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Chemical Functionalization of Graphene Family Members

Abstract:
Thanks to their outstanding physicochemical properties, graphene and its derivatives are interesting nanomaterials with a high potential in several fields. Graphene, graphene oxide, and reduced graphene oxide, however, differ partially in their characteristics due to their diverse surface composition. Those differences influence the chemical reactivity of these materials. In the following chapter the reactivity and main functionalization reactions performed on graphene, graphene oxide, and reduced graphene oxide are discussed. A part is also dedicated to the main analytical techniques used for characterization of these materials. Functionalization of graphene and its derivatives is highly important to modulate their characteristics and design graphene-based conjugates with novel properties. Functionalization can be covalent by forming strong and stable bonds with the graphene surface, or non-covalent via π–π, electrostatic, hydrophobic, and/or van der Waals interactions. Both types of functionalization are currently exploited.

Keywords: Graphene, graphene oxide, reduced graphene oxide, covalent functionalization, non-covalent functionalization, characterization

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Nanomaterials are an important product of nanotechnologies, and carbon nanomaterials are part of this family. They are getting lots of attention from different fields due to their interesting characteristics. Often, to facilitate their employment carbon nanomaterials are modified through covalent or non-covalent functionalization. In this chapter we will focus on the functionalization of graphene and its derivatives, graphene oxide (GO) and reduced graphene oxide (rGO).

1 Graphene

Graphene is a nanomaterial made of sp^2-hybridized carbon atoms, one-atom thick in the form of a planar sheet. It is a building block of graphite and was isolated for the first time in 2004 by Novoselov et al. [1]. Earlier, it was theoretically hypothesized as a part of graphite in 1940's [2] but considered thermodynamically unstable under ambient conditions [3].

Graphene presents excellent electrical and mechanical characteristics [1, 4–8]; however, it tends to form stable agglomerates or even restack to form graphite [9]. The functionalization of graphene can prevent this phenomenon because of strong polar–polar interactions of hydrophilic groups or bulky size of hydrophobic functions [10].

Due to its delocalized π-bonding system, graphene is chemically inert. This stable system limits graphene from covalent addition, but it makes complexation reaction possible through π–π, H–π, cation–π, anion–π and metal–π interactions. Compared to ideal graphene, graphene material produced until now contains vacancies, edges, curvatures and chemical impurities. Edge and vacancies in the basal plane of graphene are very reactive. The curvature, due to the occurrence of defects, diminishes instead of the overlap of the p_z atomic orbital. Thus, the reactivity of the carbon atoms is increased [11, 12]. Damages can be introduced in graphene also by the sonication procedure used to disperse it. Thus, it is mandatory not to sonicate it for a long time to preserve the integrity of its structure. To diminish the sonication time it is necessary to use solvents in which graphene is easily dispersible [13]. The defects are mainly oxidized carbon atoms at the edges of the layer. Ultrasound waves break the structure of graphene and form graphitic carbon fragments of variable sizes. This method is used to give the necessary energy to exfoliate graphite and let the solvent intercalate between the layers. Solvent exhibiting surface tension close to 40–50 mJ m^{-2} should be chosen, for example, benzyl benzoate, *N*,*N*-dimethylacetamide, γ-butyrolactone, 1,3-dimethyl-2-imidazolidinone, *N*,*N*-dimethylformamide or *N*-methyl-2-pyrrolidone [14, 15]. It is possible to decrease the damage introduced by sonication also by the use of reducing agents that prevent the formation of oxidizing radicals such as ferrocene aldehyde or tiopronin [11].

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Graphene can be functionalized on the two faces [16], at the edges and at the defect sides. Compared to carbon nanotubes (CNTs), graphene has a higher exposed surface but is less reactive because there is no bond tension caused by the curvature like on CNTs. Anyway, most of the reactions that were used on CNTs have also been applied to graphene.

Graphene can be covalently or non-covalently functionalized. In the first case, there is the formation of a stable covalent bond; in the second case weak bonds like π–π interactions, hydrogen bonds and van der Waals interactions are formed. During covalent functionalization, defects are introduced and consequently there is a partial loss of the electrical conductivity of graphene; meanwhile, in non-covalent functionalization the sp^2 structure is preserved.

1.1 Covalent Functionalization Reactions

Covalent surface modification of graphene induces rehybridization of one or more sp^2 carbon atoms of the aromatic structure, causing the loss of electronic conjugation and a strain in the plane. Indeed, because of the change of hybridization the strictly constrained sp^2 carbon atoms have to protrude out of the plane in a tetrahedral sp^3 geometry. For this reason, edge carbon atoms react easier in covalent addition reaction [12]. The covalent organic functionalization is useful to increase the dispersibility of this material in both organic solvents and water and to combine the characteristics of graphene with other functional materials such as chromophores or polymers [17, 18]. Functionalization can happen on the surface, at the edges and at the defect sites. The defects are caused by the chemical methods used to obtain graphene and include damage in the carbon lattice, structural imperfections, adatoms and solvent molecules randomly adsorbed [13, 19]. The covalent modification can be classified in free radical addition, atomic radical addition, nucleophilic addition, cycloaddition and electrophilic substitution reactions.

1.1.1 Free Radical Addition Reactions

Free radicals are highly reactive organic species that interact with the aromatic structure of graphene to form covalent bonds. This functionalization has been achieved either by thermal or by photochemical treatments. However, by employing high-energy reactants there are also unintended side reactions or deficiency in homogeneity in the functionalization reaction [20]. The most common radical addition reaction is performed using aryl diazonium salts. Other reactions include addition of peroxides, the Bergman cyclization [21] and the Kolbe electrosynthesis [14, 22]. In this section we will focus on the reaction with aryl diazonium salts.

The addition of aryl diazonium salts on graphene was first accomplished by Tour and coworkers [23]. In this reaction, the aryl diazonium ion becomes an aryl radical after the elimination of nitrogen (Figure 1). It has been postulated that the radical aryl moiety adds to sp^2 surface of graphene which donates an electron [14]. However, this reaction can lead to organic radicals that covalently react with graphene but also are susceptible to self-polymerization [20]. This reaction is strongly dependent on the number of graphene layers. It has been found by Strano et al. that single graphene sheets have a 10 times higher reactivity compared to bi- or multilayer graphene [24]. Meanwhile, the decrease in conductivity due to the disruption of the aromatic system can be controlled. It has been discovered by Tour and coworkers that the decrease in conductivity is related to the duration of the reaction [25].

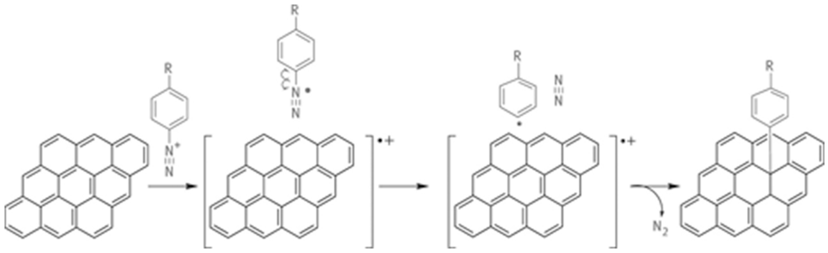

Figure 1: Mechanism of the reaction with aryl diazonium salts.

