

Chapter 2

Synthesis, Characterization and Models of Graphene Oxide

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



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

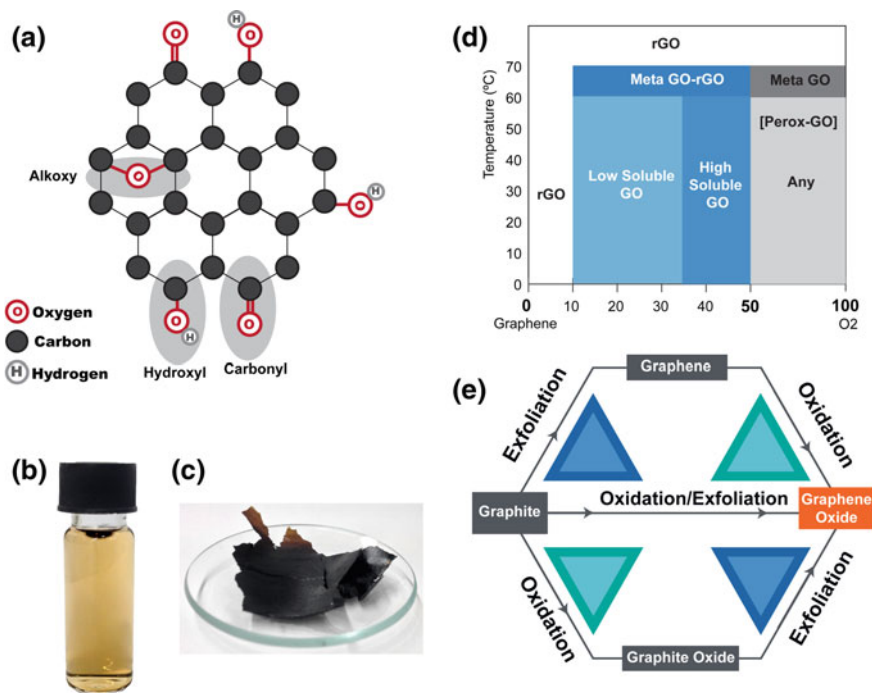


Fig. 2.1 **a** Draw of graphene oxide structure. The illustration shows the hexagonal arrangement of carbon atoms and the presence of oxygen domains. **b** A drafted diagram of the oxidation degree (%O) of graphene oxide versus temperature. Below 10 at.%O and above 70°C reduced graphene oxide is found, while over 50 at.%O a GO structure is not clear. The range between 10 and 50 at.%O shows the presence of GO possessing various degree of solubility. A meta state can be found around 60–70°C. **c** Digital photograph of 0.05 mg/mL aqueous dispersion and **d** solid graphene oxide. **e** Scheme of GO production starting from graphite as carbon source. Three paths can be described to get as final product the graphene oxide material

50 at.%O because of the sp^2 hybridization of carbon atom in the graphene hexagons. Eventually, an oxidation over the 50 at.%O may occur with a fully oxidation by peroxide groups (O_2^{2-}), but this oxidation grade is not yet observed.

2.1 Synthetic Methods for Graphene Oxide

Graphene oxide can be synthesized 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 H_2SO_4) [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 (KClO_3) and solubilized in fuming nitric acid to oxidize 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 KClO_3 , over the course of reaction. Despite that, Brodie and Staudenmaier method generates ClO_2 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 oxidize graphite improving the safe operational conditions with a drastic reducing time, from 10 to 2 days. They mixed graphite with concentrated sulfuric acid (H_2SO_4), sodium nitrate (NaNO_3) and potassium permanganate (KMnO_4) to obtain a brownish grey paste. The suspension was diluted with water and hydrogen peroxide (H_2O_2) 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

