State of the art: synthesis and characterization of functionalized graphene nanomaterials

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Abstract

Nanomaterials play nowadays a preponderant role in the field of materials science due to the wide range of applications and synergy with other fields of knowledge. Recently, carbonaceous nanomaterials, most notably bi-dimensional graphene (2D graphene), have been highlighted by their application in several areas: electronics, chemistry, medicine, energy and the environment. The search for new materials has led many researchers to develop new routes of synthesis and the expansion of the current means of production, by the anchoring of other nanomaterials on graphene surface, or by modifications of its hexagon sp² structure, through the doping of heteroatoms. By adding functional groups to the graphene surface, it is possible to increase its affinity with other materials, such as polymers, magnetic nanoparticles and clays, leading to the formation of new nanocomposites. Several covalent and non-covalent functionalization processes, their advantages and disadvantages with respect to their interactions with other chemical species, are discussed in this review. The characterization of these materials is a sensitive topic, since the insertion of functional groups over the graphene basal plane causes changes in its morphology and the so-called chemistry of surface. In this sense, beyond the classical techniques, such as x-ray Diffraction (XRD), Infrared Spectroscopy (FTIR), Raman Spectroscopy and Transmission Electron Microscopy (TEM), modern characterization techniques of graphene-based nanomaterials are discussed, focusing on those more indicated according to the proposed modifications. A significant attention was driven to environmental applications of functionalized graphenes, specifically in the removal of pollutants from wastewaters.

1. Introduction

Among the carbonaceous nanomaterials, graphene has attracted great interest from researchers worldwide due to its unique structural characteristics and application versatility. A pioneer mechanical method by which single nanosheets of graphene were obtained with a certain degree of purity was performed by Novoselov and coworkers [1]. The authors used Scotch-type tape to separate graphene layers from the graphite crystals. Their endeavor leaded Novoselov and Geim to be awarded with the Nobel Prize for Physics in 2010.

Recent applied researches have undergone a series of novel engineered nanocomposites which had been used in sports materials, as tennis racquet, shoes absorbers and fibers, cars shock absorbers. The interaction between graphene produced by Chemical Vapor Deposition (CVD) method and polymers has also been investigated, once many possibilities of practical applications arise from materials derived from 2D graphene + polymeric matrix configuration. Yet, from polymer-graphene interaction, in situ grafting of 2D graphene nanosheets into polymeric basis has been successfully developed and the nanocomposite has been employed in sensors [2]. When graphene is grafted into polymers, it confers more resistance to their derived composites; this explains the attention of industries of sports, defense and automotive products to such researches [3, 4]. Since graphene is a
transparent material, it has been employed in the base material for screens, which contributes to produce more resistant mobile phones, tablets and laptops.

In the present work, it is important to highlight the use of graphene and graphene oxide (GO) derived nanomaterials for specific applications in the most varied fields of knowledge, such as: healthcare and monitoring devices [5, 6], development of smart batteries [7], capacitors [8], thermal-transfer technologies, coating and surface treatment [3, 9], water desalination [10], sewage and wastewater treatment [11–13], capture of gaseous pollutants [14], among others. Nevertheless, a special attention to environmental aspects of many wet synthesis and functionalization of graphene nanosheets is delivered in this work, since the search for novel environmentally non-aggressive materials is growing among industries and research centers around the world. Despite of its increasing costs and scale-up challenges, graphene nanocomposites arise as a promising technological advance, once its flexibility and outstanding properties deliver many possibilities of application.

2. Graphene, an overview

2.1. Synthesis protocols

Idealized graphene is a two-dimensional sheet of pure carbon allotrope formed by hexagonal lattice structures (similar to a benzene ring structure) with a hybridized configuration sp² and with molecular weight of 106–107 g/mol. In contrast, real graphene particles have several impurities, mostly oxygen compounds and oxides [15].

In view of so many ways to synthesize graphene and its derivatives, the literature lacked standards to better define the properties of these materials. This lack of parameters took place until 2017, when ISO TS 80004/2017 established parameters of quality for graphene. From ISO TS 80004, graphene can be classified, as a matter of nomenclature, as a nanomaterial with carbonaceous hexagonal lattice in form of nanosheets and/or nanoblocks with a maximum stacking of 10 nanolayers for electrical measurements [16]. These properties can be detected through atomic force microscopy (AFM) or electron transmission microscopy (TEM). It is important to note that ISO TS 80004 does not mention GO among their parameters, hence many properties of GO (morphology/thickness, transparency, conduciveness, etc.) have been subject of investigation of early reports [17]. In their study, it is reported that the degree of oxidation plays a major role on the interlayer spacing, and it is influenced by the density of oxygen containing groups and synthesis temperature.

2.2. Top-down methods

Top-down methods of obtaining graphene are those that start from macro-structures to obtain smaller structures. Still in the 19th century, Brodie and Staudenmaier found ways to obtain graphite oxide through the use of strong acids [18, 19]. A more recent chemical protocol to synthesize graphite oxide by humid way was achieved by Hummers and Offeman [20]. However, this method must be followed by mechanic exfoliation in order to obtain GO nanosheets. Nevertheless most of exfoliation processes do not vouch satisfactory performance in the acquirement of monolayer/few-layered GO. As a result of their research, the classical methods of obtaining graphene and Graphene Oxide (GO) have been improved through the use of new routes such as electrochemical oxidation, chemical reduction, electrochemical deposition, ultrasonic and microwave exfoliation, among others [21–23].