Aryl diazonium salts can have in the para position different functional groups, such as chlorine, bromine, iodine, nitro, methoxy, carboxy and cyano groups, making this reaction highly versatile [26].

This reaction, for example, has been used to attach chlorophenyl groups to investigate the antimicrobial activity of the prepared graphene product. Graphene functionalized with chlorophenyl groups has been found to be more than twice effective as antimicrobial agent than pristine graphene [27].

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1.1.2 Nucleophilic Addition Reactions

In a nucleophilic addition graphene acts as an electron acceptor. An example is the reaction between poly-9,9′-dihexyfluorene carbazole and graphene [28, 29]. The anionic moiety is formed by using a base, leading to the generation of nitrogen anions on carbazole (Figure 2). Subsequently, the nitrogen anion reacts on the surface of graphene with the creation of a covalent bond.

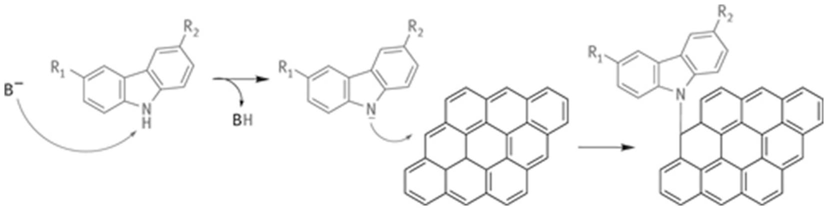

Figure 2: Mechanism of the nucleophilic addition reaction with carbazole.

1.1.3 Cycloaddition Reactions

In the cycloaddition reactions the electrons move in a circular way that includes bond cleavage and bond formation processes at the same time without the formation of anions or cations as intermediates. The following cycloadditions have been performed on graphene: [2+1], [2+2], [3+2] and [4+2]. The most famous cycloaddition is the 1,3-dipolar cycloaddition [30], which is a [3+2] cycloaddition reaction [14]. Concerning the other cycloaddition reactions, we can mention the following: (i) [2+1] cycloadditions include reactions with carbenes [31], the Bingel reaction and reactions with nitrenes [32] to form cyclopropane or aziridine adducts, respectively; (ii) [2+2] cycloaddition is the reaction with an aryne or a benzyne to form a four-carbon atoms cycle [33] and (iii) [4+2] cycloaddition is the Diels–Alder cycloaddition [34, 35] between a diene (electron rich) and a dienophile (electron deficient). Graphene is really versatile in the Diels–Alder reaction because it can act as both the diene and the dienophile. On graphene, side reactions often occur. For this reason it is difficult to control the composition of the surface modification. For example nitrenes and carbenes can react with solvents or among themselves as well [36].

In this section we will focus on the 1,3 dipolar cycloaddition reaction and the Bingel reaction. In the 1,3-dipolar cycloaddition reaction the active component is an azomethine ylide, a very reactive intermediate, obtained from a decarboxylation reaction of an α-amino acid and a carbonyl species performed under heating conditions (Figure 3).

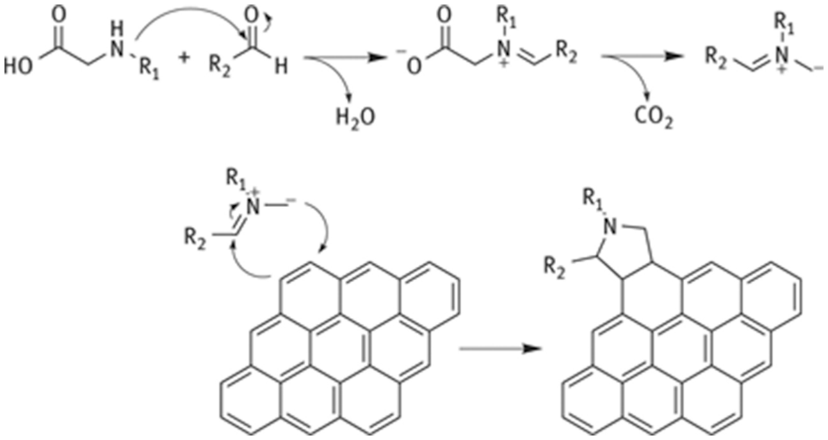

Figure 3: 1,3-dipolar cycloaddition reaction.

Trapalis and coworkers [37] were the first to perform this reaction on graphene. Meanwhile, Prato and coworkers have discovered that this reaction occurs on both the edges and the basal plane [30]. In this reaction pyrrolidine rings are formed on the surface of graphene. The 1,3-dipolar cycloaddition reaction is very versatile [11]. This is also important because it is possible to choose between several aldehydes or substituted α-amino acids as precursors, yielding in this way a large range of functional groups bound to the graphene surface [17].

With this reaction porphyrin moieties such as tetraphenylporphyrin and palladium tetraphenylporphyrin have been added onto graphene by Feringa and coworkers [38]. The quenching of fluorescence and the reduced

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excited state lifetimes suggest that there is a photoinduced energy/electron transfer between graphene and the porphyrin units.

The Bingel reaction is one of the most useful reactions for the functionalization of carbon nanomaterials, including graphene, because of the mild conditions. The reaction involves a halide derivative of a malonate ester moiety in the presence of a base (Figure 4). The halide-malonate moiety is usually generated *in situ*. The base subtracts a proton from this derivative giving an enolate that attacks a C=C bond of graphene. The carbanion formed undergoes a nucleophilic substitution with the displacement of the halide to form a cyclopropane ring [14]. Through this reaction a tetrathiafulvalene moiety has been attached onto graphene by Economopoulos et al. [39]. Tetrathiafulvalene and its derivatives are used as biosensors for sugars like fructose, and it has been demonstrated that the association with graphene enhances the sensitivity of the device [40, 41].

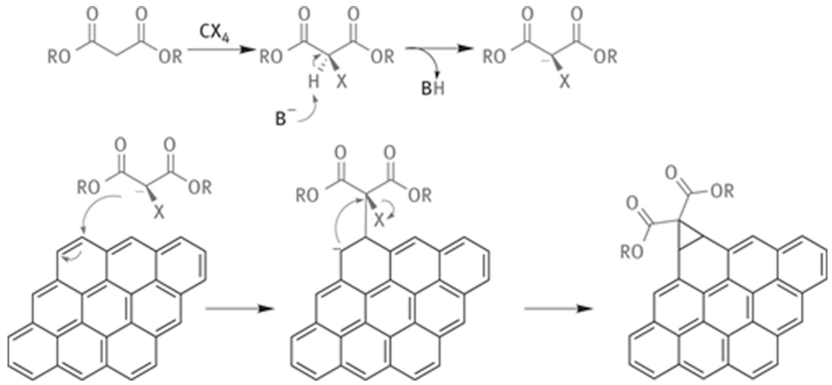

Figure 4: Mechanism of the Bingel reaction.