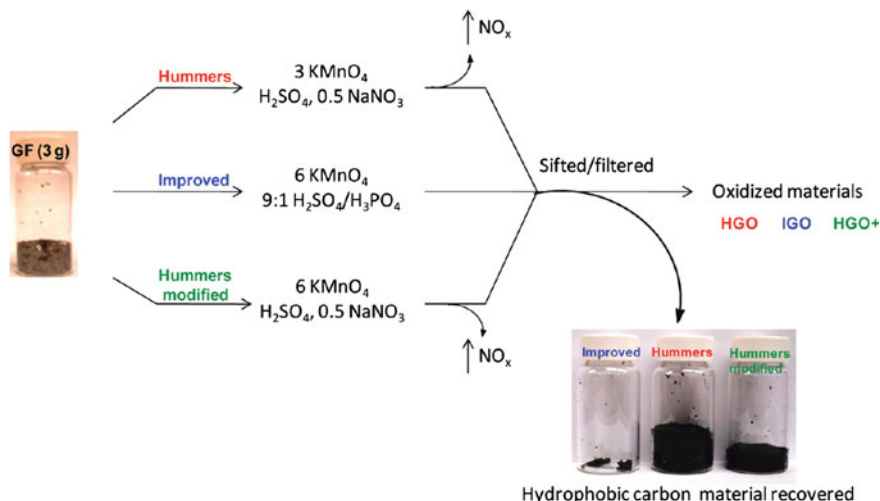


Fig. 2.2 Procedure scheme for Tour method. The starting material is expanded graphite to be used for producing graphene oxide through Tour method and in comparison with Hummers and its modification. Reprinted with permission from [31]. Copyright (2010) American Chemical Society

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 H₂SO₄/H₃PO₄ (9:1) and increasing the amount of KMnO₄. The advantage of this method consists in no generation of toxic gases, such as NO₂, N₂O₄ or ClO₂, 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

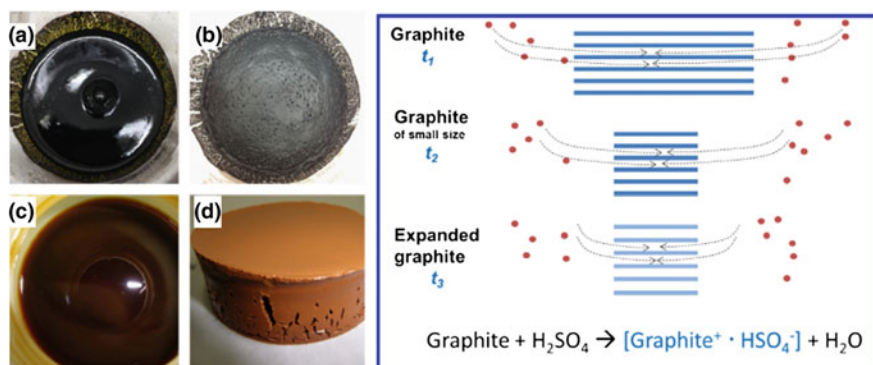


Fig. 2.3 (Left) Reaction scheme for Sun method. (Right) Photos of **a** mixture of reagent, **b** volumetric expansion (foam-like), **c** hydrolysis and **d** concentrated dispersion after purification. Reprinted from [46], Copyright (2013), with permission from Elsevier

needs strong protic acid or mixture of warm acids, such as sulphuric or nitric acid. Moreover, a strong oxidizing agent, as potassium permanganate (KMnO_4), 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 KMnO_4 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: H_2SO_4 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 (K_2FeO_4) 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 K_2FeO_4 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- KMnO_4 dispersed in concentrated sulfuric acid gets a pasty slurry. The sec-

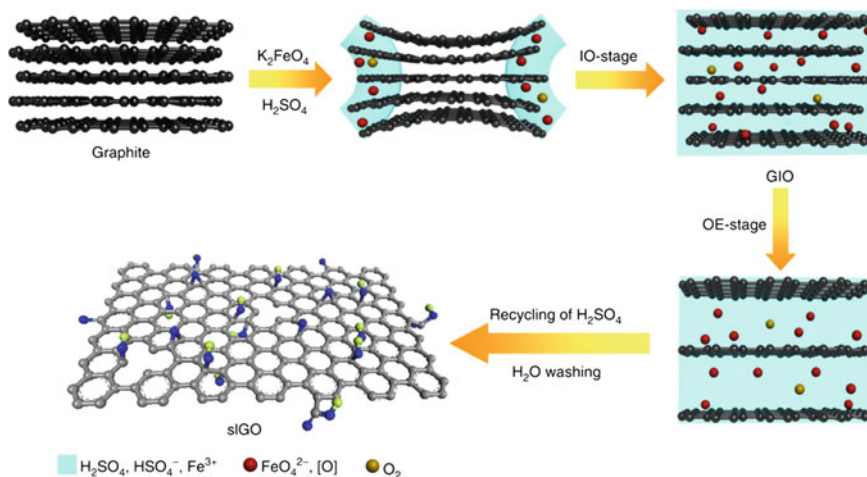


Fig. 2.4 Reaction mechanism proposed by Peng and co-workers for the synthesis of graphene oxide using K_2FeO_4 as oxidizing agent. Reprinted from [36]. This work is licensed under a Creative Commons Attribution 4.0 International License