A highly-oxidized graphite oxide is synthesized from natural graphite powder by oxidation with KMnO₄ in a concentrated strong acid, such as H₂SO₄ and HNO₃, at a low temperature (0 °C–7 °C) and under continuous stirring for homogenization [20]. The reaction time is controlled to ensure a satisfactory degree of graphite oxidation, and the oxidation time depends on the way in which the graphene is applied. Many researchers have worked to improve the Hummers method, using different types of reagents, even changing some of its steps. Changes in the variables have been studied, as well, in order to optimize the overall process. The chemical oxidation is followed by hydrolysis, washing and centrifugation [24]. Once obtained by the Hummers’ or modified Hummers’ method, the graphene oxide is chemically reduced by the addition of an electrophilic reactant. One of the most applied reduction agents is hydrazine [25]. Other researchers have reported the use of dimethylhydrazine [26], benzoquinone/hydroquinone [27], borohydrides and NaBH₄ [28]. Recently, ascorbic acid has been proved as an ecofriendly and high yield reducer of GO [29, 30]. The thermic reduction of GO is another satisfactory method applied to obtain Reduced Graphene Oxide (r-GO) by heating the samples to temperatures above 80 °C [31, 32].

Recent studies have also evaluated the use of environmentally non-aggressive biomolecules such as aminoacids [33], proteins [34, 35], and microorganisms [36], as biochemical reductants of GO, as exemplified in figure 3. Such natural or bio–compounds confers the process a higher safety from the environmental point of view, since most of them are biodegradable and non–toxic species, which allows by–product discharge without liability. The biofunctionalization of graphene nanosheets is discussed with depth in section 3.3.
Irradiation techniques, such as photoreduction and laser-controlled emission [37], belong to green alternatives through which r-GO can be obtained from oxidized graphite and graphene oxide without the use and disposal of chemical contaminants in the environment. The x-ray Photoelectron Spectroscopy (XPS) technique is employed to verify the quality of reduced graphene oxide. These processes have been observed to guarantee electron conductivity to the r-GO, by restoring the π-network on the carbon basal plane [37], so it can be possible the use of these nanomaterials in capacitors and transistors in electronic industry. However, more in-depth investigation must be carried out to assess cost-benefit of photoreduction; moreover, researchers must focus in keeping r-GO properties and quality parameters, this is a key factor.

2.3. Bottom-up methods

Graphene with high degree of purity can be obtained from the method of Chemical Vapor Deposition (CVD), in which, a volatile organic compound (alcohol, hexane, etc) is injected into a molten metal, which can be copper-nickel alloys [21]. With the effect of temperature, the organic molecules are reoriented into a sp² hexagon lattice and diffuse through the molten metal until reach its surface [38]. Despite, CVD graphene possesses a high purity, this method is very expensive in terms of energy consumption, and the amount of graphene produced is very small. In this sense, it is rather challenging to successfully scale-up CVD production.

Bottom-up method approach of in situ anchorage of graphene nanomaterials on polymeric matrices in the early stages of polymerization reaction from monomers and dimmers have been reported [2, 4]. As r-GO easily precipitates from suspensions consequently several chemical routes to reduce and stabilize the r-GO have been developed by using hydrophilic dimers, dendrimers or polymers [2]. Various advantages of these methods have been reported: the lowering of the operational temperature, short reaction time and r-GO suspension stability in water or organic solvents, as pointed by Wu and coworkers [39], who used poly(amidoamine) as a reducer agent of GO at 90 °C.

Generally, nanoparticles of metal oxides are synthesized through bottom-up methods, including sol–gel, chemical co-precipitation, hydrothermal, solvothermal, ultrasound-assisted impregnation, microwave-assisted, energy milling, reducing, etc (table 1). In this review, we analyzed the conjugation of metallic oxides with graphene. Synthesis of metallic oxides and their anchorage in graphene/GO structure might take place simultaneously. One of the most prominent examples is the synthesis of magnetite (Fe₃O₄)-functionalized graphene, in which Fe₃O₄ nanoparticles are synthesized by solvothermal (or hydrothermal) methods from hydrate salt (FeCl₃·6H₂O) (figure 1(b)).

3. Functionalization of GO, r-GO and graphene

Graphene is functionalized by non-covalent, as well as by covalent, routes according to the interactions between the ligands and the sp² carbonaceous lattice. In the non-covalent form, the extended π-electron delocalization of the graphene sheet remains intact, whereas covalent functionalization takes place via the formation of covalent bonds between the graphene and different organic functional groups [48]. These bonds are irreversible most of the times and provokes the formation of sp³ domains over the carbonaceous structure [49]. Chemically functionalized graphene can be processed further by solvent-assisted techniques, such as layer-by-layer assembly, spin-coating, and filtration. Various reagents, including aromatic molecules, surfactants, polymers, porphyrins and biological molecules, have been used to functionalize graphene and GO to improve their chemical properties [50]. Proper chemical functionalization of graphene also prevents the agglomeration of single layer graphene during reduction in the solvent phase and helps to maintain the inherent properties of graphene. GO has been widely used as a starting material for the synthesis of processable functionalized graphene [49].