1.1.4 Reaction with Atomic Radicals

If we compare the reactions performed with organic free radicals with those performed with atomic species like hydrogen, fluorine and oxygen (Figure 5), in the last cases there is a minimized possibility of side reactions. Therefore, the functionalization of graphene is uniform and homogeneous [16, 20].

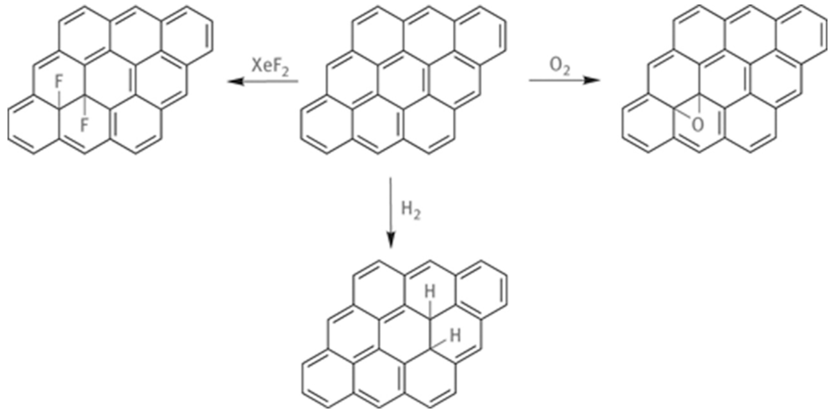

Figure 5: Mechanism of the reactions performed with gas phase atomic radicals.

In the hydrogenation, after the attachment of the first atomic hydrogen, the lattice is deformed and can react easier to form the second C–H bond. The total hydrogenated form of graphene is called graphane. The hydrogenation of graphene can be performed by exposition to hydrogen-based plasmas [42].

The fluorination of graphene is similar to the hydrogenation because fluorine also forms a single bond to carbon but with an increased binding strength. As in the case of hydrogenation, fluorination leads to high level of functionalization [43]. Fluorographene is expected to be electrically insulating. There are three main methods to produce it: (i) by exposition to XeF_2 [44], (ii) by etching using fluorinated compound [45] and (iii) by liquid phase exfoliation of bulk graphite fluoride [20, 46].

Oxygenated graphene obtained through the common Hummers' method [47, 48] is highly inhomogeneous (Section 2). In the radical addition of atomic oxygen, oxygen atoms are expected to add on graphene forming epoxides. The formation of epoxide groups has been obtained by exposing graphene at oxygen plasmas and atomic oxygen beams [49, 50].

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1.1.5 Electrophilic Substitution Reactions

This category of reactions allows to functionalize graphene owing to its electron-rich nature. Examples of substitution reactions are the Friedel–Crafts acylation [51] and hydrogen–lithium exchange [52]. The reactivity of metallated aromatics is higher than simple aromatic moieties. In the hydrogen–lithium exchange there is first the deprotonation and/or the carbometallation of graphene by BuLi (Figure 6). The lithium graphene derivative subsequently reacts with an electrophile. Once the electrophile added, the lithium graphene derivative reacts immediately with the formation of a covalent bond [14, 52].

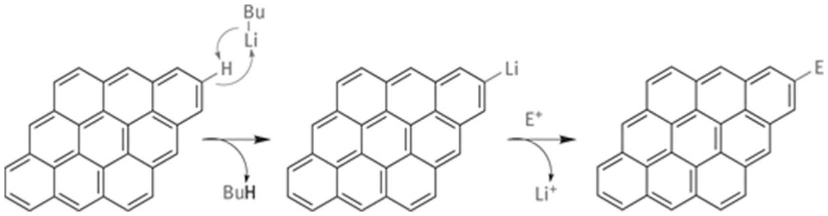

Figure 6: Mechanism of the reaction with BuLi.

The Friedel–Crafts acylation allows to introduce ketone moieties. The reactive intermediate is an acyl cation formed in the presence of a Lewis acid (Figure 7). Brominated flame-retardant high-density polyethylene composites containing graphene nanoplatelets were obtained using this reaction [53].

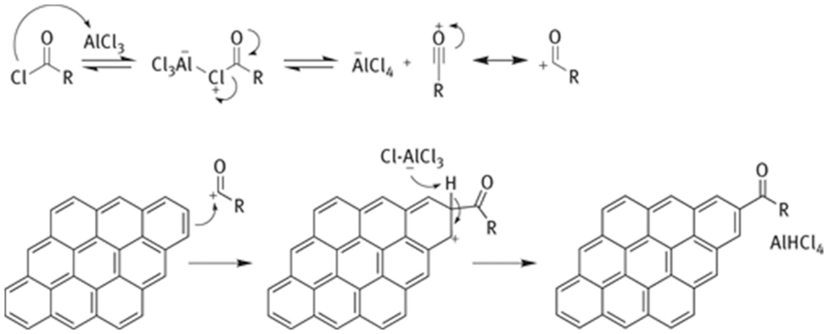

Figure 7: Mechanism of the Friedel–Crafts reaction.

1.2 Non-covalent Functionalization Reactions

Graphene has a high specific surface area that helps the physical adsorption of molecules via non-covalent interactions such as hydrophobic, van der Waals and electrostatic [54]. This way of functionalization is an interesting method to immobilize molecules without disturbing the electronic network in an easy and reversible way [55]. The non-covalent functionalization is of fundamental importance for the immobilization of proteins, enzymes, drugs and DNA, mostly in the context of devices as a little modification in the electronic characteristics of the π system can lead to a total change in the structure and properties of the system [17, 56, 57].

π-Complexes based on graphene have been extensively investigated. The interactions have been classified in non-polar gas–π, H–π, π–π, cation–π and anion–π interactions [58, 59]. The strength of these interactions is a combination of different forces that include electrostatic, dispersive and inductive interactions as attractive forces, and exchange repulsion as repulsive forces.

Non-covalently functionalized graphene can be produced from graphite by exfoliation using different types of surfactants, such as sodium cholate [60, 61], cetyltrimethylammonium bromide [62], polyvinylpyrrolidone [63], triphenylene [64] or pyrene derivatives [65]. However, in addition to single-layer graphene a big quantity of few-layer graphene or dispersed graphite is also obtained. Layers with a diameter of a few 100 nm are produced by the use of coronene carboxylate [66]. Instead, to produce larger flakes of graphene it is possible to employ perylene derivatives (Figure 8) [67, 68]. Bai et al. [69] dispersed graphene with sulfonated polyaniline and obtained non-covalent functionalized graphene nanoplatelets employed to produce water-soluble composites.

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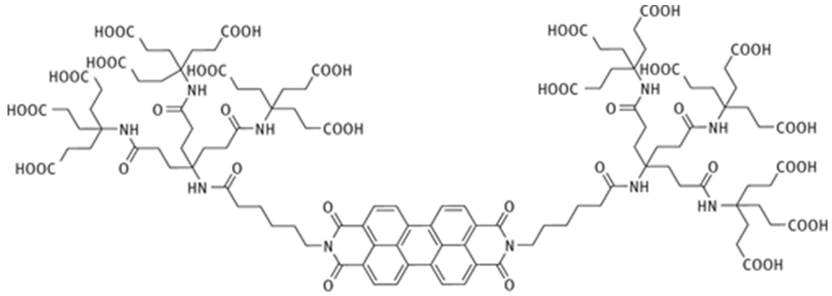

Figure 8: Example of a perylene derivative.