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 of safety operational conditions (limiting explosive reaction due to Mn_2O_7 in concentrated sulfuric acidic 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 (Mn_2O_7) 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

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

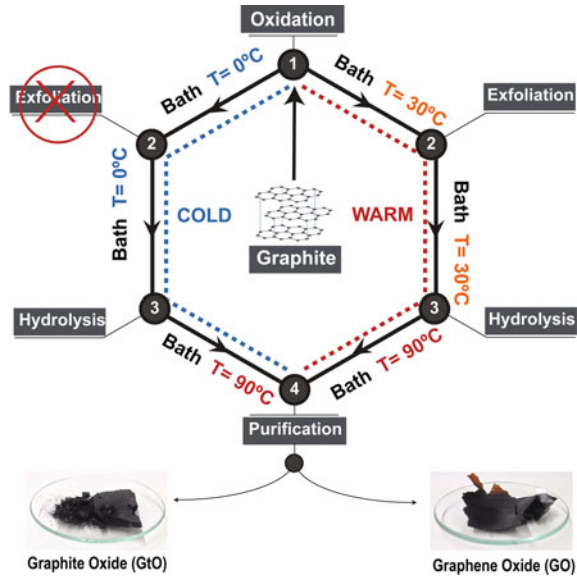


Table 2.1 Summary of the main synthetic methods used to prepare GO

Method	Oxidant	Solvent	Additive	C/O	Resistivity ^a	Ref.
Brodie	KClO ₃	HNO ₃	–	2.4–2.9	0.15–60	[5, 39–41, 51]
Staudenmaier	KClO ₃	Fuming HNO ₃	–	2.2	120	[30, 40, 45]
Hummers	KMnO ₄	H ₂ SO ₄	NaNO ₃	1.8–2.5	0.005–0.01	[23, 25, 40, 43, 51]
Tour	KMnO ₄	H ₂ SO ₄	H ₃ PO ₄	0.7–1.3	0.2–1000	[18, 26, 31]
Sun	KMnO ₄	H ₂ SO ₄	–	2.5	0.18	[46]
Peng	K ₂ FeMO ₄	H ₂ SO ₄	–	2.2	2.7	[36]
4-Steps	KMnO ₄	H ₂ SO ₄	–	3.5	23	[35]

^a 10⁵ Ω·m

varies from 0.005 to $1000 \times 10^{-5} \Omega \cdot \text{m}$, 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.

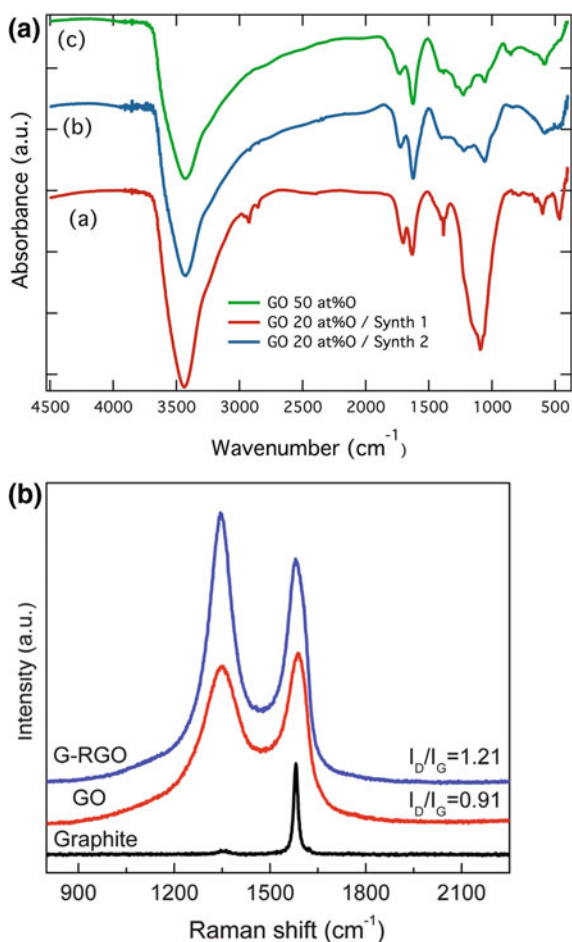
2.2 Characterizations

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 $3050\text{--}3800\text{ cm}^{-1}$, carbonyls $1750\text{--}1850\text{ cm}^{-1}$, carboxyls $1650\text{--}1750\text{ cm}^{-1}$, C=C $1500\text{--}1600\text{ cm}^{-1}$ and ethers/epoxides $1000\text{--}1280\text{ cm}^{-1}$. 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



