Abstract  The chapter gives an overview of the most important synthetic methods to produce graphene oxide via wet chemistry. Brodie-Staudenmaier-Hummers and free-water based approaches are reported and where it is considered the influence of synthesis on the graphene oxide structure. Physical chemical and morphological characterisations are described in the second part of the chapter. In the last section, details of theoretical calculation and modelling of graphene oxide structures are presented.

Keywords  Graphene oxide synthesis · Physical chemical characterization · Morphology · Molecular modelling

Graphene oxide is not a natural product and results in a non-stoichiometric “molecule”. Basically, graphene oxide is defined as a layer of graphene decorated with oxygen functionalities, such as hydroxyl (OH), carbonyl (C=O) and alkoxy (C–O–C) groups. Practically, graphene oxide is made when a pristine graphene is oxidized, following a general master equation

\[
\text{Carbon Layer} \xrightarrow{\text{Oxidation}} \text{GO}
\]  

In Fig. 2.1a–c is shown a typically representation of GO structure, a yellow-amber dispersion and an oven dry solid of graphene oxide, respectively. The description of a single unit of GO mainly depends on the size of the graphene basal plane and the number of oxygen functionalities. The size of GO is controlled by the carbon source, often graphite. Besides, the oxygen domains are subjected by the synthetic procedure. Several grades of oxidation can be found relying on the number of oxygens. The diagram in Fig. 2.1b shows that graphene oxide exists in a range 10–50 at.%O limited by temperature of about 60–70°C. In this oxidation range, pristine graphene oxide is observed with different solubility and it roughly splits into two subgroups that we name as low solubility GO (15–35°C) and high solubility GO (35–50°C), which depends on the oxidation grade. At zero oxidation (0 at.%O), pristine graphene is found, while a reduced graphene oxide (rGO) can be observed with a oxidation up to 10 at.%O. The maximum theoretical value of oxidation for graphene cannot be over
2.1 Synthetic Methods for Graphene Oxide

Graphene oxide can be synthetized in a dry or wet medium. The dry synthetic approach consists in an oxidation reaction of graphene through atomic oxygen in ultrahigh vacuum conditions [21, 47], to exposure to molecular oxygen [44, 49] and treating with ozone under ultraviolet light [10, 22]. By contrast, a suitable approach consists of wet synthesis in which graphite is typically used as graphene source, due to its natural abundance and inexpensive cost. In Fig. 2.1e, the three main
reaction routes are shown. The first approach starts with using graphene, produced with mechanical method, followed by a further oxidation, while the second one is based on exfoliation in aqueous media by means of ultrasonic treatment [4, 43]. The last route takes in a concurrent of oxidation and exfoliation process in strong acidic medium as found in Brodie-Staudenmaier-Hummers method. Overall, these paths bring to the formation of graphene oxide, but the structural properties of each type of GO are different, such as the structure or the reactivity sites.

In the following paragraphs, in chronological order, are reported approaches of preparing graphene oxide. During the last century, several methods were proposed and the three major methods are Brodie [5], Staudenmaier [45] and Hummers [23]. From these basic methods a number of variations were derived to improve the overall yield and quality of the product, for instance the Tour method [31]. Recently, a “primitive” approach was adopted by a number of researchers which consists in a free-water exfoliation and oxidation of graphite through strong oxidizing agent in a strong protic medium (often H₂SO₄) [35, 46].

2.1.1 Brodie-Staudenmaier-Hummers Based Methods

Brodie Method. The first documented synthesis of graphitic oxide material is attributed to Brodie in 1859 [5]. His study was focused on finding the weight of graphite and, as common at that time, a series of chemical reactions were investigated to elucidate the properties of a novel material. Thus, graphite was mixed with potassium chloride (KClO₃) and solubilized in fumic nitric acid to oxide the sample and inferring the molecular weight. Further oxidation processes were carried out on the sample up to any changes were visible. The elemental analysis revealed a composition of circa 60% C, 2% H and 38% O. The resulting product, a mixture of graphene and graphite oxide, was soluble in pure water.