Beside graphene stabilization in solution, non-covalent functionalization can be also exploited to immobilize molecules like epirubicin on graphene for targeted chemotherapy and photothermal therapy [70]. Another interesting approach was proposed by Lee et al. which prepared a blood-compatible graphene/heparin conjugate through non-covalent functionalization [71].

2 Graphene oxide

GO is commonly obtained through an oxidative exfoliation treatment of graphite. The flakes tend to be predominantly monolayers. This material is made of a single graphitic layer with aromatic and oxygenated aliphatic regions randomly distributed.

This oxidized form of graphene presents different reactive oxygen-bearing functional groups, such as hydroxyl functions and epoxide groups on the basal plane, while carboxyl, carbonyl, phenol, lactone and quinone groups are mainly localized at the edges. The oxygen composition of GO is still debated, in particular regarding the presence or not of carboxylic acids. There are different models in literature [72]. The most recognized is the Lerf–Klinowski model [73], in which GO presents epoxide and hydroxyl groups in the whole structure and carboxylic acids at the edges (Figure 9). One important aspect to be considered is that the surface composition of GO is strongly related to the synthesis conditions used to produce it. The presence of polar oxygen-containing species in GO makes it less hydrophobic than pristine graphene. Thus, GO is more dispersible and stable than graphene in water. Thanks to its dispersibility in water, graphene materials have already found applications in the biomedical field for biosensing [74], disease diagnosis [75], cancer targeting [76], photothermal therapy [77], and as antibacterial [78] and antiviral materials [79]. However, GO is characterized by a large quantity of structural defects that can affect its physical properties. On the other hand, the presence of oxygen-containing groups allows further functionalization. The major issue with GO is the disruption of the π-network. A reductive treatment of GO induces the removal of the functional groups and rehybridization of the sp^3 carbon atoms to sp^2, partially restoring aromaticity. GO has been often employed as a starting material for the synthesis of graphene.

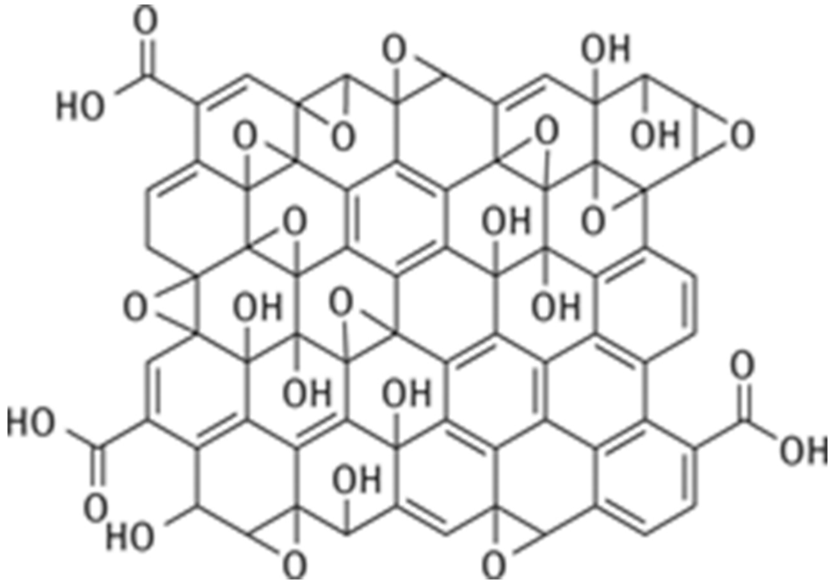

Figure 9: Schematic representation of GO based on Lerf–Klinowski model.

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Functionalization of GO can be either covalent or non-covalent. Covalent functionalization can be done on both the sp^2-hybridized areas of GO and the oxygenated functional groups present on its surface. Meanwhile, non-covalent functionalization occurs mainly by taking advantage of the aromatic portions through hydrophobic weak interactions.

2.1 Covalent Functionalization Reactions

Thanks to the presence of different types of oxygenated groups on GO, such as hydroxyls, epoxides and carboxylic acids, there are many possibilities for derivatization of GO. It is difficult to compare the reactivity of the oxygenated functions of GO with the reactivity of graphene. But, due to the high amount of defects present in GO, we can consider this material more reactive. However, because of the presence of many different functional groups, there is a high risk of secondary reactions. Moreover, the functionalization of GO has to be performed in mild conditions because of the instability of this material at high temperature.

The reactions performed on the sp^2-hybridized portions of GO are mostly the same already mentioned for graphene (see Section 1.1) as for example the free radical addition with aryl diazonium salts [80] or the hydrogen lithium exchange. A combination of BuLi and a brominated derivative has been used to functionalize GO, leading to the concomitant alkylation, etherification and esterification (Figure 10) [81].

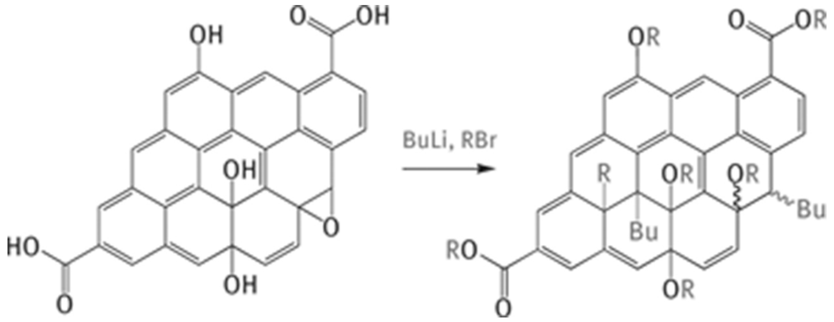

Figure 10: Reaction with BuLi. The GO model shown is simplified for clarity reasons.

The risk of side reaction during the functionalization of the oxygenated groups on the surface of GO is very high.

The functionalization of GO can be performed by derivatization of the different functional groups present on its surface. But, due to the elevated number of groups, it is difficult to obtain a good degree of selectivity.

2.1.1 Functionalization of Hydroxyl Groups

The hydroxyl groups are mainly located on the core surface of the oxidized graphene layer. They can undergo silanization [82] and etherification [83] reactions. The silanization reaction allows to functionalize the hydroxyl groups on the surface of GO. Indeed, R–O–Si bonds in silane are very reactive toward protic groups. For example, the functionalization of GO with *N*-[(3-trimethoxysilyl)propyl]ethylenediamine triacetic acid has been performed to prepare an antimicrobial system. This showed a higher antimicrobial activity compared to GO alone, which could be due to the synergic antimicrobial properties of graphene and ethylenediamine triacetic acid moiety [84]. It is believed that the silanization is a two-step reaction (Figure 11). There is first the hydrolysis of the trialkoxy groups of the silane and then the reaction between the Si–OH groups and the hydroxyl groups of GO forming a Si–O–C bond. This reaction has been done also under microwave irradiation. This procedure permits to fulfill a one-step functionalization of GO under mild conditions in a few minutes.

