

*Chapter I*

*Section A*

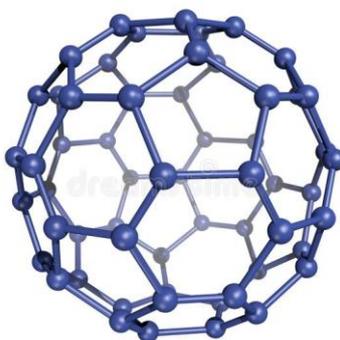
*Carbonaceous Nanomaterials*



### I.A.1 Carbonaceous nanomaterials

Carbonaceous nanomaterials are a group of amorphous solids consisting of micro crystallites with a graphite lattice. They differ from pristine graphite on the part that they have a random imperfect structures, varied pore sizes and possesses various surface functional groups over a broad range.<sup>1</sup> Commonly known carbonaceous nanomaterials include activated carbons, graphenes, carbon molecular sieves and carbon fibers. Recently, graphene fiber has been incorporated into this group.<sup>2</sup> These materials are classified into four different categories: fullerenes, graphene-based materials, carbon nanotubes (CNTs) and nanoporous activated carbon (NAC). Graphene-based nanomaterials are further subdivided into pure graphene, graphene oxide (GO), reduced graphene oxide (rGO) and chemically modified graphenes (CMGs) or graphene nanocomposites.

Fullerene is an allotrope of carbon with an enclosed cage like structure bearing fused rings of five to seven atoms. The carbon atoms are connected by single and double bonds and the molecule may be spherical, ellipsoid, tube or other shapes.<sup>3</sup> The most common being C<sub>60</sub> named after buckminsterfullerene, also called buckyballs for its resemblance with standard soccer balls (Figure I.A.1). The C<sub>60</sub> packs 12 pentagons and 20 hexagons, and all carbon atoms are arranged at the 60 vertices of a truncated icosahedron.<sup>3</sup> The structure is highly symmetrical having 32 faces. The presence of fullerenes has been predicted for long time, but it has been accidentally synthesized by Harold Kroto and co-workers in 1985.<sup>4</sup>



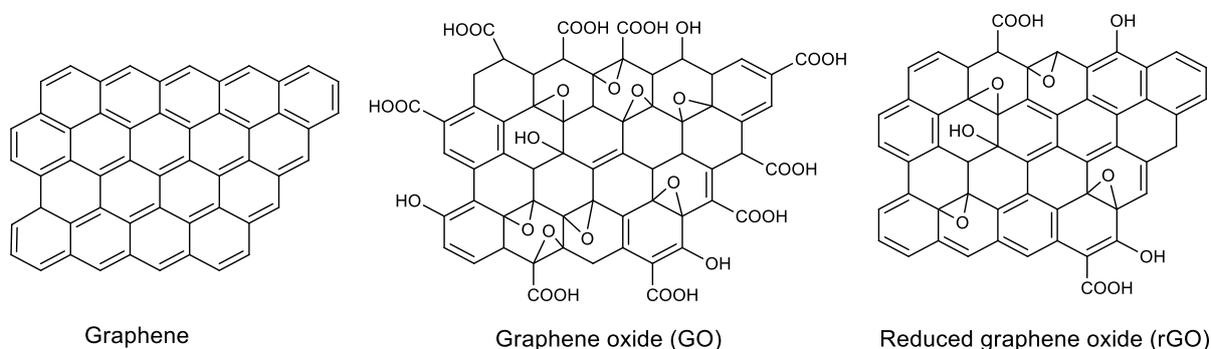
**Figure I.A.1** Model of a C<sub>60</sub> buckyball.

Graphene is an infinite two-dimensional (2D) carbon monolayer made entirely of sp<sup>2</sup> carbon atoms arrayed in a honeycomb fashion (Figure I.A.2).<sup>5,6</sup> This single-atom-thick sheet can be considered as the elementary building block for other allotropes of carbon like fullerenes and carbon nanotubes. The material has been theorized since decades but has been isolated and characterized only after 2004 by Andre Geim and Konstantin Novoselov.<sup>7</sup> It has remarkable

physical and chemical properties with immense potential for diverse applications. For example, it is the thinnest, lightest and strongest material known to man. Furthermore, it is the best conductor of heat and electricity at room temperature and also absorbs light uniformly across the visible and near infrared region of the spectrum. The surface area of graphene could reach up to  $2630 \text{ m}^2\text{g}^{-1}$ , which is much higher than many known materials.<sup>8</sup> Owing to the high surface area of this nanomaterial it exhibits exorbitantly high catalytic activity.<sup>9</sup>

The oxidised form of graphene is known as graphene oxide (GO). It is a two-dimensional graphene sheet with bountiful oxygenated functional groups on their basal plane and peripheral edges (Figure I.A.2).<sup>10</sup> During the fabrication process of GO, the  $\pi$ -conjugated arrangement is broken thereby making the material highly water dispersible. Moreover, it is the primary precursor for the synthesis of various graphene-based nanomaterials.

The reduced graphene oxide (rGO) can be considered in between graphene and graphene oxide, as it contains fewer functional groups as compared to GO (Figure I.A.2).<sup>11</sup> It is prepared from GO by chemical, thermal or electrochemical techniques. The graphene like properties of rGO makes it a suitable candidate for the fabrication of sensors, optoelectronic devices and in the preparation of composite materials.<sup>11</sup>

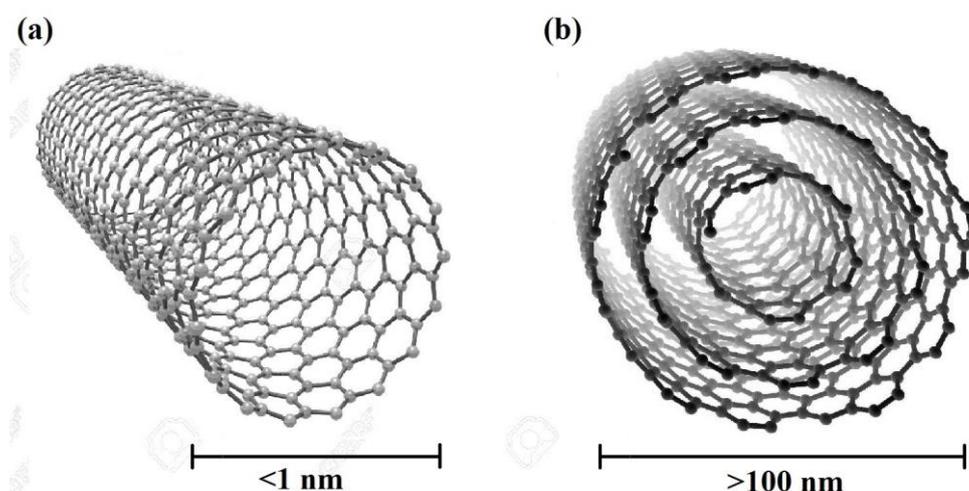


**Figure I.A.2** Structure of monolayer graphene, graphene oxide and reduced graphene oxide.

Graphene nanocomposites refers to the intertwining of graphenes with other materials like polymers, metal oxide or metal nanoparticles, metal organic frameworks (MOFs) and other porous materials like silica, zeolites, etc.<sup>12,13</sup> Graphene nanocomposites show superior chemical and physical properties as compared to conventional composite materials. These nanocomposites also exhibit multifarious properties by combining the characteristics of individual components.