Materials classified as chemically modified graphene (CMG), or modified graphene nanomaterials (MGNs), have been studied as supercapacitors, coating and insulation materials, sensors and biosensors and as potential adsorbent for dyes, metallic ions and other types of pollutants worldwide. Two of the most important characteristics of graphene is its use in effluent treatment due to its large surface area and its planar geometry [51, 52]. The functionalization of graphene promotes the modification of the characteristics of the graphene surface by the introduction of selected functional groups [53]. This use of graphene depends on the functional characteristics desired; the interactions may be through covalent bonds or weak bonds, such as π–π conjugation, van der Waals forces, hydrophobic or electrostatic interactions, that occur between the lamellae of graphene and the linker compound [47].

3.1. Covalent functionalization

The chemical functionalization of graphene and GO in dispersions or solution systems has been investigated along with the development and improvement of graphene synthesis methods by using various reactants,
Table 1. Summary of functionalized graphene nanomaterials, their synthesis and applications.

| Nanocomposite                  | Functionalization route                                                                 | Interaction between graphene and the ligands                     | Application                              | References |
|-------------------------------|-----------------------------------------------------------------------------------------|-----------------------------------------------------------------|------------------------------------------|------------|
| Aβ-42/T-Tau-graphene          | graphene/protein                                                                        | Bioconjugation, charge dispersion                               | Diagnosis                                 | [6]        |
| BMIMBF$_4$-graphene           | 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF$_4$)                             | Non-covalent, ionic bonds                                       | Electrodes, batteries                     | [8]        |
| Si-C-CVD-graphene             | CH$_4$ gas, CVD synthesis                                                               | Doping, SiC formation                                           | Electronics, conductors                  | [21]       |
| Pleurotus ostreatus-graphene  | biofunctionalization                                                                    | Electrostatic repulsion, surface charge density                | Biosensors                               | [40]       |
| Polyvinyl alcohol-rGO         | rGO/PVA addition, ultrasound                                                            | H-bonds                                                       | Protective films, anti-corrosion          | [9]        |
| Polyelectrolyte-rGO           | Layer by layer coating                                                                  | Covalent bonds                                                 | Electronics, electromagnetic shielding   | [3]        |
| Casein-phosphopeptides-GO     | Amino acids                                                                             | Covalent, H-bonds                                              | Flame retardant                          | [41]       |
| Amino-graphene                 | Aromatic/non-aromatic amines, microwave-assisted reactions                             | Covalent bonds                                                 | Supercapacitors                          | [42]       |
| B, N-doped graphene           | Doping by N and B, predicted by DFT model                                               | Heteroatom, covalent bond                                      | Water desalination                       | [10]       |
| MOF-graphene                  | Metal organic frameworks (MOF)                                                         | Dispersive interactions                                        | Capture of greenhouse gases             | [14]       |
| Chitosan-NH$_4$ quaternary salt-GO | Amidation reaction, N,N-dimethyloctadecane-1-amine                                 | π-stacking interactions                                       | Adsorption, dye removal from solutions   | [43]       |
| Fe$_3$O$_4$-GO                | Solvothermal reaction by FeCl$_3$·6H$_2$O                                             | Non-covalent, electrostatic attraction                         | Adsorption, wastewater remediation       | [44]       |
| ZnO-GO                        | Zn(NO$_3$)$_2$·6H$_2$O, ultrasound irradiation-assisted                               | Non-covalent, electrostatic attraction                         | Photocatalysis, AOPs, wastewater remediation | [45]       |
| IL-GO                         | 1-hexyl 3-decahexyl imidazolium                                                        | Non-covalent, coordination bonds                               | Adsorption, wastewater remediation       | [46]       |
including hydrogen, oxygen, or halogens, which lead to partially functionalized graphene \[54, 55\]. The need to synthetize a versatile nanocomposite that can be used in diverse applications has led to the search for new reactants and more complex functionalization agents and methods in recent years.

In principle, covalent functionalization allows formation of covalent binding, such as nucleophilic addition, cycloaddition, free radical additions, substitutions and rearrangements, on both sides of the graphene plane, accompanied by the rehybridization of C atoms from sp\(^2\) to sp\(^3\) \[54, 56\]. Sainsbury and coworkers \[57\] studied graphene functionalization with carbene and had verified that the covalent attachment of dibromocarbene groups resulted in rehybridization of the C atoms via the formation of cyclopropyl groups, whose defect degree on the covalent functional group was confirmed by Raman Spectroscopy. Additionally, functional aromatic organic compounds, such as benzoquinone and anthraquinone, participate on a carbon surface as an electron donor in donor-acceptor complexes with adsorbed molecules. This phenomenon results in a delocalization of \(\pi\)-electrons over the carbonaceous lattice \[58\], which certainly favor \(\pi-\pi\) conjugation and, with less intensity, electrostatic interactions between sorbent and sorbate in an aqueous medium.