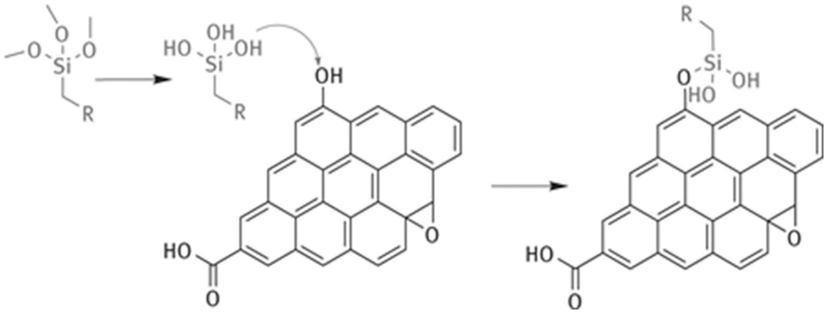

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Figure 11: Mechanism of the silanization reaction.

The Johnson–Claisen rearrangement is a modified Claisen reaction in which an allylic alcohol with an orthoester is used instead of the allyl vinyl ether. On GO only the hydroxyl functions that are allylic alcohols are subjected to this reaction. Therefore, not all hydroxyl groups present on the surface of GO will be functionalized. In this reaction there is first the reaction with the triethyl orthoacetate to give an ester, and then the rearrangement and the formation of a C–C bond with the graphitic surface (Figure 12) [85].

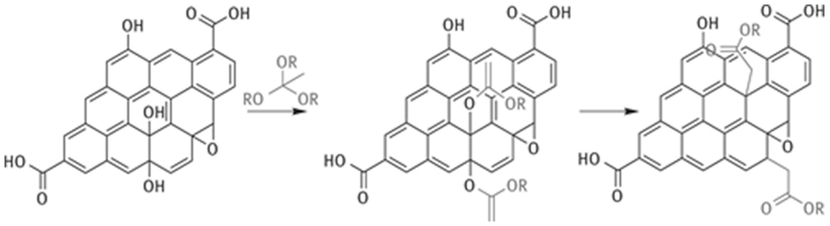

Figure 12: Mechanism of the Johnson–Claisen rearrangement.

2.1.2 Functionalization of Carboxylic Acids

The carboxylic acids of GO are located mainly at the edges. These functional groups can react with amines to form amides or with alcohols and phenols to form esters. The amidation reaction on the carboxylic acid groups of GO can be performed in harsh or mild conditions (Figure 13). In the first case the carboxylic acid is activated to form an acyl chloride using thionyl or oxalyl chloride. Then, the amino derivative is added to form the amide. In the second case, coupling agents are employed, like *N,N′*-dicyclohexylcarbodiimide or 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and hydroxybenzotriazole. However, thionyl or oxalyl chlorides are not selective for the carboxylic acid groups as they react with the hydroxyl groups too, causing side reactions. Various amino chains have been attached onto GO [86–89]. For example, Xu et al. prepared a porphyrin-graphene nanohybrid [86].

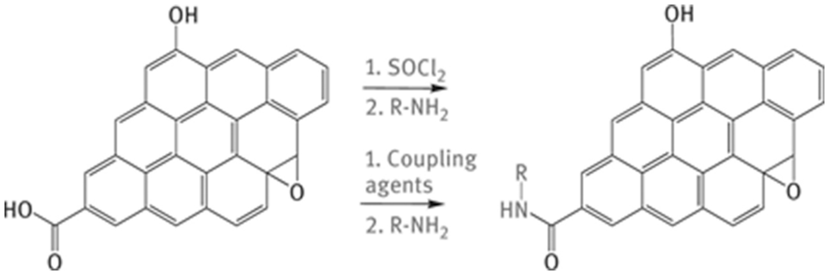

Figure 13: Mechanism of the amidation reaction. In this scheme the side reaction, opening of the epoxide, is not shown.

We would like to highlight that, once we add an amino chain, an important side reaction can happen due to the reaction with the epoxide groups, with a consequent opening of the ring and covalent introduction of the amino chain forming a secondary amine bond (see Section 2.1.3 about nucleophilic addition on epoxides). The amidation reaction has often been used to obtain biocompatible GO by introducing polymers like polyethyleneglycol [90], dextran [91] and chitosan [92].

The esterification reaction is another way to functionalize the carboxylic acids on the surface of GO. As in the case of amidation, thionyl (or oxalyl) chloride can be employed to obtain the acyl chlorides. Then, a base has to be used to deprotonate the alcohol, resulting in the formation of an ester bond. Meanwhile, if coupling agents such as EDC and 4-dimethylaminopyridine (DMAP) are instead utilized, a base is not necessary. The conditions using EDC/DMAP are commonly known as the Steglich esterification. The Steglich conditions were first applied on graphene by Mei et al. to obtain a double functionalized GO [93]. The activation of the carboxylic acids via the formation of acyl chlorides has been used to graft a poly(3-hexylthiophene) molecule, to design heterojunction photovoltaic devices [94].

2.1.3 Functionalization of Epoxides

The epoxides are mainly located on the basal plane of GO. The epoxy ring can be functionalized with amine-terminated molecules or sodium azide through a nucleophilic ring-opening reaction. The opening of the epoxy

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ring is mainly performed with amino moieties (Figure 14). Thanks to this nucleophilic addition reaction, chromophores and polymers have been introduced on GO. For example poly-*L*-lysine has been grafted to enhance the dispersibility of GO in water and its biocompatibility [95].

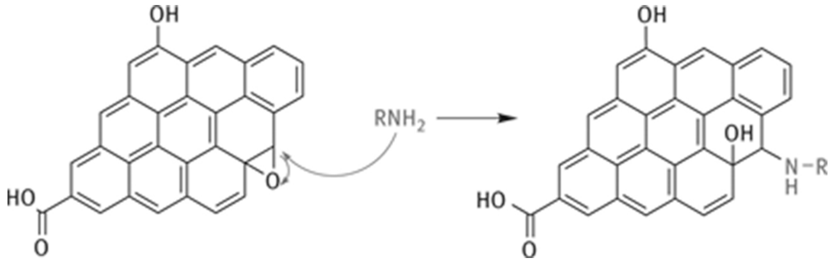

Figure 14: Mechanism of the opening of epoxide with a nucleophile.

2.1.4 Reaction with Isocyanate

Often, due to the high amount of functional groups on the surface of GO, the reagents can interact with more than one functional groups, as it is the case for amidation reactions. Organic isocyanate derivatives can react with both carboxyl and hydroxyl groups of GO with the generation of carbamates and amides (Figure 15) [96, 97]. The addition of isocyanate compounds has been used in various GO derivatives, in particular to get a pillared lamellar hybrid porous material [98].