Staudenmaier Method. In 1898 Staudenmaier [45] improved the Brodie’s reaction by adding sulfuric acid, to increase the acidity of the mixture, and several aliquots of solid KClO₃, over the course of reaction. Despite that, Brodie and Staudenmaier method generates ClO₂ toxic gas which rapidly decomposes in air giving explosions. These modifications led to a more oxidized graphitic material and a simplification of the reaction.

Hummers Method. In 1958, Hummers and Offeman [23] proposed an alternative way to oxide graphite improving the safe operational conditions with a drastic reducing time, from 10 to 2 days. They mixed graphite with concentrated sulfuric acid (H₂SO₄), sodium nitrate (NaNO₃) and potassium permanganate (KMnO₄) to obtain a brownish grey pasty. The suspension was diluted with water and hydrogen peroxide (H₂O₂) was added to get a higher oxidation degree and to eliminate manganese from the dispersion (yellow-brown mixture). Finally, the sample was filtered and washed with warm water. They achieved the same degree of oxidation reported by Staudenmaier, however, the amount of GO results very little. The weakness of this
method includes a time-consuming of the separation and purification process. From Hummers method a huge number of variation/optimization approaches has been developed and a typical GO product is made by flakes of about 1 nm and a lateral size of 1 µm.

**Tour Method.** An improvement of Hummers method was proposed by Tour’s group at Rice University in 2010 [31]. They have substituted the sodium nitride with phosphoric acid in a mixture of H$_2$SO$_4$/H$_3$PO$_4$ (9:1) and increasing the amount of KMnO$_4$. The advantage of this method consists in no generation of toxic gases, such as NO$_2$, N$_2$O$_4$ or ClO$_2$, in the reaction and an easy temperature control. The authors claim that the presence of phosphoric acid generates a more intact graphitic basal plane. A comparison of the improved method with the conventional and modified Hummers’s procedures can be seen in Fig. 2.2. The advantage of the Tour method consists in a production of graphene oxide having a higher hydrophilic degree, in contrast with GO produced by Hummers method (see Table 2.1). Hence, this graphene oxide results more oxidized and soluble.

### 2.1.2 Free-Water Oxidation Method

The Free-Water Oxidation method takes advantage of a reaction between expanded graphite and oxidizing agent in a free-water medium. Because of inorganic carbon is essentially inert at room temperature, its solubilization/ dispersion in a solvent
needs strong protic acid or mixture of warm acids, such as sulphuric or nitric acid. Moreover, a strong oxidizing agent, as potassium permanganate (KMnO₄), ensures the bonds of oxygen functionalities to inorganic carbons. From historical reason, the free-water oxidation methods derived from a modification of the Hummers method in which some limitations, such as hazardous reagents, were improved.

**Sun Method.** In 2013, Sun and Fugetsu at Hokkaido University [46] introduced a more direct method to produce graphene oxide. They used expanded graphite as carbon precursor. The potassium permanganate had twofold effects: intercalating agent and oxidizing agent. The intercalation of KMnO₄ between graphitic layers produced a further *spontaneous expansion* which looks like a foam of graphitic material, as shown in Fig. 2.3b. The reaction occurs in acidic medium of sulfuric acid. The ratio Graphite:H₂SO₄ was reduced to 1:20 and additional reagents were eliminated from the reaction procedure. For this reason, Sun protocol can be considered as one of the first green procedure of among the wet synthetic methods.

**Peng Method.** Very recently (2015), Peng and co-workers [36] proposed a scalable and green method (Fig. 2.4) to produce graphene oxide, using potassium ferrate (K₂FeO₄) as strong oxidant. This compound avoids the introduction of heavy metals or the formation of toxic gases during the preparation. In this method, a mixture of graphitic flakes and K₂FeO₄ dispersed in concentrated sulphuric acid, were loaded into a reactor and stirred for 1h at room temperature. The product was water-washing by repeated centrifugation to obtain highly water soluble graphene oxide.