Carbon nanotubes (CNTs), also called buckytubes, are cylindrical molecules that consist of rolled-up sheets of single layer carbon atoms (graphene).<sup>14</sup> They can be divided into single-

walled CNTs (SWCNTs) with diameter of less than 1 nm, or multi-walled CNTs (MWCNTs) with diameter more than 100 nm (Figure I.A.3). The SWCNTs are made up of single layer carbon atoms, while MWCNTs consists of several multilateral graphene sheets that are rolled upon itself in concentric tubes.<sup>15</sup> Just like graphene, the carbon atoms in CNTs are  $sp^2$  bonded with each other. There are various methods for the synthesis of CNTs, which include chemical vapor deposition (CVD), the arc-discharge method, flame synthesis method and other modified methods.<sup>16</sup> Owing to their unique structures; CNTs exhibit exceptional properties such as high electrical conductivity. Moreover, their large specific area, rich hollow and layered structure renders remarkable applications in diverse fields.



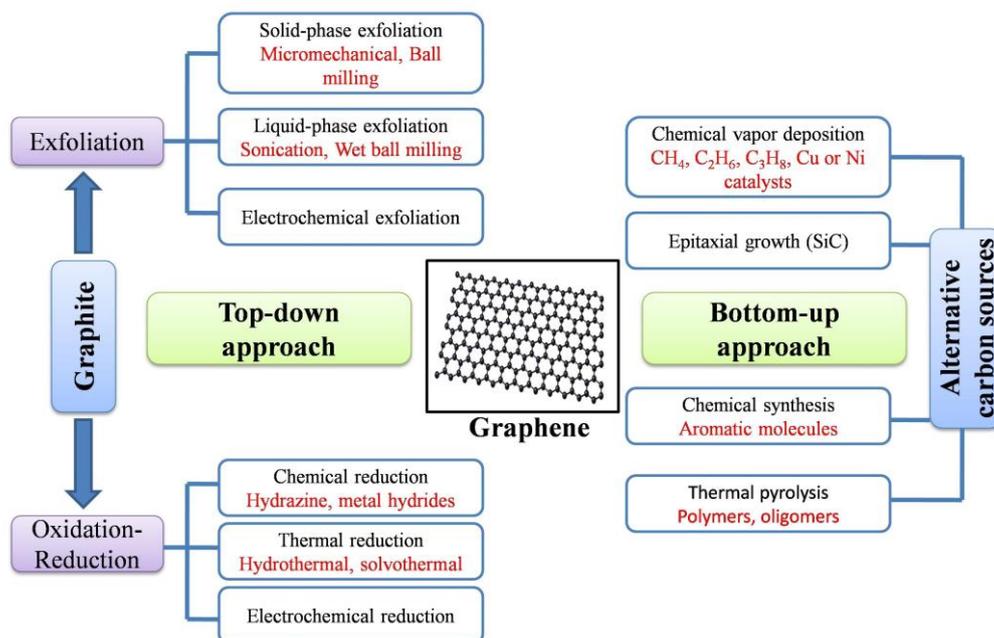
**Figure I.A.3** Molecular representations of (a) SWCNT and (b) MWCNT.

Among the various carbonaceous nanomaterials, our studies has been primarily focussed on the synthesis and catalytic applications of graphene-based nanomaterials (GO and CMGs).

### **I.A.2 The wonder material graphene: A breakthrough invention in nanoscience**

Ever since the isolation of graphene by Andre Geim and Konstantin Novoselov, the perception of how we see the nano world has changed entirely. In 2004, they isolated graphene by repetitive peeling of graphite layers using a scotch tape.<sup>7</sup> Although, this ‘scotch tape’ method undeniably gives a single layer of carbons, the method has been less useful for practical purposes due to very low yield. The synthesis of graphene has been based on two different methods, the ‘top-down’ approach and the ‘bottom-up’ approach. While the ‘top-down’ approach involves the separation of stacked layers of graphite to yield single layer graphene sheets, the ‘bottom-up’ approach comprises of the synthesis of graphene form alternative carbon sources (Figure I.A.4). In spite of the different routes to synthesize

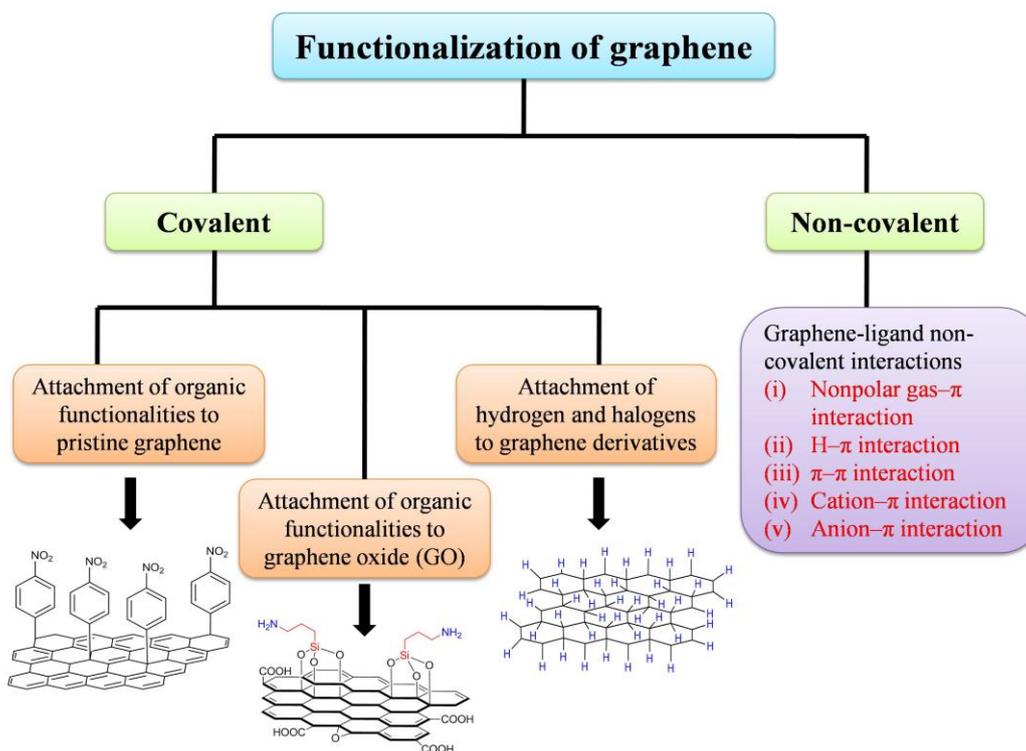
graphene, its large scale production in an affordable manner still continues to be a considerable challenge.