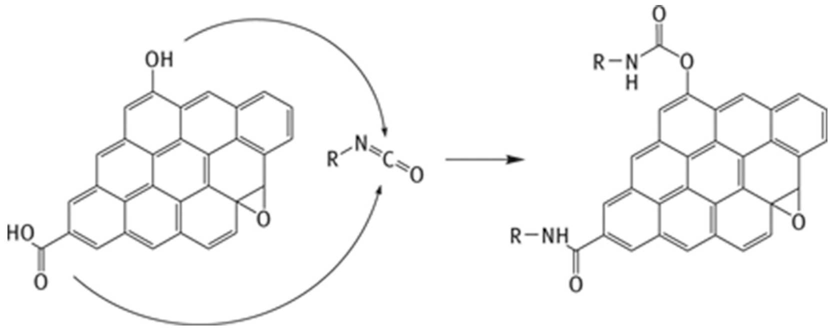

Figure 15: Mechanism of the reaction with isocyanate.

2.2 Non-covalent Functionalization Reactions

The non-covalent functionalization of GO occurs through π–π, electrostatic binding, H-bonding, van der Waals, H–π, cation–π and anion–π interactions [99–102]. Non-covalent interactions are usually formed with surfactant molecules or amphiphilic polymers. For example, anticancer drugs were adsorbed onto PEGylated GO nanocarrier [90]. An electrochemical supercapacitor was produced by non-covalent functionalization of GO with sulfanilic acid azocromotrop and consecutive reduction of GO [103].

3 Reduced GO

The procedure to produce graphene is expensive, the production yields are low and the graphene has the tendency to reaggregate. For this reason, the research in this field in the last years faced a fast raise to develop methods to obtain cheaper graphene at the industrial scale. Thus, the easiest way to produce graphene is through the oxidation and exfoliation of graphite, followed by the reduction of the resulting GO into graphene [104]. Nevertheless, rGO is constituted of graphene layers that contain a higher number of defects in the basal plane (e.g., holes), compared to graphene (Figure 16) [68]. A complete reduction of GO to graphene has not been achieved yet [17]. This material can be obtained starting from GO with different methods: (i) thermal reduction, (ii) chemical reduction and (iii) electrochemical reduction [105–107].

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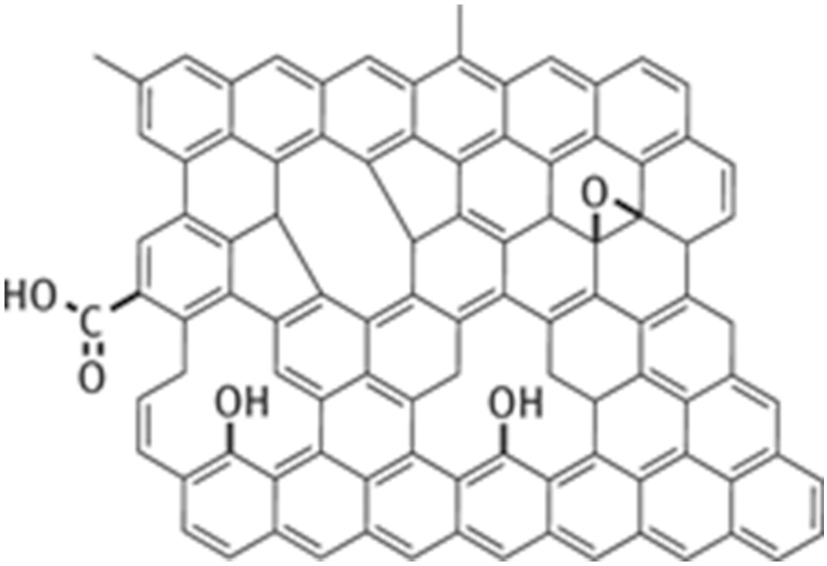

Figure 16: Molecular structure of rGO.

Through heat treatment at different temperatures or chemical reduction, not only water but also carbonaceous groups like CO_2 and CO are removed, causing the formation of defects. However, thanks to theoretical and experimental studies, it has been concluded that the elimination of carbonaceous groups is temperature specific. Depending on the temperature there are transformations of various functional groups, starting from the epoxides and carboxylic acids, to thermodynamically stable hydroxyl and carbonyl groups [108, 109]. Like graphene and GO, rGO can also be covalently and non-covalently functionalized. Indeed, rGO presents characteristics of both materials. It is prevalently aromatic like graphene, but it is more reactive due to the high amount of defects and the presence of remaining oxygen-bearing functional groups.

3.1 Covalent Functionalization

Covalent functionalization can happen on both the aromatic structure and the oxygen-containing groups. However, rGO has a lower amount of oxygenated functions. In addition, the quantity of oxygenated functional groups depends on the reduction conditions. Thus, it is necessary to assess which functions are present and to which extent. Anyway, rGO is mainly functionalized on its aromatic surface. All covalent reactions already mentioned for graphene can be applied on rGO (see Section 1.1). For example, rGO has already been functionalized with phenyldiazonium derivatives [110, 111] and through carbene addition (Figure 17) [112].

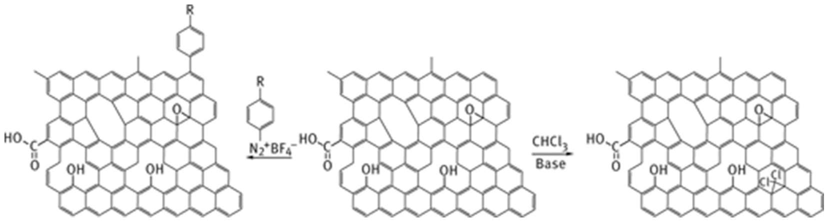

Figure 17: Aryl diazonium salt radical addition and carbene addition reactions on rGO (Possible side reactions are not shown).

As already mentioned the covalent functionalization of the oxygenated functional groups depends on the type of the groups that are present on the surface. Considering that the main groups found on rGO are the hydroxyls, the functionalization reactions are mainly performed on these functions [108, 109].

The functionalization reactions that can be applied have been already mentioned in the section about the covalent functionalization of the oxygenated groups on the surface of GO (Section 2.1). In a rGO sample with residual oxygen-bearing species on the surface, an amine linker was introduced through nucleophilic opening of the epoxide ring [113].

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3.2 Non-covalent Functionalization Reactions

As for GO, rGO can be non-covalently functionalized with different types of polymers and small molecules through π–π stacking or van der Waals interactions [114]. Shen et al. decorated rGO with polystyrene–polyacrylamide copolymer to obtain an amphiphilic graphene that can be dispersed in polar and non-polar solvents [115].

4 Characterization of Graphene Family Members

There are many challenges in the nanotechnology field on the identification of the products. A precise assessment of their structure is of fundamental importance. Different characterization techniques for the identification of graphene, GO, rGO and derivatives exist. In this section the UV-visible spectroscopy, Fourier transform infrared (FTIR) spectroscopy, atomic force microscopy, transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and the thermogravimetric analysis (TGA) will be discussed in detail.

4.1 UV-Visible Spectroscopy

The UV-visible spectroscopy does not give much information on graphene materials. For GO a peak around 224 nm is due to the π–π* transitions of C=C bonds; meanwhile, a shoulder at 300 nm is attributed to the n–π* transition of C=O bonds (Figure 18). Through this technique it is also possible to estimate the number of layers of graphene because it is related to the transparency of the sample [54, 116].