**4-Steps Method.** This method derived from the basic exfoliation-oxidation procedure and was improved by Pendolino and co-workers [35]. The method consists of 4 reaction steps controlled by temperature, which affects strongly the final product. A scheme of reactions is shown in Fig. 2.5 in which two paths are proposed depending on temperature. In the first step the oxidation process for the mixture graphite-KMnO₄ dispersed in concentrated sulfuric acid gets a pasty slurry. The sec-
ond step (warm) consists of the exfoliation of graphite and is the most critical one. In fact, the production of graphene oxide is limited by temperature and only occurs when the water bath is around 30°C. By contrast, the exfoliation is suppressed for lower temperature with a resulting graphite oxide (cold). The hydrolysis, at 90°C for 1 h, completes the third step. The purification of product is performed by centrifugation using warm water up to the neutrality of the dispersion, at the forth step.

Through the 4-Steps method two different products can be synthesized just controlling the temperature along the reaction. The advantage of this method is related to the improved safety operational conditions (limiting explosive reaction due to Mn₂O₇ in concentrated sulfuric acid for temperature above 55°C) and the production of a type of GO which contains an amount of oxygen domains lower to about 20–30 at.%O. This type of GO can be employed for filter/remediation or biosystems due to the low toxic effect.

In all the above synthetic methods to prepare graphene oxide some limitations are encountered. Primary, lab safety ascribed to hazardous reagents [12, 13, 19]. The use of sodium nitrate or potassium chlorate in Brodie or Staudenmaier methods results explosive, while sodium nitrate (Hummers) or fuming nitric acid, introduce heteroatoms or defects on the GO structure that affects the reactivity [9, 11]. Next, the presence of dimanganese heptoxide (Mn₂O₇) in a solution of sulphuric acid detonates with a temperature over 55°C. An other important factor is the quality and the grain size of graphite. In fact, defect free structure gives higher quality of graphene oxide, as reported by Chen et al. [8] and the size of grain establishes the size for the graphene basal plane. Moreover, the ratio C/O ranges from 0.7 (~55 at.%O) to 3.5 (~20 at.%O) relying on the synthetic method, as well as, the resistivity...
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Fig. 2.5 Reaction scheme for the 4-Steps method. The temperature influences the final product according with the “warm” or “cold” path. The graphene oxide is only obtained when the warm path is followed, and, by contrast, graphite oxide is produced at lower temperature below 30°C.

Table 2.1 Summary of the main synthetic methods used to prepare GO

<table>
<thead>
<tr>
<th>Method</th>
<th>Oxidant</th>
<th>Solvent</th>
<th>Additive</th>
<th>C/O</th>
<th>Resistivity(^{a})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brodie</td>
<td>KClO(_3)</td>
<td>HNO(_3)</td>
<td>–</td>
<td>2.4−2.9</td>
<td>0.15−60</td>
<td>[5, 39–41, 51]</td>
</tr>
<tr>
<td>Staudenmaier</td>
<td>KClO(_3)</td>
<td>Fuming HNO(_3)</td>
<td>–</td>
<td>2.2</td>
<td>120</td>
<td>[30, 40, 45]</td>
</tr>
<tr>
<td>Hummers</td>
<td>KMnO(_4)</td>
<td>H(_2)SO(_4)</td>
<td>NaNO(_3)</td>
<td>1.8–2.5</td>
<td>0.005−0.01</td>
<td>[23, 25, 40, 43, 51]</td>
</tr>
<tr>
<td>Tour</td>
<td>KMnO(_4)</td>
<td>H(_2)SO(_4)</td>
<td>H(_3)PO(_4)</td>
<td>0.7−1.3</td>
<td>0.2−1000</td>
<td>[18, 26, 31]</td>
</tr>
<tr>
<td>Sun</td>
<td>KMnO(_4)</td>
<td>H(_2)SO(_4)</td>
<td>–</td>
<td>2.5</td>
<td>0.18</td>
<td>[46]</td>
</tr>
<tr>
<td>Peng</td>
<td>K(_2)FeMO(_4)</td>
<td>H(_2)SO(_4)</td>
<td>–</td>
<td>2.2</td>
<td>2.7</td>
<td>[36]</td>
</tr>
<tr>
<td>4-Steps</td>
<td>KMnO(_4)</td>
<td>H(_2)SO(_4)</td>
<td>–</td>
<td>3.5</td>
<td>23</td>
<td>[35]</td>
</tr>
</tbody>
</table>