**Figure I.A.4** Schematic illustration for the synthesis of graphene by ‘top-down’ and ‘bottom-up’ approaches.

### I.A.2.1 Functionalization of graphenes

The two main ways for functionalization graphenes have been based on covalent and non-covalent methods (Figure I.A.5). Covalent functionalization of graphenes has been achieved by direct attachment of organic functionalities either to pristine graphene or to graphene oxide (GO). Graphene oxide itself can be considered as functionalized graphene along with its reduced form, the reduced graphene oxide (rGO). On the other hand, non-covalent functionalization of graphenes takes place through  $\pi$ - $\pi$  interaction between the graphene surface and other moieties (Figure I.A.5). Another route for the functionalization of graphene involves the deposition of metal and metal oxide nanoparticles (NPs) on the surface of graphene sheets. The type of interaction between graphene and the nanoparticles can either be covalent or non-covalent, depending on the method of preparation of the composite material and the nature of the nanoparticles involved. For instance, palladium has a higher affinity towards graphene due to the partial covalent nature of binding between them.<sup>17</sup> The immobilization of metal and metal oxide NPs on graphene and functionalized graphenes have been dealt in detail in Chapter 2, Section A.

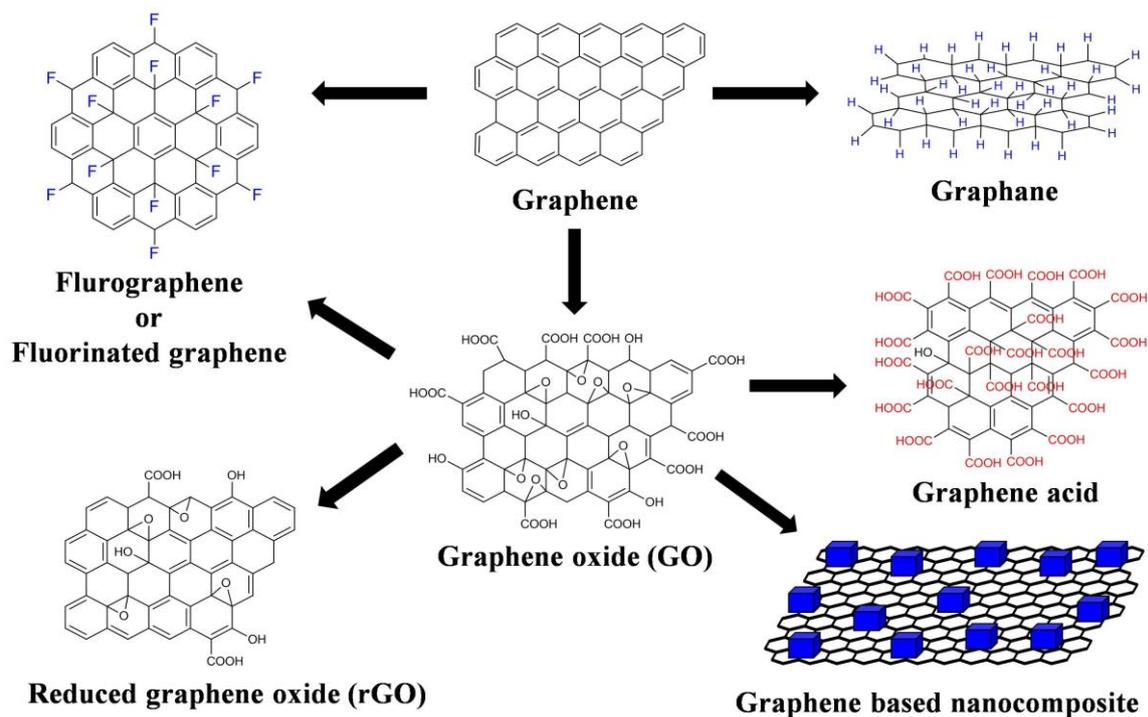


**Figure I.A.5** Different routes for the functionalization of graphene.

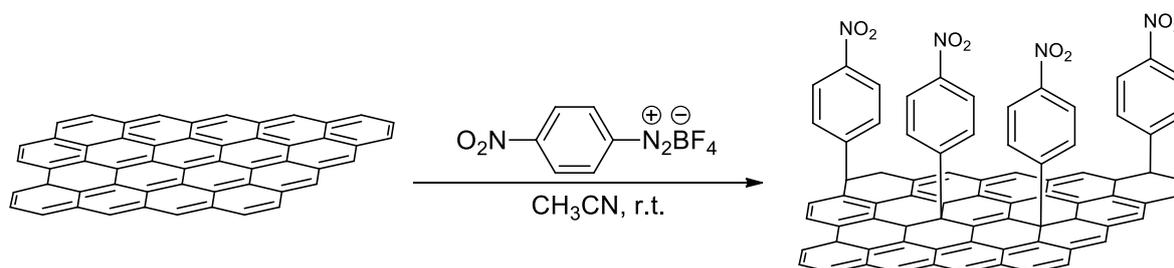
### I.A.2.2 Covalent functionalization of graphene

The covalent functionalization of graphenes has been done by three different routes, one involving the formation of covalent bonds between free radicals or dienophiles and C=C bonds of pristine graphene. The second route and by far the most explored one involve graphene oxide (GO) as the starting material (Scheme I.A.1). In this case, the formation of covalent bond occurs between different functional groups and oxygenated functional groups of GO. Moreover, GO can be transformed into reduced graphene oxide (rGO) which can then be further functionalized. The third one involves direct attachment of hydrogen and halogens to graphene derivatives leading to the formation of ‘graphane’ and fluorographene (graphene fluoride).

Tour and co-workers,<sup>18</sup> have decorated graphene with nitrophenyls via heating diazonium salt to produce highly reactive free radical, which subsequently reacts with  $sp^2$  carbon atoms of graphene (Scheme I.A.2). This covalent functionalization of graphene results in decrease in the conductivity of graphene in a controlled manner, due to disruption of the  $\pi$  network. Moreover, it has been found that this covalent attachment of nitrophenyls leads to the introduction of a band gap.<sup>19</sup> Thus functionalization of graphene in this way could make them potentially useful for fabrication of semiconducting nanomaterials.