Amino-functionalization of GO takes place by reaching hydroxyl groups by an amine-compound, at high temperatures (up to 180 °C) \[12, 47\]. At lower temperatures (50 °C–120 °C), a primary amine can break GO epoxide ring bonds, forming amine and amides, as result of a chemical reduction of GO \[59\]. At temperatures above 250 °C, reaction with amine, however, may provoke breaks in the carbon sp\(^2\) configuration, forming heteroatom structures with nitrogen over GO lattice \[47\], as depicted in figure 1(a). Similar to aromatic organic moieties, amines have the power to increase graphene \(\pi\)-stacking configuration, by the delocalization of \(\pi\)-electrons resulting from the nitrogen electronic pairing \[42\]. The increase of delocalized \(\pi\)-electrons over graphenic structure is responsible for a strong enhancement in GO’s electrochemical properties \[42\], which might contribute to develop novel supercapacitors. Moreover, this change leads to a facilitation of \(\pi-\pi\) stacking interactions between reactive dyes molecules and the amino-functionalized graphene \[12\].

Studies of molecular simulations describe the intercalation of functional moieties in the graphenic plane holes and their biding over the edges via covalent bonds \[60\]. Similar investigation reported heteroatom (N and B) doping over graphene nanosheets \[10\]. This is a tendency that researchers should follow to better understand the interactions of functional groups and graphene in molecular level. For that, some software available in the market have powerful tools based on the density functional theory (DFT) in their portfolio, which allow the calculation of bond length, energy and the angles between them.

### 3.2. Non-Covalent functionalization

The non-covalent functionalization of graphene and GO is mostly based on van der Waals forces, hydrogen bonds, electrostatic or \(\pi-\pi\) interactions with organic molecules or polymers that meet some basic criteria. The energies involved in a single non-covalent interaction on the surface of the adsorbent are relatively low in comparison to the covalent bond energy; however, when combined over large surfaces, they can match some covalent bonds. This is particularly interesting from the point of view of the preservation of the conjugated \(\pi\)
Together with the ionic compounds, some surfactants agents have been used for the production of non-covalent functionalized graphene or GO [61], due to their capacity to establish interactions between the graphene surface and the ionic type ligands (chemical functional groups) of these species and their high stabilizing power.

3.2.1. Metallic oxide nanoparticles
With respect to adsorption of pollutants from water and atmosphere, one of the major challenges of working with graphene nanosheets is the recovery of nanomaterials after the pollutant removal. Solid-liquid separation is very difficult when GO nanosheets are employed in an aqueous medium, due to the hydrophilic properties of GO [62]. Moreover, the use of GO in water/wastewater treatments becomes a liability when it is considered that GO has been proved as toxic for aquatic fauna [63]. This is sufficient to drive the researchers’ attention towards the control of the release of by-products in the environment through toxicity assessment and chemical mapping by advanced techniques, such as chromatography (GC-LC) and mass spectrometry (MS) detection.

An efficient method to solve this problem is to introduce magnetic nanoparticles (MNPs), such as Fe3O4, α-Fe2O3, or Fe2O3n, in the reduced graphene or graphene oxide structure [44]. In these metalized structures, it is possible to apply a magnetic field to easily separate the sorbent from the sorbate. This calls for an in-depth discussion on mass magnetization saturation, coercive field and temperature influence to obtain a better understanding of the magnetic properties of magnetite-functionalized graphene. Moreover, magnetization measurements can be used to reveal the saturation point of the ferromagnetism and whether the material shows characteristics of diamagnetism or paramagnetism [64]. The saturation of the ferromagnetic signal for Fe3O4-functionalized graphene is between 27–45 emu·g−1, and it saturates when a high magnetic field is applied, in agreement to the data found in the literature [64].

Titanium dioxide (TiO2) and oxide of zinc (ZnO) are powerful photocatalysts for the UV-assisted degradation of water pollutants in wastewater treatments [13, 45] and other advanced oxidation processes (AOPs), as seen in Table 1. There are several research works which deal with the treatment of organic pollutants, most of them, dyes. Despite the innovative character of these nanomaterials, the literature nowadays lacks the investigation of other types of aquatic pollutants. As an example, TiO2-Ag3PO4-graphene catalysts have shown excellent performance in the degradation of the dye Acid Blue 25 [13], however the investigation of this and other similar nanomaterials in the treatment of real textile effluents remains a research gap. Recently, GO has been investigated as support of TiO2 catalysts and applied in oxygen reduction reaction with great catalytic selectivity and stability [65].

3.2.2. Ionic and poly(ionic ions)
The abundance of metallic species in nature has led researchers to develop organic molecules capable of increasing the adsorptive power of graphene against toxic and reactive metals in their ionic form. Non-covalent functionalization with polymers containing heteroatoms or with ionic liquids (IL) [such as 1-methylimidazolium, as depicted in Figure 2] and poly(ionic liquids) [PIL] improves the electrical conductivity of flexible graphene electrodes, according to published reports [8]. Moreover, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF4) functionalization of graphene electrodes increased their discharge time, which can be compared to Li-based batteries. These findings bring great perspectives to the application of PIL/graphene in the research of novel capacitors. Among PIL species, it has been used polythiophene [66], polyvinylimidazole [67], polyfuran [68], among others.