\(^{a}\)10^5 \, \Omega \cdot m

varies from 0.005 to 1000 × 10\(^{-5}\) \, \Omega \cdot m, as shown in Table 2.1. Details on synthesis and functionalization of graphene oxide can be consulted at [6, 16, 17, 53].

Furthermore, the purification is overlong and time-consuming. The filtration using paper filter is not a practicable approach because of the unpurified mixture possesses a colloidal behaviour. Dialysis or centrifugation required a large number of washing cycles. All these aspects strongly affect the final product. To conclude, there is not an exhaustive method or procedure for producing a “standard” graphene oxide, because of for each synthetic method a different type of graphene oxide is produced. Hence, graphene oxide exhibits different physical chemical properties, such as structure and reactivity. The discrepancy between the structure and reactivity of graphene oxide
is in the most of the cases due to the synthetic method and the carbon source, as reported in literature. The standardization of synthesis appears one of the major obstacle in using GO for advanced applications. Nevertheless, different type of graphene oxide, produced with different methods, can enlarge the implementation range of this material by modulating its properties and opening new operating routes. Therefore, different type of GO can be considered an advantage for a future use of this nanomaterials.

### 2.2 Characterizations

The physical chemical characterization of graphene oxide is not often of easy interpretation because this material is made of carbons and oxygens as the majority of organic molecules. Thus, the peculiar spectroscopic signals are blended by conventional carbon and oxygen signals. In the following paragraphs, the most regular techniques and the representative interpretation to identify the GO are shown.

**FTIR.** The FTIR is an efficient tool for a rapid characterization of GO. It becomes common to interpret FTIR signals as referred to hydroxyl (OH), epoxy (C−O−C) and ketone (C=O) groups. The corresponding vibrational frequencies for the stretching mode are around 3400 cm\(^{-1}\), 1090 cm\(^{-1}\) and a doublet at 1700 cm\(^{-1}\), respectively. A typical FTIR spectrum is reported in Fig. 2.6a. It is obvious that the fingerprint region of the IR spectrum of GO varies. The plots a and b show a spectrum of two different synthesis of GO having a oxygen content of 20 at.%O, while plot c represents a commercial GO possessing 50 at.%O. The most of the difference are found for peaks at 1090 cm\(^{-1}\) and the first peak of the doublet around 1700 cm\(^{-1}\). An other example of FTIR spectrum is reported by Bagri et al. [3]. They obtained the following vibration frequencies: hydroxyl 3050–3800 cm\(^{-1}\), carbonyls 1750–1850 cm\(^{-1}\), carboxyls 1650–1750 cm\(^{-1}\), C=C 1500–1600 cm\(^{-1}\) and ethers/epoxides 1000–1280 cm\(^{-1}\). A different interpretation for the two peaks around 1700 cm\(^{-1}\) is reported by Pendolino et al. [33] for GO spectrum having an oxygen content of about 20–30 at.%. Similar frequencies are reported for pristine GO from water dispersion, bands a centred at hydroxyl 3410 cm\(^{-1}\), carbonyls 1730 and 1620 cm\(^{-1}\), and ethers/epoxides 1090 cm\(^{-1}\). Authors argue that these peaks (1730 cm\(^{-1}\), 1620 cm\(^{-1}\)) are not different carbonyl/carboxyl groups but the doublet are interpreted as a keto-enol tautomers, an equilibrium that occurs in molecules carrying keto and enol groups. As reported previously [34], the tautomeric equilibrium is shifted toward the enol form when the dielectric constant is increased, while has an intensity ratio 1:1 in water dispersion. This fact makes evidence of the interpretation for keto-enol tautomerism.