**Scheme I.A.1** Schematic representation for the functionalization of graphene.

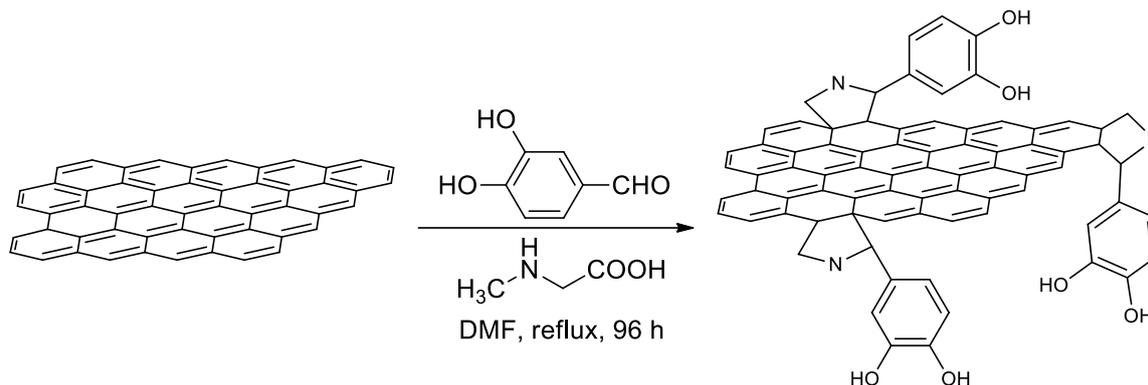


**Scheme I.A.2** Covalent attachment of nitrophenyls with graphene.

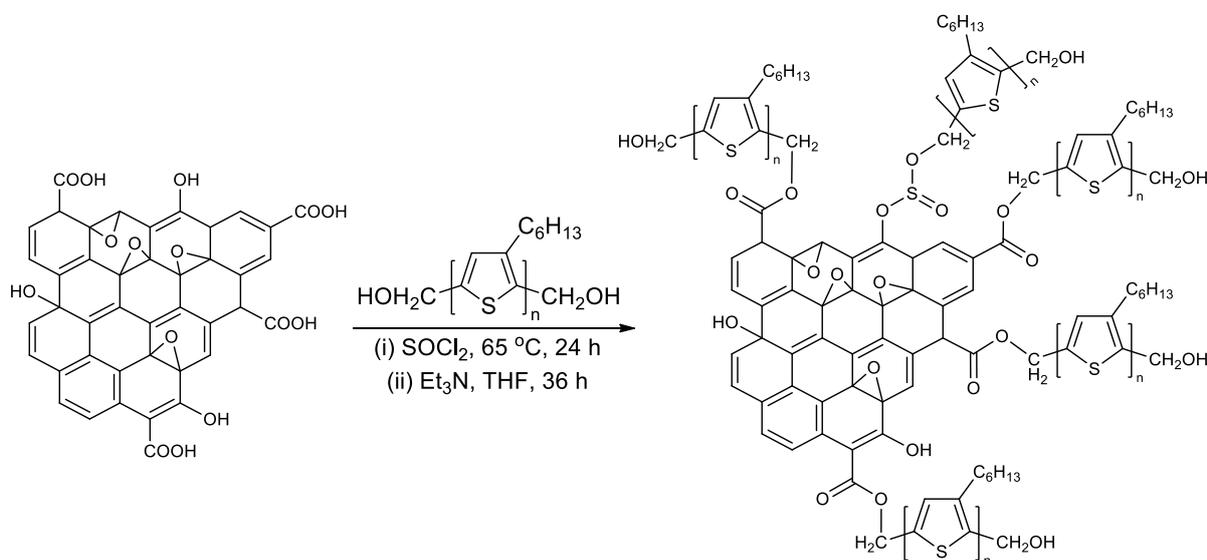
The reaction of graphenes with dienophiles is another common route for the covalent functionalization. Azomethine ylide has been utilized as the prevalent dienophile for this purpose. For instance, graphene sheets have been decorated with dihydroxyphenyl groups through attachment with pyrrolidine rings (Scheme I.A.3). The attachment takes place via a 1,3-dipolar cycloaddition of azomethine ylide. The introduction of hydroxyl groups into graphene increases its dispersibility in polar solvents.<sup>20</sup>

Owing to the rich chemistry of hydroxyl, carbonyl, epoxy and carboxyl functional groups, GO has been selected as the primary precursor for the synthesis of various functionalized graphenes through covalent attachment. For instance, GO functionalized with  $-\text{CH}_2\text{OH}$  terminated regioregular poly(3-hexylthiophene) ( $\text{P}_3\text{HT}$ ) has been accomplished through the

formation of ester linkage with the carboxyl groups of GO (Scheme I.A.4). The presence of abundant –OH groups in the material facilitated its solubility in common organic solvents. The investigators designed a photovoltaic device by further combining this composite material (P<sub>3</sub>HT/GO) with C<sub>60</sub>. This combination resulted in a 200% increase in the power conversion efficiency in comparison to P<sub>3</sub>HT/C<sub>60</sub> system. This exceptional increase has been due to the extended electron delocalization that took place after the covalent attachment of P<sub>3</sub>HT with GO.<sup>21</sup>