($\sim 1350 \text{ cm}^{-1}$) 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 $\lambda = 230 \text{ nm}$ which is attributed to $\pi \rightarrow \pi^*$ transitions in conjugated systems. The shoulder occurs at around $\lambda = 300 \text{ nm}$ 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

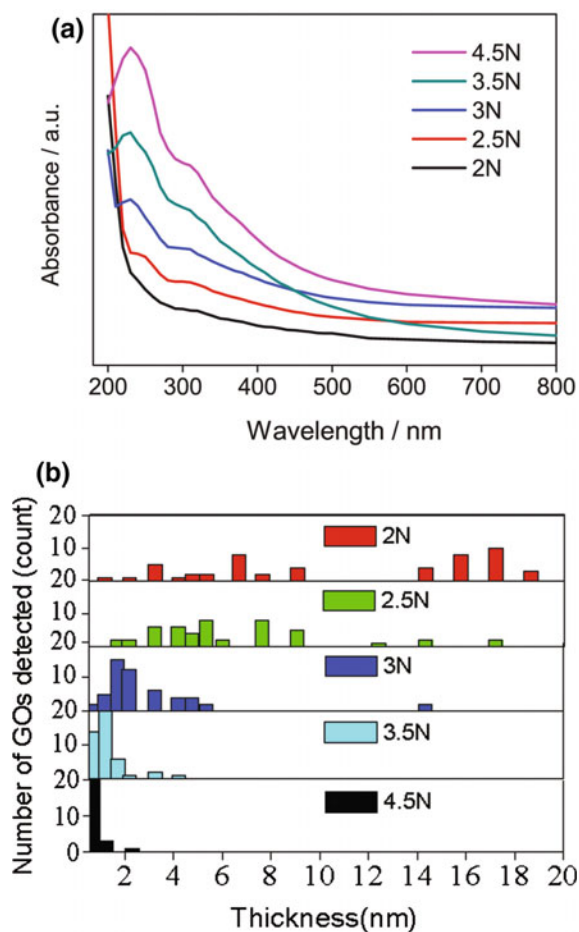
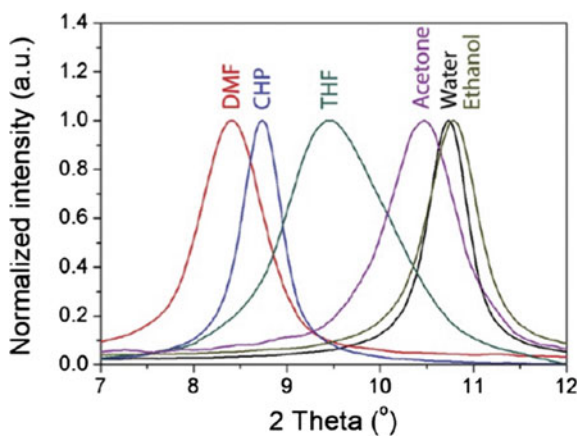


Fig. 2.8 XRD patterns from GO dispersion in DMF, CHP, THF, Acetone, water and ethanol solvent. Reprinted with permission from [24]. Copyright (2013) American Chemical Society