**Raman.** Raman spectrum for the GO shows only two broaden peaks which represent the G and D band (Fig. 2.6b). The first band is found around 1580 cm\(^{-1}\) and is attributed to the in-phase vibrations of ordered crystal structure while the D band
**Fig. 2.6 a** FTIR spectra for GO. The profile a GO with a oxygen content of 20 at.%O following the 4-step synthetic method, profile b different synthesis of GO with a oxygen content of 20 at.%O following the 4-step synthetic method, profile c commercial GO with a oxygen content of 50 at.%O. 

**b** Raman spectra for graphite, GO and reduced GO by γ ray. Reproduced from Ref. [52] with permission from the Royal Society of Chemistry.

(~1350 cm\(^{-1}\)) is assigned to the disorder crystal structure. This fact correlates the G band to the sp\(^2\) carbon and the D band to the presence of sp\(^3\), hence, to oxygen domains [28, 52].

**UV-vis.** The UV-vis spectra for GO shows one adsorption signal followed by a shoulder in the range 190–900 nm. The region 400–900 nm is not affected by any absorptions. The maximum absorbance is found around \(\lambda = 230\) nm which is attributed to \(\pi \rightarrow \pi^*\) transitions in conjugated systems. The shoulder occurs at around \(\lambda = 300\) nm and is often assigned to the \(n \rightarrow \pi^*\) transitions of a carbonyl group. The optical absorption is changing with the number of layers, as reported by Lai et al. [29]. They observed a disappearance of maximum adsorption band towards a lower wavelengths of 196 nm for thick-layer > 10 layers (Fig. 2.7).
Fig. 2.7  a UV-vis spectra for GO dispersions at different sonication time and b histograms vs thickness. Reproduced from Ref. [29] distributed under a Creative Commons Attribution 3.0 Unported License.

Fig. 2.8  XRD patterns from GO dispersion in DMF, CHP, THF, Acetone, water and ethanol solvent. Reprinted with permission from [24]. Copyright (2013) American Chemical Society.
XRD. X-ray diffraction (XRD) pattern of pristine graphene oxide shows only a broad peak around 11° [1, 7, 20, 24, 27, 31]. This peak is associated with the interlayer distance $\sim$1 nm due to the presence of functional groups onto GO. This distance varies depending on the solvent in which GO is dispersed. Jalili et al. [24] reported an interlayer minimum distance of 0.82 nm for ethanol and 1.17 nm in the case GO is dispersed in DMF, as shown in Fig. 2.8.

SEM/TEM. Figure 2.9a, b show SEM images of oven dry GO. The morphology of GO appears as a tightly packed layers with a corrugate surface that sometimes is wrinkled [35].

The TEM image is useful to identify a single layer of graphene oxide, as shown in Fig. 2.9c. This technique shows highly electron transparent corrugated or wrinkled
structure of GO layer. Typical examples of GO single and multilayers are reported by Aunkor et al. [2] and Wang et al. [48].

**AFM.** Atomic force microscopy (AFM) is able to characterize the lateral size and the thickness of GO layer. Typically, the height profile reveals a thickness of 1–1.2 nm while the lateral size can range in the order of tens to hundreds micrometers, depending on the synthesis and the post-synthesis treatment, e.g. sonication. A representative AFM image is shown in Fig. 2.9d, where it can be noted that the lateral size of GO single layer ranging from 500 nm to 50 μm. It can be observed an overlapping of multiple layers with a height of 1 nm for each step [50].