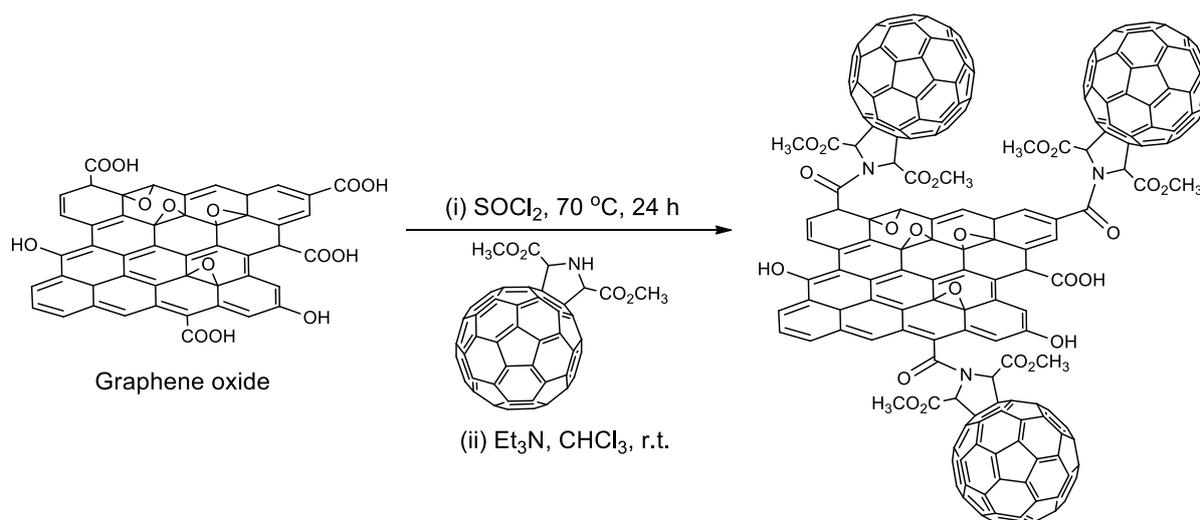


**Scheme I.A.3** Functionalization of graphene via 1,3-dipolar cycloaddition of azomethine ylide.



**Scheme I.A.4** Synthesis of P<sub>3</sub>HT grafted graphene.

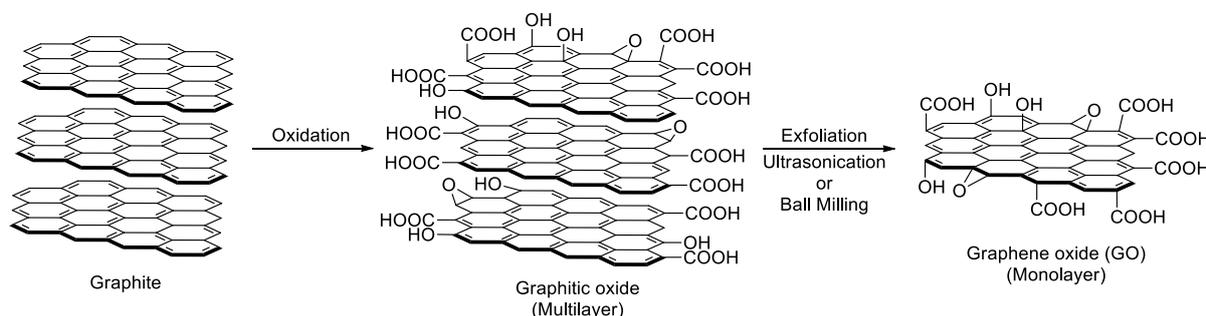
In another approach a hybrid material has been prepared by covalent attachment between graphene oxide and pyrrolidine ring anchored C<sub>60</sub> fullerene.<sup>22</sup> The pyrrolidine ring of C<sub>60</sub> formed an amide linkage with the carboxyl groups present of the surface of GO (Scheme I.A.5). Such GO–C<sub>60</sub> hybrid materials could find application in the fabrication of optoelectronic devices due to their excellent optical and electronic properties.



**Scheme I.A.5** Formation of GO–C<sub>60</sub> hybrid material from graphene oxide.

### I.A.2.3 Graphene oxide (GO)

Graphene oxide (GO), the oxidised form of graphene has been primarily used as precursor for bulk scale production of graphene based materials. Although the name suggests similarity with graphene, GO exhibits widely different properties from pristine graphene. This is due to the disruption of the conjugated  $\pi$  network of graphene during its chemical treatment. Whereas pristine graphene is composed of  $\text{sp}^2$  carbons spread endlessly, GO is highly functionalized with diverse oxygenated functional groups like hydroxyl, epoxy, carboxyl, etc.<sup>10</sup> The hydroxyl and epoxide groups lie on the basal plane and the carboxyl groups are located at the peripheral edges of GO sheets (Scheme I.A.6). Thus graphene oxide can be considered as a single layer of graphite sheet with a variety of different hydrophilic oxygenated functional groups.



**Scheme I.A.6** Schematic representation for the synthesis of graphene oxide (GO).

Owing to the presence of carboxyl and hydroxyl groups, graphene oxide has been found to be slightly acidic in nature (pH 4.5 at 0.1 mg mL<sup>-1</sup>).<sup>23</sup> Furthermore, in solution graphene oxide shows three different  $\text{pK}_a$  values of 4.3, 6.6 and 9.0 corresponding to carboxyl, phenolic and

hydroxyl groups respectively.<sup>24,25</sup> The presence of ionisable groups has been reflected in their high dispersibility in aqueous medium. However, the solubility of GO in aqueous medium decreases with the decrease in the pH value of the dispersion because the repulsive force between GO sheets gets weakened due to the protonation of carboxyl and phenolic groups. Moreover, exfoliated graphene oxide also forms stable colloidal dispersions in water due to the electrostatic repulsion between the GO sheets resulted after ionisation of the carboxyl and phenolic groups.

#### **I.A.2.4 Milestones in the synthesis of graphene oxide**

The synthesis of multilayer graphene oxide can be classified into three different categories based on the type of chemical oxidising agents used. They are the chlorate method, the permanganate method and the third method comprising of novel oxidants like chromate,<sup>26</sup> ferrate,<sup>27</sup> benzoyl peroxide,<sup>28</sup> etc.

##### **I.A.2.4a Chlorate methods**

The first synthesis of multilayered graphene oxide dates back to 1859, when Benjamin Brodie heated lamellar graphite in presence of strong oxidising agents.<sup>29</sup> The main objective was to unravel the chemical structure of this material. In his experiment, Brodie treated graphite with a mixture of potassium chlorate (KClO<sub>3</sub>) and fuming nitric acid (HNO<sub>3</sub>) at 60 °C for 3-4 days. At that time KClO<sub>3</sub> was commonly used as a source of molecular oxygen and nitric acid was known to react strongly with aromatic carbons. The product obtained after repeated oxidative treatments was found to be acidic in nature, which led Brodie to coin the term ‘graphic acid’ for this new material.

In 1898 L. Staudenmaier,<sup>30</sup> modified the Brodie’s method by adding potassium chlorate in small portion during the course of the reaction. Moreover, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) was also added in small amounts in order to increase the acidity of the mixture and shortening the overall reaction time. The main objective behind the use of H<sub>2</sub>SO<sub>4</sub> was to reduce the amount of fuming nitric acid, thereby evading large emission of toxic gases (NO<sub>2</sub>, N<sub>2</sub>O<sub>4</sub>) and making the process comparatively safer. The material thus obtained in this was found to possess similar properties to that of Brodie’s graphic acid.

Forty years later, Hofmann,<sup>31</sup> attempted to develop an even safer alternative method by using KClO<sub>3</sub> and non-fuming nitric acid. Although the material formed in this way possessed similar properties, the level of oxidation was found to be lower.

#### I.A.2.4b Permanganate methods

Almost one hundred years after the initial discovery of Brodie, Hummers and Offeman,<sup>32</sup> developed the fastest, safest and most convenient method for the synthesis of graphene oxide. Their method of oxidative chemical exfoliation consisted of potassium permanganate along with sulfuric acid and a small amount of sodium nitrate. The level of oxidation was similar to that of Brodie's method; however, the absence of  $\text{KClO}_3$  prevented the release of explosive  $\text{ClO}_2$  gas. Although the release of  $\text{ClO}_2$  gas could be eliminated, the formation of other toxic gases ( $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ ) could not be avoided. Moreover, the GO synthesized by Hummers' method contains traces of sulfur and nitrogen presumably as covalently bonded sulphates and nitrates. Nevertheless, Hummers' method remains as a fundamental process for producing large quantities of graphite oxide even today.