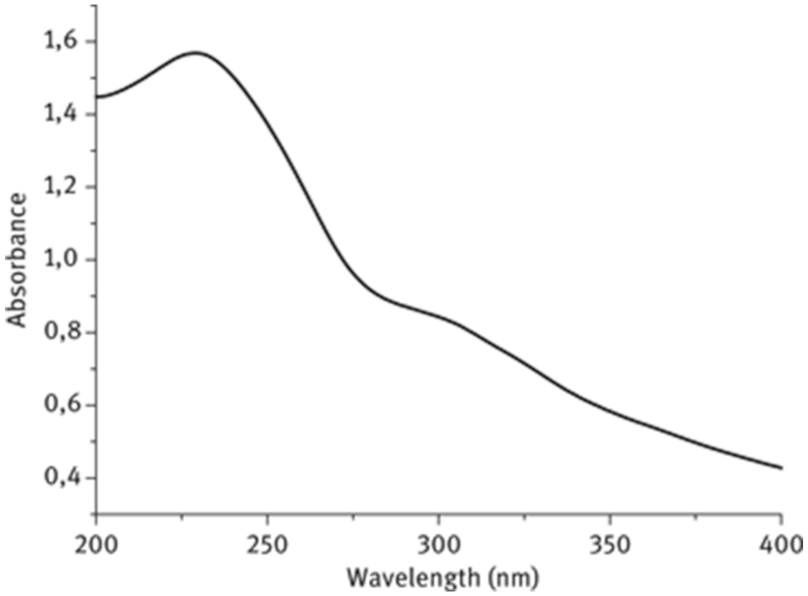

Figure 18: UV spectrum of GO.

4.2 Fourier transform infrared Spectroscopy

The FTIR spectroscopy is used to determine the functional groups of a molecule. While no significant peaks were found in graphene, for GO there are the characteristic peaks of the oxygenated functional groups (Figure 19). However, GO has a high humidity content due to the presence of oxygenated species. The adsorbed water is difficult to eliminate through thermal treatment because of GO thermal instability. For this reason, it is also possible to detect in GO spectra the strong signals of water. In the spectrum of GO, we can identify the following stretchings: the hydroxyl group and the adsorbed water at 3,800–2,200 cm^{-1}, the carbonyl group at 1,714 cm^{-1}, the vibration of the trapped water or of oxygen surface compounds and the skeletal vibration of the sp^2 carbon atoms at 1,620 cm^{-1}, the C–O groups at 1,063 cm^{-1}, and the epoxy and ether functionalities at 1,266 cm^{-1} [116–118].

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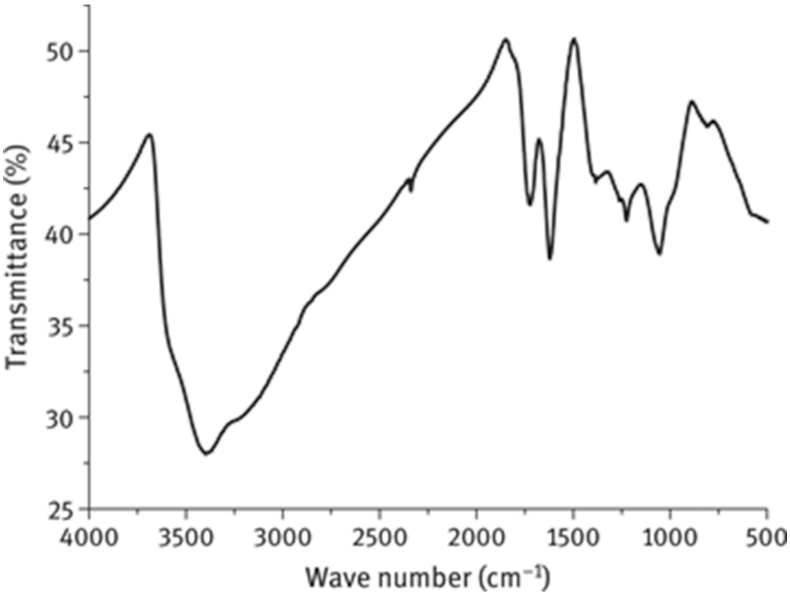

Figure 19: FT-IR spectrum of GO.

4.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is a high-resolution method used to visualize the surface topology of the materials in three-dimensional detail at the nanometer scale (Figure 20). In this technique a tip gathers the surface of the material to scan the surface. It is possible, through this method, to determine the lateral size, the number of layers and the thickness of graphene and GO. In GO, due to the presence of oxygen groups, the distance between layers is increased to 0.7 nm, almost two times more compared to graphene [117].

Figure 20: AFM image of GO on the top and its high profile on the bottom.

4.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) allows to observe graphene samples and assess their size, thickness, morphology and purity. By analyzing an elevated number of images, it is possible to do flake thickness statistics of graphene materials (Figure 21). Meanwhile, the transparency of graphene sheets gives indications about the thickness of the graphene samples. More precisely, looking at the edges it is possible to count the number of layers [54].

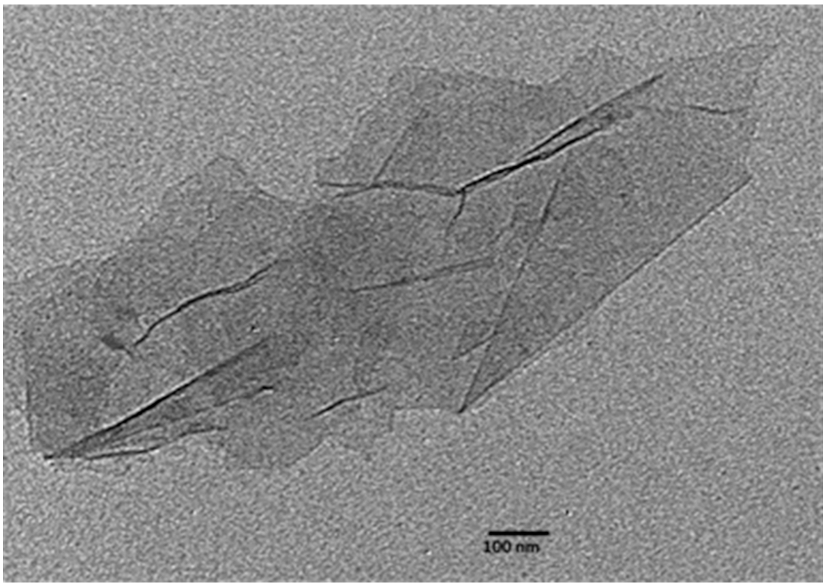

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Figure 21: TEM image of GO.

4.5 Raman spectroscopy

Raman spectroscopy is a technique used for sample identification and quantification that gives information about the molecular vibrations. For carbon nanomaterials it is used to define the disorder and the order in the carbon skeleton of sp^2- and sp^3- hybridized structures. Graphene displays three main peaks at 1,350 cm^{-1} (D band), at 1,580 cm^{-1} (G band) and at 2,700 cm^{-1} (2D band) (Figure 22). The G band is caused by planar vibrations of carbon atoms. The D band is due to the amount of defects present in the material. The 2D band gives instead information on the number of layers of the graphite material. In the case of graphite this band has a width of around 45–60 cm^{-1}; meanwhile, for single-layer graphene it is around 24 cm^{-1}.