Regarding the capturing of pollutants from water, PIL can enable mechanisms involving the electrostatic interaction between the lone pair of the heteroatom and the positively charged ions [46]. In this sense, 1-hexyl-3-decahexyl imidazolium-functionalized GO has proved to have a high adsorption capacity for the removal of Sulfamethoxazole (SMZ), carbamazepine (CBZ), and ketoprofen (KET) from an aqueous solution in comparison to pristine GO [46]. However, the novel adsorbent showed considerably lower reusability than GO (especially for CBZ samples), which might be pointed as a setback. Finally, 1-amino-3-methylimidazole chloride functionalized GO was successfully synthetized by Gholami-Bonabi and coworkers [69], who used it to adsorb Phenol. The authors reported significant phenol uptake of 95%.

3.3. Biofunctionalization
Compounds from natural extracts (bio extracts) contain functional groups capable of binding to graphene through a series of intermolecular interactions (Figure 3). Bioconjugated nanocomposites have been successfully applied in wastewater remediation by biosorption and photocatalysis [43, 71]. Most carbohydrates establish H-bonds between their functional moieties and the hydrogens of hydroxyl and carboxyl groups of GO structure. Moreover, π–π and π-cation relationship between them and sp2 system of graphene plane is also reported [43].

The vast amount of oxygenated groups (most of them hydroxyl) of carbohydrates and amino acids eases their
conjugation with graphene. Moreover, intermediate doping of graphene nanostructure with amines and thio compounds can improve the yield of biofunctionalization [71]. Magnetic nanoparticles can also be anchored on biofunctionalized graphene structures without interfere in their targeted properties. Moreover, Fe₃O₄-biofunctionalized-graphenes are easily separated from aqueous medium by a magnet [72].

Recent reports have investigated the increasing sensibility and selectivity of protein-imprinted graphene in the detection of AD biomarkers in biofluids [6] (table 1). High sensitivity of these biosensors is consequence of the increasing of doping effects on graphene surface, since these biomarkers have different charges. In their work, the authors investigated the different stages of interactions between two proteins (Aβ₁-42 and t-Tau) and graphene and how these interactions influenced in the transmission signals. This contributes to early detection of Alzheimer’s and other degenerative diseases.

Between the many advantages of these compounds it merits to be mentioned their low cost, mild synthesis conditions and ecofriendly properties, since their by-products are non-toxic and biodegradable [40]. Other benefits of orientation-controlled bioconjugation can be pointed is the tailoring of specific morphologies over graphene plane, which enhance its specific surface area. Consequently, high surface area increases the composite adsorptive power and reactivity towards toxic chemicals. The probability of employment of biofunctionalized graphene nanocomposites over an extended variety of remediable pollutants is marked as another advantage [73]. Finally, the undesirable agglomeration (much common for GO), sedimentation and retention throughout aqueous media might be mitigated by the increase of hydrophobic interactions by the groups over biofunctionalized GO surface.

The main disadvantage, however, is that parallel reactions might take place, since natural extracts are composed by different species of chemicals. Depending of the substrate (e.g. bacteria, proteins and enzymes),
some bio-nanocomposites might degrade with the course of time. Therefore, the lifetime of these nanocomposites becomes a drawback in relation to manufactured chemicals.

Many of these bio extracts have been investigated in the enhancement of properties of graphene nanocomposites, such as porosity, surface area, thermal resistance; among others. One of the most reported natural extracts for biofunctionalization is the chitosan, a biopolymer with glycose and several oxygenated functional groups over its structure. Chitosan has been used in crosslinking functionalization of carbons, clays and, more recently, a broad range of carbonaceous nanomaterials [43, 73]. Amino acids, such as Casein-phosphopeptides, bestow outstanding properties to graphene with aims to its application as fire retardant. Liu and coworkers [41] report high thermal conductivity and excellent flame retardancy of GO nanoplatelets after their Casein-phosphopeptides functionalization.

4. Characterization

The most common techniques used to characterize graphene and identify the presence of functional groups and morphological modifications on the graphene sheets surface are: Raman Spectroscopy, Fourier-Transform Infrared Spectroscopy (FTIR), x-ray Diffraction (XRD), x-ray Photoelectron Spectroscopy (XPS), Transmission Electron and Atomic Force Microscopies (TEM and AFM) and Thermogravimetric Analysis (TGA).