Recently, an improved method for the preparation of graphene oxide has been developed. Tour and co-workers,<sup>33</sup> ameliorated Hummers' method by replacing sodium nitrate with phosphoric acid for the oxidative chemical exfoliation of graphite. The GO produced through this method has a higher yield, more uniform structure and a higher level of oxidation. Hence, this method has been regarded as the fourth principal method for the preparation of GO.

#### I.A.2.4c Other methods

Apart from the chlorate and permanganate method, several modern ways to oxidise graphite have evolved. For instance, potassium chromate has been used as oxidant either using Jones conditions,<sup>27</sup> or in combination with  $\text{HNO}_3$  or  $\text{HClO}_4$ .<sup>34</sup> Moreover, potassium ferrate has also been used to oxidise graphite in presence of sulfuric acid at room temperature,<sup>27</sup> or with hydrogen peroxide in aqueous media at 50 °C.<sup>35</sup> Other routes for the preparation of graphene oxide include benzoyl peroxide,<sup>28</sup> and acid-free oxidation in presence of oxone.<sup>36</sup> The key routes for the oxidative exfoliation of graphite towards the synthesis of GO are listed in Table I.A.1.

**Table I.A.1** Prevalent strategies for the synthesis of GO

Classification	Method	Conditions	Year
Chlorate	Brodie	$\text{KClO}_3$ , fuming $\text{HNO}_3$ , 60 °C, 3-4 d	1859
	Staudenmaier	$\text{KClO}_3$ , $\text{HNO}_3$ + $\text{H}_2\text{SO}_4$ , 60 °C, 1-2 d	1898
	Hofmann	$\text{KClO}_3$ , $\text{HNO}_3$ (non-fuming)	1937
Permanganate	Hummers	$\text{KMnO}_4$ + $\text{NaNO}_3$ , $\text{H}_2\text{SO}_4$ , 35 °C, 2 h	1958
	Tour	$\text{KMnO}_4$ , $\text{H}_2\text{SO}_4$ + $\text{H}_3\text{PO}_4$ , 50 °C, 12 h	2010

	Mechanochemical	KMnO <sub>4</sub> , ball mill, 500 rpm, 3 h	2013
	Microwave assisted	KMnO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , 250 W, 150 s	2014
	Room temperature	KMnO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , 10-25 °C, 4-8 h	2019
Chromate	Jones	H <sub>2</sub> CrO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub>	1978
	Cr(VI)	K <sub>2</sub> CrO <sub>4</sub> , HClO <sub>3</sub> , HNO <sub>3</sub> , 50 °C, 24 h	2012
Ferrate	Room temperature	K <sub>2</sub> FeO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , r.t., 1 h	2015
	Fe(VI)	K <sub>2</sub> FeO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> O, 50 °C, ~ 4 h	2016
Peroxide	Organic process	C <sub>14</sub> H <sub>10</sub> O <sub>4</sub> , 110 °C, 10 min	2009
Oxone	Acid-free	KHSO <sub>5</sub> , DMF, heat	2015

Besides these methods there are several other procedures which employ combination of different reagents, co-oxidants and physical promoters. Furthermore, the electrochemical approaches are also used for large scale production of high quality graphene oxide. These methods are considered more environmentally benign than chemical methods in terms of low waste generation.<sup>37,38</sup> A careful optimization of the amount of water and the temperature of the reaction leads to the formation of either hydroxyl- and epoxide-rich GO sheets or more carbonyl-rich domains.<sup>39</sup>

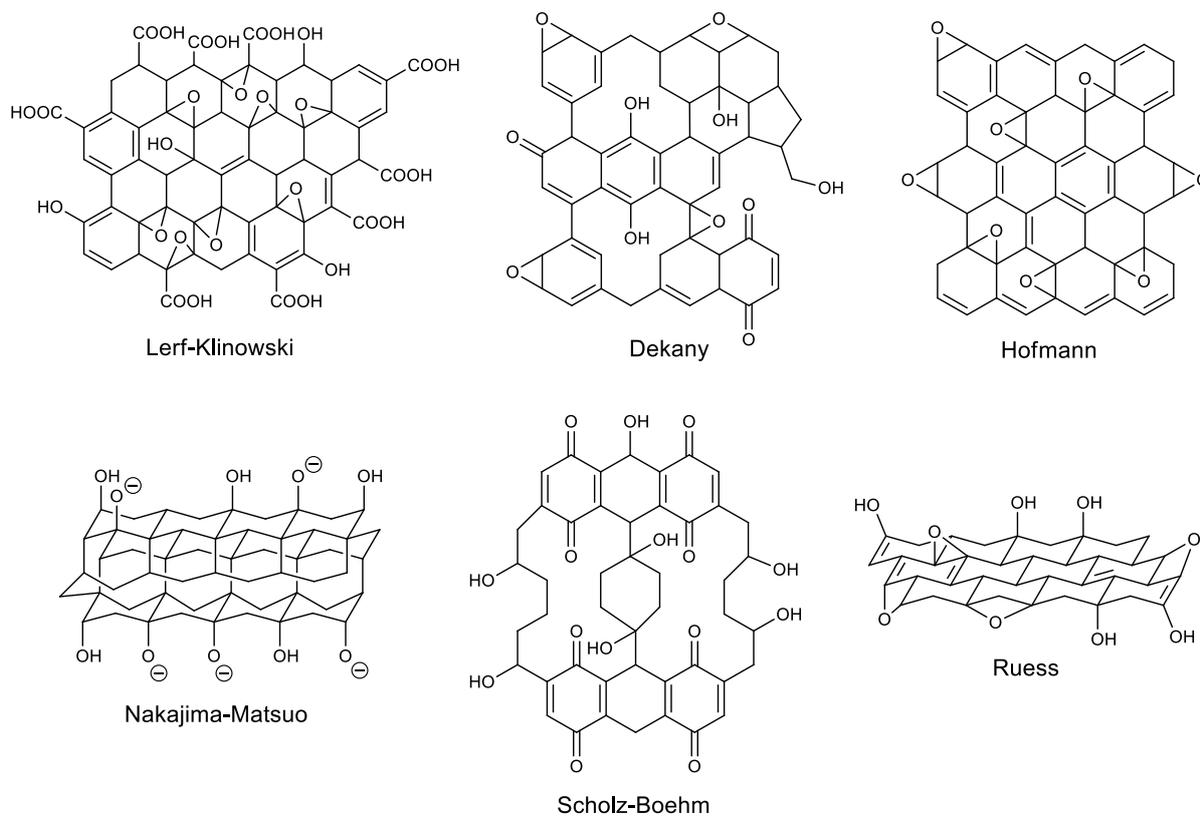
### I.A.2.5 Structure of graphene oxide

Among the various known models for the structure of graphene oxide, the model that accounts for most of the experimental observations has been proposed by Lerf-Klinowski in the late 1990s.<sup>40-43</sup> After a series of analytical studies using <sup>1</sup>H, <sup>13</sup>C solid state NMR and FT-IR, Lerf-Klinowski concluded that GO contains two different regions. Those are aliphatic regions with six-membered rings and aromatic regions with non-oxidized benzene rings. The actual distribution of oxygenated functional groups on GO is not fully understood due to its non-stoichiometric composition. Nevertheless, several different models for the structure of GO have been suggested by different groups which are presented in Figure I.A.6.

