effect, highest charge transport and thermal conductivity originated from graphene’s 2-dimensional structures have not been observed earlier from most conventional three-dimensional materials. A large amount of research publications in the past 5 years signifies the importance of graphene that might surpass silicon research in the development of microelectronics. While silicon based research is at its mature stage to overcome the technological barrier, graphene is being extensively investigated as it holds the future for micro to nano scale electronics. The inherent semi-metal characteristic of graphene has been modified to realize the applications in transistors. Graphene nanoribbons and bilayer graphene are the results of such modification that leads to a suitable band gap and allows the applications in FET. However, graphene as a new material still faces many challenges ranging from synthesis and characterization to the final device fabrication. The exceptional properties were observed in the defect free pristine graphene prepared by graphite exfoliation using scotch tape method which is not appropriate for any large scale device manufacturing. The alternative methods have progressed to CVD and epitaxially grown single, bilayer and few-layer graphene. Recent reports demonstrated the scalability using CVD method to wafer scale on different substrates and facile transfer of graphene layer for subsequent device fabrication. These breakthroughs offer novel and exciting opportunities for semiconductor industries. The chemical exfoliation of graphite into GO followed by thermal and chemical reduction, has offered a cost-effective production route of reduced graphene oxide on a large scale. However, the chemical and thermal modification lowers the electrical and mechanical properties, along with its chemical reactivity leading to lack of control in functionalization by other groups. The controlled oxidation/reduction and functionalization are very important in tuning the material properties such as band gap, electrical conductivity, and mechanical properties. Therefore, controlled modification of graphite, GO, and RGO is crucial in expanding the applications of graphene-based materials. In addition, the large surface of low density GO and RGO in mass production may possess handling difficulty, which can lead to a health risk due to inhaling and handling toxic reducing chemicals. The health risk associated with graphene and their derivatives needs to be evaluated through the investigation of the toxicity and biocompatibility of these novel carbon structures and its derivatives.

The possible applications of graphene-based material include transparent flexible electrodes, graphene/polymer composites for mechanical parts, energy storage, sensors and organic electronics. Graphene/polymer composites have showed the lowest percolation threshold for electrical conductivity and improved mechanical, thermal, and gas barrier properties. However, the core issues such as the homogeneous distribution of individual graphene platelets, their orientation, connectivity, and interface bonding with matrix still require more investigation. The charge mobility of RGO is considerably higher than that of the amorphous silicon and existing semi-conducting conjugated polymers, enlightening the probable path for the application in electronics. The main hurdles with any device fabrication using RGO including defects at atomic level, the folding/wrinkling of RGO and the over lapping of RGO at macro-scale require continuous research endeavors.

The visibility of monolayer graphene under an optical microscope requires the suitable substrate to create contrast between different layers due to interference. Current detection of graphene using an optical microscope depends on the substrate thickness and incident light wavelength. More research is needed to develop a simple detection method of pristine graphene that is independent of support material. Aberration corrected high resolution TEM made it possible to reveal defect structures and graphene quantum dot at atomic resolutions, providing opportunities to visually examine the doping and defects at atomic levels.

Although the advanced deposition technique of single layer and bilayer made it possible to fabricate large area devices, creating band gap in a controlled and practical manner is still challenging for the application in logic devices. Several methods aiming at tuning the substrates properties and nano-ribbon dimension have been proposed to introduce tunable band gap essential for nanoelectronics.
Particularly, this energy band gap can be achieved through quantum confinement, bilayer graphene, and chemical functionalization. The former, quasi-one-dimensional graphene nanoribbon has been considered with either edge localization or Coulomb blockade effects. Graphene nanoribbon with appropriate dimension (i.e. 10 nm) is expected to provide right band gap for efficient FET devices. Cutting graphene into nanoribbon has shown great promise for FET logic applications, but associated with the electron scattering at the rough edges and disorder from the back substrate. On the other hand, FETs based on graphene bilayer still require large on/off ratio for logic applications. The new options such as tunnel FETs and bilayer pseudospin FETs have been suggested to tackle the challenge of the graphene devices problems based on the conventional FET principle. These concepts are supported by simulation studies but need to be experimented. The latter, oxides form of graphene (GO), has triggered significant research interest due to large scale integration. However, the electronic band structure is not clearly understood due to the nanoscale inhomogeneity. Recent atomic scale systematical investigation and geometrical microscopic studies provided the evidence of tunable band gap through varying oxidation level and reduction process. Therefore band gap opened graphene based through GNR and GO have been encouraged to become future practical nano electronic devices comparable to complementary metal oxide semiconductor circuits.

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