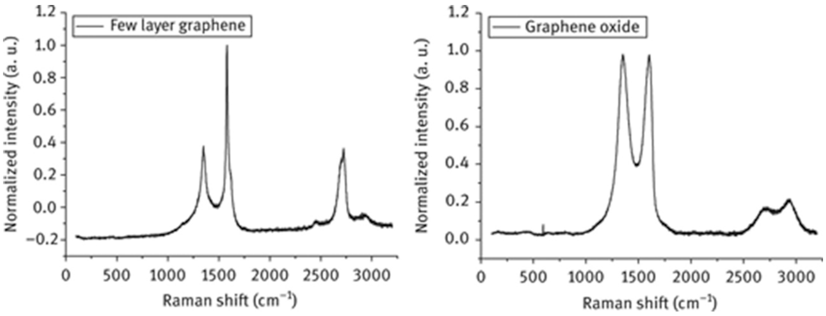

Figure 22: Raman spectra of few-layer graphene (left) and GO (right).

In GO the G band is larger and shifted to higher values (around 1,590 cm^{-1}), the D band has an increased intensity due to the higher amount of defects and the 2D band decreases and becomes wider (Figure 22) [117].

4.6 X-Ray Photoelectron Spectroscopy

XPS is a semi-quantitative spectroscopic technique giving information on the elemental composition, the empirical formula, the chemical state and the electronic state of the elements in a sample. In this technique the sample is irradiated with a beam of X-rays in ultra-high vacuum conditions exiting the core electrons into unoccupied atomic/molecular orbitals. XPS measures the kinetic energy and the number of electrons that are emitted from the top of the analyzed material. This technique gives information about not only the elemental composition, but also the ratios of the elements detected and the identity of the functional groups. In graphene, mainly one peak can be localized in the C1s spectral region, at 284.5 eV corresponding to the sp^2 C–C. In GO the peaks are more complex, as we can find the sp^2 and sp^3 carbon atoms, the hydroxyl, epoxy, carbonyl and carboxylic acid groups at 284.5, 285.2, 286.4, 287.1, 288.0, 289.2 eV, respectively, in the C1s region (Figure 23) [117, 119].

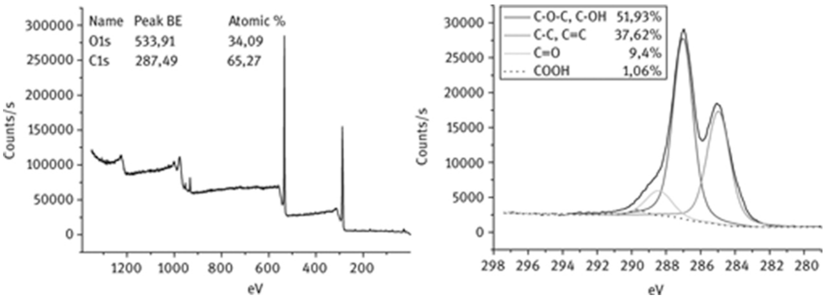

Figure 23: XPS spectra of GO. In the image on the left there is the survey spectrum of GO; in the one on the right the C1s spectral region.

4.7 Thermogravimetric Analysis

TGA allows to establish the amount of functional groups by calculating the weight loss while increasing the temperature (Figure 24). There are different factors that can cause this weight loss. These factors depend on the analyzed compound. Graphene is stable at high temperatures; therefore, the weight loss of the functionalized sample corresponds to the amount of functional groups introduced. Meanwhile, the thermal profile of GO shows a weight loss between 150°C and 400°C that can be assigned to the thermal decomposition of the unreacted oxygenated groups. If we analyze instead functionalized GO, the weight loss in this interval is caused by both, the unreacted oxygenated groups and the molecule covalently introduced. Therefore, to establish the amount of molecule introduced, the difference between the weight loss of GO and functionalized GO has to be calculated.

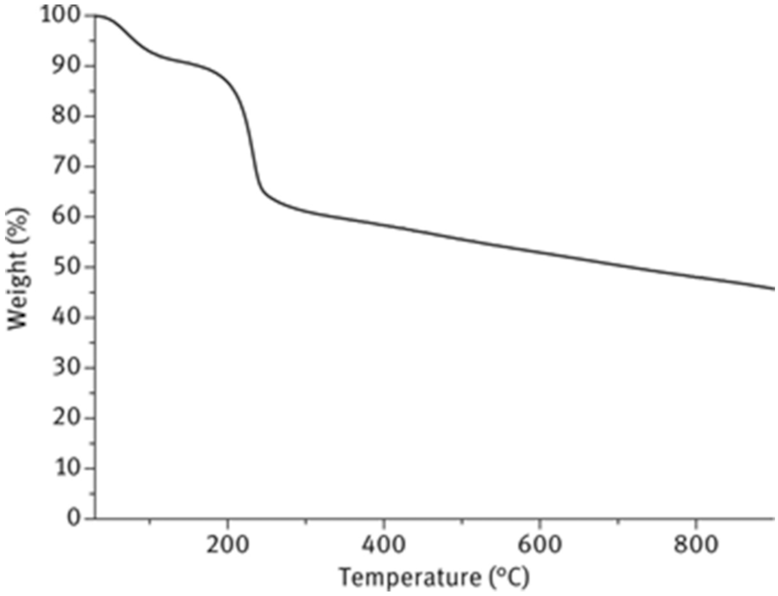

Figure 24: Thermogravimetric analysis of GO.

5 Conclusions

Even if graphene, GO and rGO are part of the same family, they present different characteristics and can undergo different reactions. Graphene can be covalently functionalized directly on the sp^2 carbon atom surface through free radical addition, atomic radical addition, nucleophilic addition, cycloaddition and electrophilic substitution reactions. It can be non-covalently functionalized by the formation of hydrophobic, van der Waals and electrostatic interactions with molecules such as perylene derivatives. GO instead is mainly covalently functionalized on its oxygenated functions, via the amidation and the esterification reactions on the carboxylic acids, the silanization and the Johnson–Claisen rearrangement of the hydroxyl groups and the nucleophilic addition to the epoxides. It can be non-covalently functionalized by π–π, electrostatic binding, H-bonding, van der Waals, H–π, cation–π and anion–π interactions. rGO can be considered between these two materials. It is more similar to graphene or GO, depending on the degree of reduction. The total reduction of GO to graphene has not been achieved yet. However, an important difference between graphene and rGO concerns the presence of defects in the latter one.

Which material to choose between graphene, GO and rGO depends on the purpose. GO, for instance, is mainly explored for composites and biomedical applications because of its high dispersibility. Graphene, instead, is more useful in electronics because of its electrical properties. Graphene and its derivatives are studied only for few years; therefore there is still a lot that has to be understood and discovered. Moreover, because of the complexity of this family of materials, much work remains to be done in developing reliable characterization methods that will aid to obtain precise and unambiguous chemical and structural identification.

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