4.1. Raman spectroscopy

Raman Spectroscopy is a simple, fast and non-destructive method that uses monochromatic excitation laser to verify the structure of the material. In Raman Spectroscopy of graphene, there are three response peaks of interest [74]. The in-plane vibrations of the conjugated π-bonds exhibit characteristic Raman spectra: 1327, 1584, 2643 cm⁻¹ for D, G and 2D, respectively (figure 4(a)) [31, 75]. The D peak can be used to characterize graphene-based materials with defects, which refers the presence of sp³ carbons in the basal carbon plane, such as disordered graphene and graphene oxide [31, 76]. The G and 2D band peaks are characteristic of monolayer graphenes, which generally appear at 1582 cm⁻¹ and 2700 cm⁻¹, respectively. The G band is approximately twice the D band frequency, however, a two-phonon band (2D) is described for second-order Raman spectra of graphene without any kind of disorder or defects [77]. However, if a structural modification is made, changes in D, G, and 2D-bands peaks may appear as a result of successive introduction of ‘holes’ or sp³ centers in the graphene surface or basal plane depending on the chosen functionalization route. This happens due to ‘defects’ caused by the application of the covalent bond-forming chemicals on the carbon framework, which leads to changes in the vibrational excitation response quite distinct from that caused by localized, physical defects in sp²-conjugated carbon [49]. Hence, graphite oxidation and consequent functionalization leads to the
appearance of some Raman peaks, 746 cm\(^{-1}\) (C–S stretching), 524, 1062, 1102, 1130 cm\(^{-1}\) (skeletal vibrations, CCCC \textit{trans} and \textit{gauche}), 1294 (twisting), 1440, 1461 (C–H deformation, scissoring), 2848 and 2884 cm\(^{-1}\) (C–H stretching)\cite{75}. Raman spectra of poly(ionic liquid)s functionalized r-GO (PIL-rGO) revealed the typical D (1341 cm\(^{-1}\)) and G (1589 cm\(^{-1}\)) bands, similar to those of GO and r-GO, indicating the presence of sp\(^3\) defects and a sp\(^2\) conjugated carbon network in the hexagonal plane in G and GO\cite{78}. Finally, the I\(_D\)/I\(_G\) ratio can provide a substantive notion regarding sp\(^2\) degree of disorder and the presence of defects, impurities or chirality from functionalization or doping processes.

4.2. FTIR infrared spectroscopy

FTIR Spectroscopy is widely employed to detect functional groups and to characterize graphene nanocomposites, however, is not the most recommended technique to detect the presence of metallic species on the surface of graphene or GO. According to stretching in specific wavelengths it is possible to discover the functional groups present in the sample from specific bands located at certain wavenumbers (cm\(^{-1}\)). With proper FTIR analysis, one can be sure if the functionalization route was successful. For alcohols and phenols, FTIR spectra are used to detect the presence of functional groups on the graphene surface. These can be easily detectable on the IR spectra through their O–H stretching absorption, which presents very pronounced bands at 3590–3650 cm\(^{-1}\). The adsorption bands also are high for other oxygen-functional groups such as –COOH (1727 cm\(^{-1}\)), C–O–C (1052 cm\(^{-1}\)) and –COH (1225 cm\(^{-1}\)). Amines, on the other hand, show bands at 3300–3500 cm\(^{-1}\), originally from vibration of N–H stretching; and bands at 1580 cm\(^{-1}\), which are attributed to N–H binding vibration\cite{82}, as seen in figure 4(b). Furthermore, in amino-functionalization of GO, amiation reactions also take place generating amides (figure 1(c)), which can be detected by bands which reveal the presence of C=O bonds, adjacent to N, by strong bands at 1700–1750 cm\(^{-1}\)\cite{28, 42, 83}. Thio compounds can also be detected by FTIR through the appearance of peaks at 616, 1070 and 1423 cm\(^{-1}\), which are assigned to the C–S vibration, C=S vibration and C–N (in N–C=S) of the dithiocarbamate groups\cite{83}. The presence of amino and carboxyl binding stretching on the FTIR spectra on the broad band 1650–1730 cm\(^{-1}\) is an indication of the presence of poly(ionic liquid) poly(1-vinylimidazole) on the r-GO surface\cite{84}.

4.3. X-ray diffraction

Although XRD is not a perfect tool for identifying single-layer graphene, the analysis may help to differentiate between graphite and graphene samples. Pristine graphite exhibits a basal reflection (002) peak at 2\(\theta\) = 26.6\(^\circ\) (d spacing = 0.335 nm) in the XRD pattern. According to Spyrou and Rudolf\cite{85}, after graphite oxidation and before the exfoliation process, the graphite oxide intermediate basal (002) reflection peak is shifted to 11.2\(^\circ\), corresponding to a d spacing of 0.79 nm. This increase in the interlayer space is attributed by the researchers to the intercalation of water molecules between the oxidized graphene layers. XRD analysis has been applied to explain the presence of metallic compounds in graphene structures. Moreover, the interaction of x-rays with a graphitic crystalline phase results in the creation of a diffraction pattern\cite{74}. Zhao and coworkers\cite{84} performed by the non–covalent functionalization of r-GO with two poly(ionic liquids) (PIL), poly(1-vinylimidazole) (PVI) and 2-bromopropionyl bromide and evaluated that PIL–r-GO diffractograms showed the disappearance of a sharp diffraction peak of GO at 2\(\theta\) = 11.8\(^\circ\). This behavior is in agreement with the reported data, and a small increment in the intensity of the GO characteristic peak in 2\(\theta\) = 44.5\(^\circ\) (101), referent to the basal reflexing plane of tri-dimensional graphite\cite{86, 87}. The r-GO patterns showed an intriguing appearance of an intense peak at 2\(\theta\) = 26\(^\circ\) (002) (figure 4(d)), which corresponds to a d spacing of 0.335 nm\cite{85}, and is also characteristic of graphite basal reflection. This peak suggests that the oxidation process was not sufficient to fully oxidize the graphite\cite{80}. The grafting of 2-bromopropionyl bromide and PVI revealed a peak at 21\(^\circ\), which can be related to a significant increase in the distance between interlayer sheets after the functionalization.