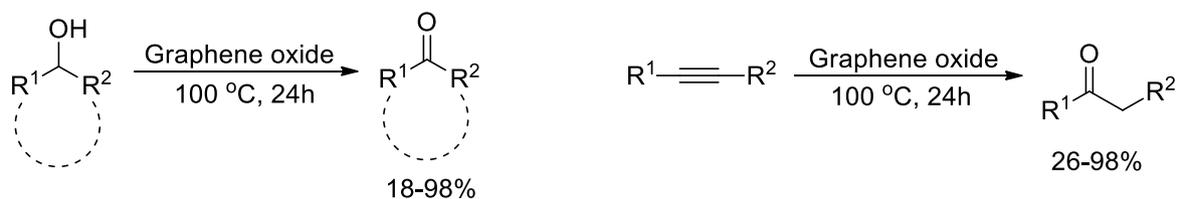
Owing to the presence of different oxygenated functionalities in GO, it has been frequently used as catalyst in diverse organic reactions. Few examples of graphene oxide as a carbocatalyst in organic transformations are presented below.

In 2010 C. W. Bielawski,<sup>44</sup> was the first to demonstrate the oxidative property of GO in synthetic organic transformation. They employed GO (200 wt%) for the oxidation of alcohols

to carbonyl compounds and hydration of alkynes to corresponding ketones, thus establishing the propensity of GO towards oxidation reaction (Scheme I.A.7).

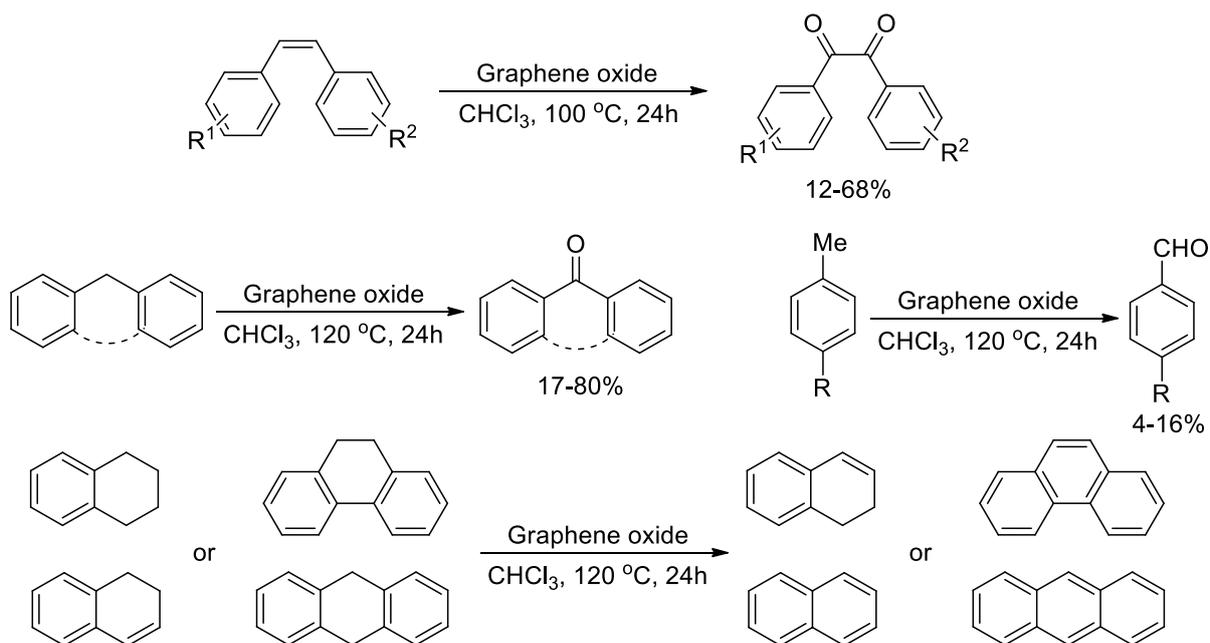


**Figure I.A.6** Different structural models of GO.



**Scheme I.A.7** Graphene oxide mediated oxidation and hydration reactions.

The same group reported graphene oxide as an effective oxidant for the C–H oxidation of various olefins, methyl benzenes and diarylmethanes.<sup>45</sup> Moreover, the catalyst was also used successfully for dehydrogenation of aromatic hydrocarbons. The advantage of the protocol was that no additional co-oxidants or transition metal catalysts were required (Scheme I.A.8). Bielawski and co-workers,<sup>46</sup> accomplished the oxidation of thiols and sulfides to disulfides and sulfoxides using graphene oxide. The heterogeneous nature of the catalyst led to easy isolation and purification of the final products (Scheme I.A.9).