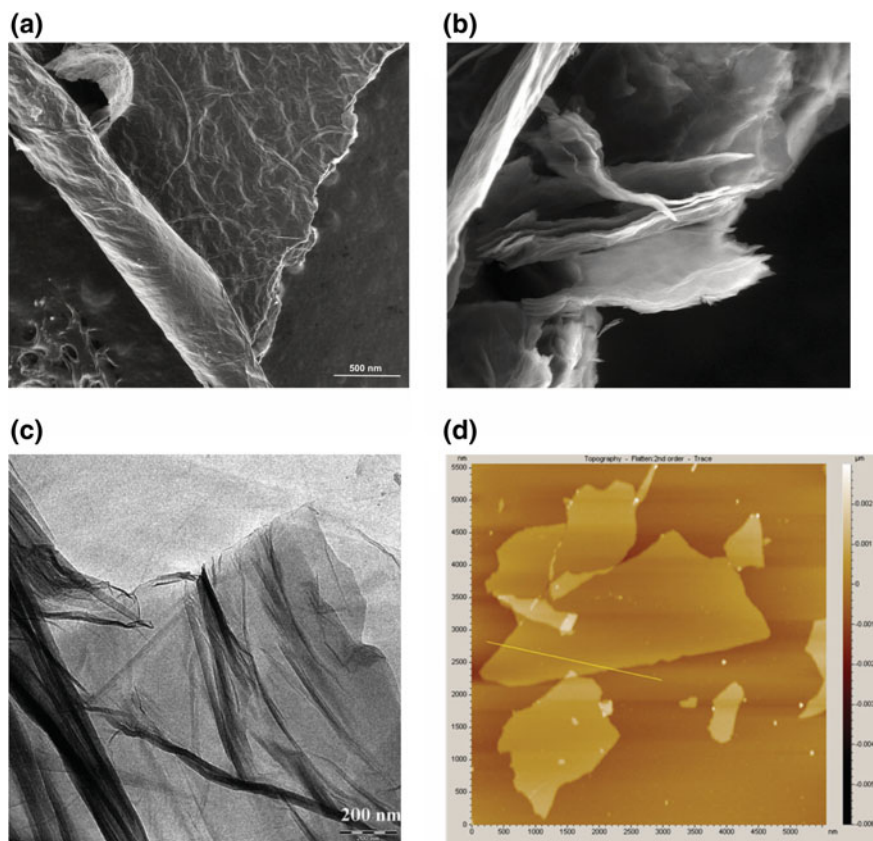


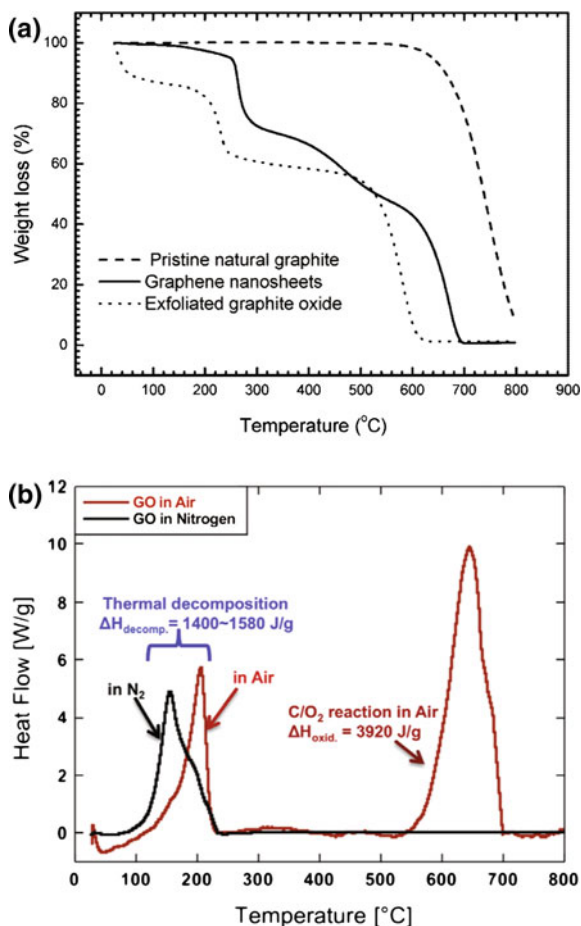
Fig. 2.9 SEM images of **a** layered structure of GO with rounded layer and **b** detail of packed GO structure. Representative TEM images of GO. **c** Reproduced from Ref. [2] with permission from the Royal Society of Chemistry. **d** AFM image of GO. Reprinted with permission from [50]. Copyright (2014) 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 ~ 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

Fig. 2.10 **a** DSC profiles for GO under air and N_2 atmosphere at 10 K min^{-1} . Reprinted with permission from [48]. Copyright (2008) American Chemical Society. **b** TGA profiles for graphite, graphene and graphene oxide in dry air. Reprinted from [37], Copyright (2013), with permission from Elsevier