**Thermogravimetric Analysis (TGA).** The thermal decomposition of GO is shown in Fig. 2.10a and reported by Wang et al. [48]. Despite the oxygen concentration, GO is generally unstable to the temperature with starting around 60°C. The material are
lost about the 60% of its weight up to 300°C and lose almost all its mass reaching 900–1000°C. A fast heating process causes a detonation.

**Differential Scanning Calorimetry (DSC).** A DSC profiles for GO in air and N₂ was reported by Qiu et al. [37] in Fig. 2.10b. Few information can get from DSC of GO up to 800°C. The main signal appears over 200°C with exothermal effect which corresponds to an explosion under nitrogen atmosphere. Authors measured an enthalpy of 1600 J g⁻¹ for thermal decomposition under nitrogen and 3920 J g⁻¹ for the second exothermic peak under air pressure.

### 2.2.1 Models and Modelling

Many efforts have been devoted to the structural description of graphene oxide (Fig. 2.11) and several models were proposed [13, 53]. Since the first description, Hoffman and Holst proposed to locate on the basal plane of graphite, with sp² hybridization, net molecular form C₂O, made by epoxy groups. Later, Ruess reformulated this model and, considering the presence of hydrogen in GO species, introduced hydroxyl moieties in the basal plane of graphite. With this modifications, this model, which acquired a sp³ character, is considered formed by a repeat unit where 1/4 of cyclohexanes with epoxide groups localized in the 1, 3 positions and hydroxilated in 4 position. In the Scholz and Boehm model the epoxide and ether groups have been substituted by quinoidal species in a corrugated backbone. In these

![Fig. 2.11 Example of proposed graphene oxide structure. Reproduced from Ref. [13] with permission from The Royal Society of Chemistry](image)
models, however, a misinterpretation is present: the graphene oxide is treated as a materials built up by repetitive units. Lerf and Klinowski abandoned the assumption of the GO periodicity and expressed the model in which the structure is composed by a random distribution of aromatic and wrinkled regions. After all, it is difficult to establish an unique structure for GO because of strictly connected with the synthetic methods.

Besides the interpretation of experimental data to elucidate the GO structure, theoretical studies were carried out approaching towards the fully understand of issue. The first key problem, in a computational study of GO, is related to size of graphene basal plane that usually is too large to be calculated with precision. Several algorithms and methods were referred to the GO structure theoretically. Samarakoon and Wang [38] identified a twist-boat conformation by DFT calculations for a fully-oxidized GO layer with randomly decorated hydroxyl and epoxide groups. Paci et al. [32] explored the formation fo GO structure by means of Monte Carlo method. Here, epoxide and hydroxyl functional groups dominate and are randomly distributed on both side of the graphene plane. They found a set of hydroxyl-hydroxyl and hydroxyl-epoxide hydrogen-bonding interactions and, occasionally, defects made by small holes. In addition, carbonyl and alcohol groups are even molecule of water were observed. Fonseca et al. [14] examined three classical force fields methods. They used Reactive Empirical Bond Order for carbon, third generation of the Charge Optimized Many Body (COMB3), hydrogen and oxygen (REBO-CHO) and Chemistry at HARvard Macromolecular Mechanics (CHARMM) force field to study the properties of GO and to simulate GO structures. Their conclusion is that the COMB3 was considered as the best prediction for almost all properties to investigate physical and chemical properties of different GO structures. Recently, Sk et al. [42] looked into the oxidative process of graphene at edges using DFT. Their results showed that the oxidation is more favourable along the edges comparing with the central part of the graphene basal plane. Froning et al. [15] employed a density functional theory calculations to confirm experimental data for the oxidation process of graphene. They studied the progressive oxidation, using UV/ozone, of a graphene surface by AFM and then compared with DFT and MD simulation to explain that the oxidation starts is susceptible of graphene edges.

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