4.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is an analytical technique employed to detect chemical species through a photoelectric effect under x-ray stimulation. XPS is a non-destructive analysis, which can supply atomic information of the sample surface or near-surface regions. XPS analytical precision is in the order of parts per billion, since the species are concentrated on the adsorbent surface\cite{88}. XPS technique is also applied to determine the amount of oxygen on the graphene and GO surfaces as well as to identify the types of the bonds\cite{31, 89}. On XPS spectra, the characteristic peak of graphenic carbons can be clearly seen at 285.0 eV (figure 4(f))\cite{90}. Moreover, strong peaks can be seen at 289.3 eV in the XPS C1s region which is associated with the carboxylic group species; peaks at the region of 287.0 eV can be attributed to species such as alcohol and epoxides, and to C(II) species such as ketones (figure 4(e))\cite{91}. Amine functional groups present on functionalized graphene, show characteristic (N1) peaks in the binding energy region of 400.0 eV\cite{91}, however, a closer analysis reveals two peaks at 399.9 and 401.4 eV, which correspond to the C–N and C–N–H bonds\cite{92}. 
In contrast to the previous analysis, Zhao and coworkers [84] reported the presence of amine C–N bond on the PVI-r-GO surface given the appearance of a less intense peak at 286.0 eV, which possibly corresponds to reveal amide groups. According to Thomas [93], functionalization of graphene with sulfur organic groups can be explained by the appearance of XPS S 2p spectrum, and it is fitted with 2p3/2 components at 161.9 eV, relative to lower binding energy component of spin–orbit split doublet, assigned to a S–S bond, 163.5 eV and 164.5 eV (H–S–C and R–S–C), and 168.0 eV (S–O). The main drawback in performing XPS analyzes is regarding the equipment installation and maintenance, once they are very costly and it is necessary vibrations-free facilities and a clean room standard in order to allow the operation of x-ray photoelectron spectroscopes. If these standards are not fulfilled, it may occasion damages in the equipment.

Finally, successful non-covalent functionalization of graphene can be confirmed by the appearance of characteristic peaks in the x-ray Photoelectron Spectra (XPS) [94]. According to [95], the presence of magnetic nanoparticles anchored on the GO surface can be detected by two distinguished peaks at 729 and 715.3 eV. Moreover, it is reported the occurrence of peaks attributed to C=O (285 eV) and C=O (286.2 eV) and C–O–O (289 eV) bonds of the XPS C1 spectrum after Fe3O4-functionalization. Despite the authors have not compared the spectra of Fe3O4-GO with pristine GO, the assessment exhibited evidences of the successful anchoring of Fe3O4 over GO surface.

4.5. Transmission electron and atomic force microscopies
Transmission Electron Microscopy (TEM) analysis accurately exhibits the morphology of a graphene sample. Moreover, TEM images are powerful tools for the detection of morphologic changes in the nanostructures, such as the existence of very small (less than 2 nm) micropores between the layers [96]. TEM scans (figures 5(a), (b), and (d)) deliver images with higher precision than other methods, such the Scanning Electron Microscopy (SEM), shown in figure 5(e). TEM photographs of GO (figure 5(a)), and mainly r-GO (figures 5(b), (d) and (e)), show an agglomeration of graphene sheets after reduction. Additionally, Atomic Force Microscopy (AFM) (figures 5(c) and (f)) can be employed to determine morphological features of graphene, such as layer thickness, number of layers and lateral dimensions of a well dispersed sample. Hence, the nanometer thickness of these nanocomposites can be confirmed with satisfactory precision [31, 97].

Depending on the morphological state of a nanosorbent, the number of stacked nanosheets and the way in which they are pillared, the adsorption of certain types of pollutants may be negatively influenced. This phenomenon occurs since there is a tendency for the decrease of sorbent specific surface area, and consequently of its active site availability. On the other hand, the distance between layers analyzed for the nanomaterial is a determinant for the removal efficiency (%) of some contaminants. This distance, however, must be sufficient to...
retain molecules of certain sizes and then promote their retention in the solid phase. Some works have reported that the functionalization of graphene led to a decrease in its surface area because the ligands had reached some active sites of the nanosorbents, promoting their pillaring, re-stacking or agglomeration [99, 100]. These changes can be easily confirmed through Specific Surface Area and Pore Volumes (BET) and Dynamic Light Scattering (DLS) techniques, usually associated with TEM and/or AFM microscopy [101].

It is important to keep in mind the necessary care in the installation and operation of atomic force microscopes. Like the x-ray Photoelectron Spectrometer, the AFM equipment must be installed in a clean room standard facility in order to avoid contamination of the samples, as well as possible damage to the microscope systems. Such requirements are yet another factor that makes analyzes more expensive and, consequently, the final product.