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 $^{\circ}\text{C}$. 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 hydroxylated 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

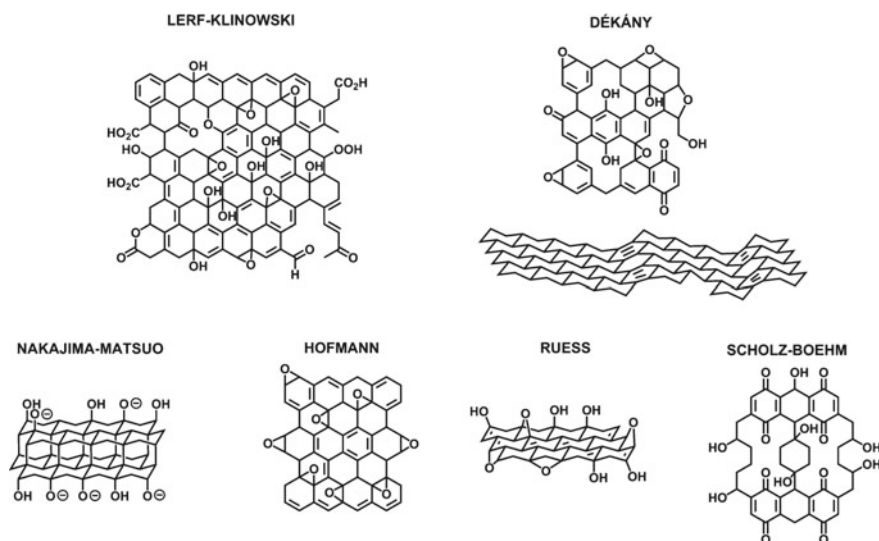


Fig. 2.11 Example of proposed graphene oxide structure. Reproduced from Ref. [13] with permission from The Royal Society of Chemistry

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 of 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.

References

1. Aboutalebi SH, Gudarzi MM, Zheng QB, Kim JK (2011) Spontaneous formation of liquid crystals in ultralarge graphene oxide dispersions. *Adv Funct Mater* 21(15):2978–2988
2. Aunkor MTH, Mahbubul IM, Saidur R, Metselaar HSC (2015) Deoxygenation of graphene oxide using household baking soda as a reducing agent: a green approach. *RSC Adv* 5(86):70461–70472
3. Bagri A, Mattevi C, Acik M, Chabal YJ, Chhowalla M, Shenoy VB (2010) Structural evolution during the reduction of chemically derived graphene oxide. *Nat Chem* 2(7):581–587
4. Bosch-Navarro C, Busolo F, Coronado E, Duan Y, Marti-Gastaldo C, Prima-Garcia H (2013) Influence of the covalent grafting of organic radicals to graphene on its magnetoresistance. *J*