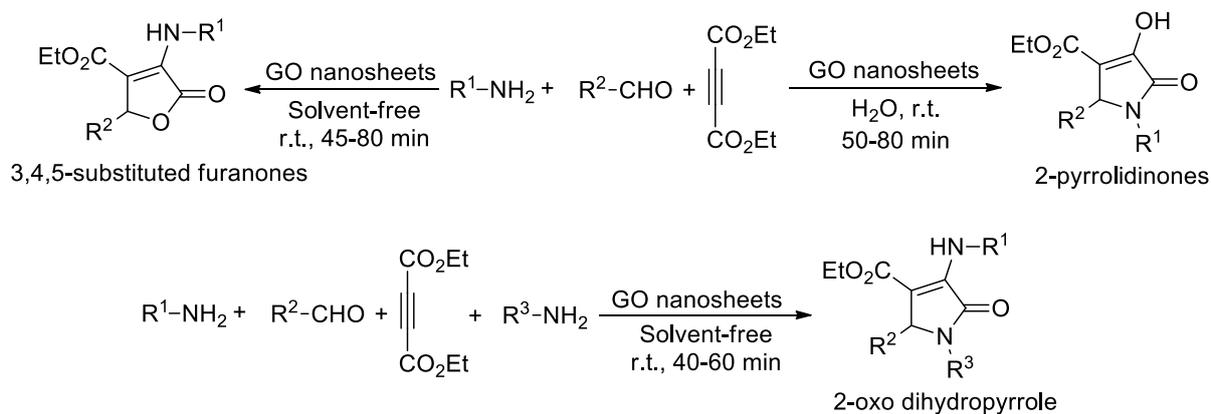


**Scheme I.A.8** GO mediated oxidation and dehydrogenation reactions.



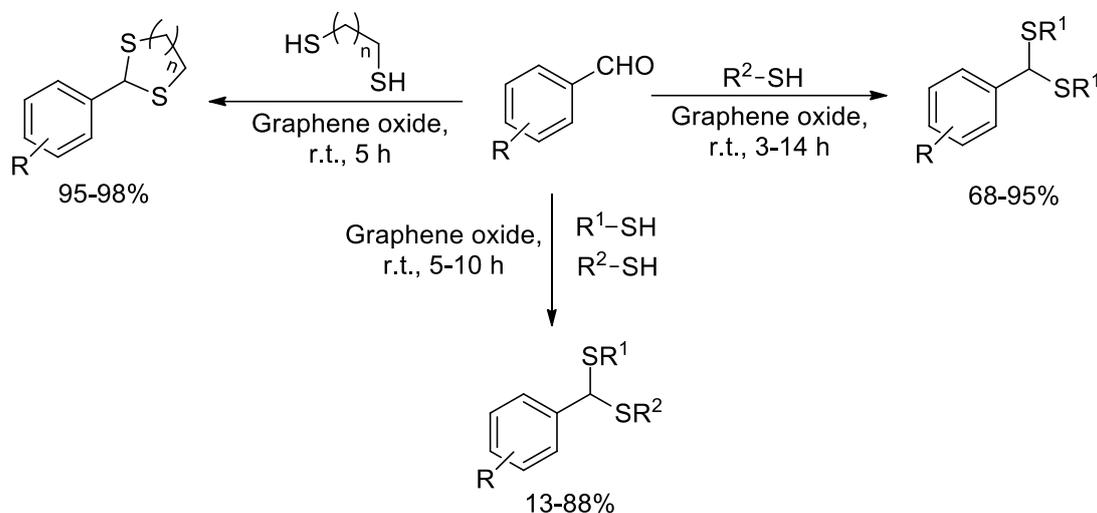
**Scheme I.A.9** Oxidation of thiols and sulfides in presence of GO.

Apart from oxidation reactions, GO nanosheets have been successfully employed as catalyst in the synthesis of diversely functionalized heterocyclic compounds like 2-pyrrolidinones, furanones and 2-oxo dihydropyrroles (Scheme I.A.10).<sup>47</sup>



**Scheme I.A.10** GO nanosheets catalyzed synthesis of heterocyclic compounds.

The acidic nature of GO has been utilized in the thioacetalization of aldehyde under solvent-free conditions.<sup>48</sup> A range of symmetrical as well as unsymmetrical thioacetals have been synthesized using catalytic amount of GO (Scheme I.A.11).



**Scheme I.A.11** GO catalyzed thioacetalization of aldehydes.

### I.A.2.6 Reduced graphene oxide (rGO)

The reduced form of graphene oxide generated by reductive exfoliation treatment of GO has been regarded as reduced graphene oxide (rGO). This material has mechanical and optoelectronic properties very close to that of pristine graphene.<sup>11</sup> Reduced graphene oxide possesses graphene-like basal plane with specific zones containing oxidized chemical entities. The graphene-like properties makes this material a suitable candidate for myriads of application and fabrication of optoelectronic and energy storage devices.<sup>49</sup> Reduced graphene oxide can be easily prepared in large quantities from GO by thermal,<sup>50</sup> electrochemical,<sup>51,52</sup> microwave- and photo-assisted methods.<sup>53,54</sup> During the reduction process of GO, the removal of epoxy and hydroxyl groups are more facile than that of carboxyl groups. The carbon-oxygen ratio determines the level of reduction that has been achieved. Henceforth, it is noteworthy to mention that the quality and property of rGO depends on the method by which it has been prepared. Chemical reduction of GO has been generally performed by using hydrazine hydrate and other hydrazine derivatives.<sup>55</sup> Other commonly used reducing agents include sodium borohydride,<sup>56</sup> sodium borohydride in combination with sulfuric acid,<sup>57</sup> hydroiodic acid,<sup>58</sup> etc. Apart from these reagents, some organic reducing agents like ascorbic acid,<sup>59</sup> amino acids and various leaf extracts have been employed for the synthesis of rGO.<sup>60</sup> Since, most of the oxidising and acidic functionalities are lost during the reduction process, rGO have been seldom used as catalyst. However, rGO is used for immobilization of

metal NPs or in the preparation of diverse nanocomposite materials, which subsequently exhibits exceptional catalytic property.<sup>61</sup>

### **I.A.2.7 Other graphene derivatives**

Apart from graphene oxide (GO), reduced graphene oxide (rGO) and chemically modified graphenes (CMGs), there are few other graphene derivatives that have emerging in the recent years. These include graphane (fully hydrogenated graphene), graphol (hydroxyl form), thiographene, graphene acid, halogenated graphene, graphene fibers, etc. Sofo and co-workers,<sup>62</sup> theoretically predicted the existence of graphane and fluorinated graphane. The material could be synthesized by exposing graphene to cold hydrogen plasma.<sup>63,64</sup> The characterization of graphane indicated conversion of  $sp^2$  domains into  $sp^3$  without the loss of hexagonal symmetry. Owing to the complete loss of conjugation in graphane, it behaves as an insulator.

Fluorographene or graphene fluoride has been synthesized by the treatment of  $XeF_2$  on graphene at room temperature.<sup>65</sup> During fluorination the  $sp^2$  carbon atoms reorganize to  $sp^3$  carbon in fluorographene, which changes its structure and optical properties. Fluorographene behaves as an insulator and shows anisotropic negative magnetoresistance.<sup>66</sup>

Graphene fiber is a new generation of macroscopically assembled carbonaceous fiber comprising of individual units graphene and its derivatives.<sup>67</sup> Graphene fibers have been prepared by wet spinning of graphene oxide liquid crystals followed by reduction.<sup>68</sup> The material is expected to possess extreme mechanical and transport properties which could find application in textiles, electronic devices, photodetectors, supercapacitors and batteries.

### **I.A.2.8 Non-covalent functionalization of graphene**

Graphene sheets are hydrophobic in nature and forms multilayer due to  $\pi$ - $\pi$  stacking. To avoid this  $\pi$ - $\pi$  stacking, non-covalent functionalization of graphene is essential. Non-covalent functionalization is an attractive method since it allows attachment of different functional groups to graphene without disturbing the  $\pi$ -electronic network.<sup>69</sup> The type of contact through which graphenes could be non-covalently functionalized includes nonpolar gas- $\pi$  interaction, H- $\pi$  interaction,  $\pi$ - $\pi$  interaction, cation- $\pi$  interaction and anion- $\pi$  interaction.

### **I.A.3 References**

References are given in BIBLIOGRAPHY under Chapter I, Section A.