4.6. Thermogravimetric analysis
TGA can be a complementary technique to FTIR and is especially useful to unravel the presence of functional groups on graphene. From thermograms, it can be seen the decrease of mass in certain temperature range, which can be associated to the uptake of moisture, oxygenated groups and nitrogenized compounds. Moreover, some papers report the degree of oxidation by TGA when it is not possible to carry out XPS analyses [80]. Thermogravimetric Analysis (TGA) is a useful tool to determine the functionalized graphene or functionalized GO weight loss under aggressive temperatures. Many authors have applied it to trace changes in the structure of graphitic materials before and after functionalization of graphene sheets [85]. Hydroxides and the water elements are removed after the temperature reaches the first 100 °C; followed by the combustion of organic compounds weakly linked to the solid matrix [102]. When the temperature reaches 250 °C–400 °C, the oxygen-containing functional groups (hydroxyl, carboxyl, epoxide, etc) such as carboxyl and hydroxyl begin to decompose, and the loss beyond this temperature is due to carbon skeleton pyrolysis [103] (figure 4(c)). Roughly stating, TGA is commonly applied by researchers to calculate the oxidation degree of GO, based in the uptake of oxygenated functional groups. Differently, r-GO samples show no significant weight loss in the first 500 °C; yet, presenting an intense decrease after the temperature reaches 700 °C, due to the decomposition of graphitic structures. In this sense, it is important to note that GO start to reduce at temperatures greater than 80 °C [31]. The acquirement of GO with high degree of purity requires care in drying processes, especially in ovens, where high temperatures (> 100 °C) should be avoided. For that, is strongly recommended the drying in vacuum systems, under environmental temperature.

4.7. Specific surface area and pores volume
BET Specific Surface Area and Pore Distribution is one of the techniques which are widely used to estimate the maximum adsorption capacity of some materials. For adsorptive and catalytic processes, the surface area and pore size distribution have a considerable influence on their efficiency, capacity and yield [74]. Therefore, BET technique has not been extensively employed by researchers in works related to the use of functionalized graphene as adsorbent of liquid pollutants; moreover, not always the nanosorbents with greater specific surface area (SBET, given in m²·g⁻¹) show great maximum adsorptive capacity (qm, given in mg·g⁻¹). On one hand, the surface interactions determine the adsorption performance of functionalized graphene composites; on the other hand, the influence of intraparticle diffusion mechanisms and porous microstructure on the adsorption of dyes onto functionalized graphene composites has a role, although secondary. Altogether with the N₂ adsorption method limitations for microporous materials [104], the maximum surface area of GO in water is accessible only in very low concentrations (< 35.0 µg·ml⁻¹) and the functionalized-GO measured BET Specific Surface Area is much lower than the GO theoretical surface area, which can be attributed to the aggregation and packing formation of graphene nanosheets [49, 105]. Moreover, sorbent higher specific surface area does not guarantee by itself a higher adsorption capacity. Measurement errors and low reproducibility are other aspects which make it difficult to use BET Specific Surface Area and Pores Distribution technique, with analytical errors that may reach 9.86% of the measurements [106]. Moreover, 91.0% of the deviances in SBET are regarding to gravimetric imprecisions, as reported by Hackley and Stefaniak [107]. According to Fan and coworkers [108], the BET method also involves unrealistic assumptions, such as constant surface energy, localized adsorption in the top layers which can be reached by N₂ molecules in the BET analyzer, reduced N₂ pressure range, and the necessity of choosing need to choose a theoretical molecular projection area. These are some reasons why many authors prioritize the FTIR, Raman, XPS and even XRD analysis to achieve a better understanding of the factors that may favor or hinder the mechanisms of surface interaction between modified graphene and the chemical species to be removed by adsorption.
5. Conclusions and perspectives

Graphene and its derivatives are attracting the attention of many researchers nowadays due to their outstanding properties, such as high surface area, transparency, malleability, thermic and electric conductivity, chemical selectivity, among others. These properties are enhanced when certain functional groups are inserted over the graphenic plane and edges. It is reported a substantial increase in graphene chemical selectivity with organic dyes after its functionalization with a primary amine. However, functionalization, doping and anchoring consist in another step in nanocomposite production and therefore increases in their production costs.

It was observed that each novel material must be well characterized after each modification by doping or by functionalization. Moreover, in order to obtain sufficient information from the new nanomaterial after modification process, it is necessary to carry out repeated analyzes in order to obtain a complete picture of each stage of production. Additionally quality parameters of nanocomposite are established based on their characterization and these properties are not always easily replicated. Therefore, it is very clear that such continuous monitoring makes the process more expensive, since the cost of characterization will certainly be embedded in the price of the final product.

Novel routes for graphene oxide production and functionalization with low environmental impact tend to be investigated to substitute or improve the classical processes, such as Hummers, and CVD method. In this sense, several works have reported novel methods to reduce GO into r-GO through the addition of natural and biological reductants, such as C vitamin, plants extracts and microorganisms. The elimination or reduction of by-products during GO synthesis is another source of research following this trend. Finally the scale-up of graphene-derived nanomaterials production is a significant challenge in terms of cost and reproducibility. In this sense, new efforts are needed in the design and development of new equipment in order to increase the production volume and the quality of graphene-based nanomaterials.

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