- Mater Chem C 1(30):4590–9
5. Brodie BC (1859) On the atomic weight of graphite. *Phil Trans R Soc Lond* 149:249–259
 6. Chen D, Feng H, Li J (2012) Graphene oxide: preparation, functionalization, and electrochemical applications. *Chem Rev* 112(11):6027–6053
 7. Chen J, Li Y, Huang L, Li C, Shi G (2015) High-yield preparation of graphene oxide from small graphite flakes via an improved Hummers method with a simple purification process. *Carbon* 81:826–834
 8. Chen ZL, Kam FY, Goh RGS, Song J, Lim GK, Chua LL (2013) Influence of graphite source on chemical oxidative reactivity. *Chem Mater* 25(15):2944–2949
 9. Chua CK, Pumera M (2014) Chemical reduction of graphene oxide: a synthetic chemistry viewpoint. *Chem Soc Rev* 43(1):291–312
 10. Chung MG, Kim DH, Lee HM, Kim T, Choi JH, Dk S, Yoo JB, Hong SH, Kang TJ, Kim YH (2012) Highly sensitive NO₂ gas sensor based on ozone treated graphene. *Sens Actuators B Chem* 166–167:172–176
 11. Dimiev AM, Tour JM (2014) Mechanism of graphene oxide formation. *ACS Nano* 8(3):3060–3068
 12. Dreyer DR, Park S, Bielawski CW, Ruoff RS (2010) The chemistry of graphene oxide. *Chem Soc Rev* 39(1):228–240
 13. Dreyer DR, Todd AD, Bielawski CW (2014) Harnessing the chemistry of graphene oxide. *Chem Soc Rev* 43(15):5288–5301
 14. Fonseca AF, Liang T, Zhang D, Choudhary K, Sinnott SB (2016) Probing the accuracy of reactive and non-reactive force fields to describe physical and chemical properties of graphene-oxide. *Comput Mater Sci* 114:236–243
 15. Froning JP, Lazar P, Pykal M, Li Q, Dong M, Zboril R, Otyepka M (2017) Direct mapping of chemical oxidation of individual graphene sheets through dynamic force measurements at the nanoscale. *Nanoscale* 9(1):119–127
 16. Gao W (2015) Graphene oxide: reduction recipes, spectroscopy, and applications. Springer: New York
 17. Georgakilas V (2014) Functionalization of graphene. Wiley, New York
 18. Gilje S, Han S, Wang M, Wang KL, Kaner RB (2007) A chemical route to graphene for device applications. *Nano Lett* 7(11):3394–3398
 19. Guerrero-Contreras J, Caballero-Briones F (2015) Graphene oxide powders with different oxidation degree, prepared by synthesis variations of the Hummers method. *Mater Chem Phys* 153:209–220
 20. Hong Y, Wang Z, Jin X (2013) Sulfuric acid intercalated graphite oxide for graphene preparation. *Sci Rep* 3:132
 21. Hossain MZ, Johns JE, Bevan KH, Karmel HJ, Liang YT, Yoshimoto S, Mukai K, Koitaya T, Yoshinobu J, Kawai M, Lear AM, Kesmodel LL, Tait SL, Hersam MC (2012) Chemically homogeneous and thermally reversible oxidation of epitaxial graphene. *Nat Chem* 4(4):305–309
 22. Huh S, Park J, Kim YS, Kim KS, Hong BH, Nam JM (2011) UV/ozone-oxidized large-scale graphene platform with large chemical enhancement in surface-enhanced Raman scattering. *ACS Nano* 5(12):9799–9806
 23. Hummers WS, Offeman RE (1958) Preparation of graphitic oxide. *J Am Chem Soc* 80(6):1339–1339
 24. Jalili R, Aboutalebi SH, Esrafilzadeh D, Konstantinov K, Moulton SE, Razal JM, Wallace GG (2013) Organic solvent-based graphene oxide liquid crystals: a facile route toward the next generation of self-assembled layer-by-layer multifunctional 3D architectures. *ACS Nano* 7(5):3981–3990
 25. Jung I, Field DA, Clark NJ, Zhu Y, Yang D, Piner RD, Stankovich S, Dikin DA, Geisler H, Ventrice Jr CA, Ruoff RS (2009) Reduction kinetics of graphene oxide determined by electrical transport measurements and temperature programmed desorption. *J Phys Chem C* 113(43):18480–18486

26. Kovtyukhova NI, Ollivier PJ, Martin BR, Mallouk TE, Chizhik SA, Buzaneva EV, Gorchinskiy AD (1999) Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations. *Chem Mater* 11(3):771–778
27. Krishnamoorthy K, Veerapandian M, Yun K, Kim SJ (2013) The chemical and structural analysis of graphene oxide with different degrees of oxidation. *Carbon* 53:38–49
28. Kudin KN, Ozbas B, Schniepp HC, Prud'homme RK, Aksay IA, Car R (2008) Raman spectra of graphite oxide and functionalized graphene sheets. *Nano Lett* 8(1):36–41
29. Lai Q, Zhu S, Luo X, Zou M, Huang S (2012) Ultraviolet-visible spectroscopy of graphene oxides. *AIP Adv* 2(3):032146
30. Ma HL, Zhang HB, Hu QH, Li WJ, Jiang ZG, Yu ZZ, Dasari A (2012) Functionalization and reduction of graphene oxide with p-phenylene diamine for electrically conductive and thermally stable polystyrene composites. *ACS Appl Mater Interfaces* 4(4):1948–1953
31. Marcano DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun Z, Slesarev A, Alemany LB, Lu W, Tour JM (2010) Improved synthesis of graphene oxide. *ACS Nano* 4(8):4806–4814
32. Paci JT, Belytschko T, Schatz GC (2007) Computational studies of the structure, behavior upon heating, and mechanical properties of graphite oxide. *J Phys Chem C* 111(49):18099–18111
33. Pendolino F, Capurso G, Maddalena A, Lo Russo S (2014a) The structural change of graphene oxide in a methanol dispersion. *RSC Adv* 4(62):32,914
34. Pendolino F, Parisini E, Lo Russo S (2014b) Time-dependent structure and solubilization kinetics of graphene oxide in methanol and water dispersions. *J Phys Chem C* 118(48):28162–28169
35. Pendolino F, Armata N, Masullo T, Cuttitta A (2015) Temperature influence on the synthesis of pristine graphene oxide and graphite oxide. *Mater Chem Phys* 164:71–77
36. Peng L, Xu Z, Liu Z, Wei Y, Sun H, Li Z, Zhao X, Gao C (2015) An iron-based green approach to 1-h production of single-layer graphene oxide. *Nat Comms* 6:5716
37. Qiu Y, Collin F, Hurt RH, Külaots I (2016) Thermochemistry and kinetics of graphite oxide exothermic decomposition for safety in large-scale storage and processing. *Carbon* 96:20–28
38. Samarakoon DK, Wang XQ (2011) Twist-boat conformation in graphene oxides. *Nanoscale* 3(1):192–195
39. Schniepp HC, Li JL, McAllister MJ, Sai H, Herrera-Alonso M, Adamson DH, Prud'homme RK, Car R, Saville DA, Aksay IA (2006) Functionalized single graphene sheets derived from splitting graphite oxide. *J Phys Chem* 110(17):8535–8539
40. Scholz W, Boehm HP (1969) Untersuchungen am Graphitoxid. VI. Betrachtungen zur Struktur des Graphitoxids. *Z Anorg Allg Chem* 369(3–6):327–340
41. Shin HJ, Kim KK, Benayad A, Yoon SM, Park HK, Jung IS, Jin MH, Jeong HK, Kim JM, Choi JY, Lee YH (2009) Efficient reduction of graphite oxide by sodium borohydride and its effect on electrical conductance. *Adv Funct Mater* 19(12):1987–1992
42. Sk MA, Huang L, Chen P, Lim KH (2016) Controlling armchair and zigzag edges in oxidative cutting of graphene. *J Mater Chem C* 4(27):6539–6545
43. Stankovich S, Da D, Piner RD, Kohlhaas KA, Kleinhammes A, Jia Y, Wu Y, Nguyen ST, Ruoff RS (2007) Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* 45(7):1558–1565
44. Starodub E, Bartelt NC, McCarty KF (2010) Oxidation of graphene on metals. *J Phys Chem C* 114(11):5134–5140
45. Staudenmaier L (1898) Verfahren zur Darstellung der Graphitsäure. *Ber Dtsch Chem Ges* 31(2):1481–1487
46. Sun L, Fugetsu B (2013) Mass production of graphene oxide from expanded graphite. *Mater Lett* 109:207–210
47. Vinogradov NA, Schulte K, Ng ML, Mikkelsen A, Lundgren E, Mårtensson N, Preobrajenski AB (2011) Impact of atomic oxygen on the structure of graphene formed on Ir(111) and Pt(111). *J Phys Chem C* 115(19):9568–9577
48. Wang G, Yang J, Park J, Gou X, Wang B, Liu H, Yao J (2008) Facile synthesis and characterization of graphene nanosheets. *J Phys Chem C* 112(22):8192–8195

49. Yamamoto M, Einstein TL, Fuhrer MS, Cullen WG (2012) Charge inhomogeneity determines oxidative reactivity of graphene on substrates. *ACS Nano*
50. Yang H, Li H, Zhai J, Sun L, Yu H (2014) Simple synthesis of graphene oxide using ultrasonic cleaner from expanded graphite. *Ind Eng Chem Res* 53(46):17878–17883
51. You S, Luzan SM, Szabó T, Talyzin AV (2013) Effect of synthesis method on solvation and exfoliation of graphite oxide. *Carbon* 52:171–180
52. Zhang Y, Ma HL, Zhang Q, Peng J, Li J, Zhai M, Yu ZZ (2012) Facile synthesis of well-dispersed graphene by γ -ray induced reduction of graphene oxide. *J Mater Chem* 22(26):13064
53. Zhao J, Liu L, Li F (2015) Graphene oxide: physics and applications. *Springer Briefs in Physics*. Springer, Berlin

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