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Review

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Graphene oxide films, fibers, and membranes

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Abstract: Graphene oxide (GO) macroscopic films, fibers, and membranes have become important applications of this interesting two-dimensional material due to their specific properties and great potential as new high-performance materials. After chemical or thermal reduction, GO is transformed into an electrically conductive material termed reduced GO (RGO). These materials hold great potential because they can be prepared in large quantities at low costs, and consequently they are particularly suitable for applications in packaging, textiles, energy devices, and separation technologies. In the following years, the use of GO- and RGO-based films, fibers, and membranes is expected to grow; however, several challenges regarding its processing conditions must be resolved. In this review, we addressed some of the recent work regarding these important technologies and summarized the state of the art of GO films, fibers, and membranes.

Keywords: gas separation; graphene; nanocomposite; nanostructured materials; water purification.

1 Introduction

For thousands of years, carbon materials had been scarcely used as structural materials until methods to prepare carbon fibers with robust mechanical properties were developed in the late 1950s [1, 2]. Soon after the era of carbon fibers emerged, researchers realized the potential of carbon as a strong, lightweight, corrosion-resistant, and electrically conductive material. However, it was only after the discovery of the fullerenes [3], and especially after the discovery of carbon nanotubes [4, 5], that carbon nanomaterials captured the attention of researchers. The use of carbon nanotubes received a boost when its large-scale synthesis was developed [6] and researchers realized the extraordinary mechanical and electrical properties of individual carbon nanotubes [7]. sp^2 Hybridized carbon nanomaterials can be classified in groups by taking into account its dimensionality (D) [8]: 0D, 1D, 2D, and 3D. The isolation of graphene and the characterization of its unique physical properties [9] caught considerable interest in 2D nanocarbons. This group of nanomaterials are characterized by a small thickness (going to an atom-thick layer) and a comparatively large lateral size, and include not only graphene but also graphene nanoribbons, graphene oxide (GO), and reduced GO (RGO), among others.

While graphene has dominated the electronic applications, GO is one of the most attractive 2D carbon materials for bulk applications, such as composites, films, fibers, and membranes. GO is derived easily by exfoliation from graphite oxide, which was first synthesized by Brodie in 1859 [10]. Graphite oxide remained as an uninteresting compound for many years, and only recently has been investigated with prospects of applications [11–14]. GO can be produced in large scale by chemical oxidation of graphite, and is water dispersible; thus, it can be processed in environmentally friendly methods without using organic solvents [11]. Unlike graphene, or pristine carbon nanotubes, GO contains various functional groups that enable a variety of covalent chemical modification methods with relative simplicity. In water, GO sheets have a strong negative charge, thus enabling its processing through electrostatic assembly [15]. Due to its large anisotropic shape, GO can self-assemble into layered systems. However, most interestingly, GO can be reduced by numerous methods, resulting in an electrically conducting material, reduced GO (RGO). RGO resembles many of the graphene properties, such as being atomically thick, electrically conductive, 2D, and exhibiting a very similar chemical composition.

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However, because of the presence of defects within its structure, caused by the lack of full crystalline order and the presence of residual oxygen functional groups, RGO possesses attractive physical and chemical properties that are very different from those of graphene. GO and RGO can be prepared in large quantities by the modified Hummer's method using potassium permanganate as an oxidizer, instead of Brodie's method [10], which involved potassium perchlorate. In order to prepare structural materials, GO sheet size plays an important role in order to provide high viscosity to the dispersions and long-range mechanical stability to the materials. GO with large sheet size and high oxidation degree has been reported recently [16, 17]. Some of the conditions needed to keep the large sheet size in GO dispersions are to avoid overoxidation to minimize the exposure to high shears, and to avoid ultrasonic treatment during purification [18]. In addition, small sheets and multilayered particles of GO must be removed by centrifugation fractionation. The viscosity of aqueous GO dispersions is a factor that should be considered in order to develop successful processing methods. The sheet size of GO dispersions plays a similar role to that of molecular weight in polymer solutions. Indeed, the viscosity of both dispersions/solutions is highly dependent not only on the mass fraction of solids but also on the molecular weight or sheet size [19]. In both cases, degradation of sheet size or molecular weight is accompanied by a large decrease in viscosity, and usually a change of its physical properties. Another factor is the oxidation degree of GO, because the higher the oxidation the more hydrophilic GO becomes, and the weight loss after reduction also increases. GO sheets charge must also be considered because in water dispersion, GO sheets have a strong negative charge that is also pH dependent. This behavior of GO is similar to an anionic polyelectrolyte, and thus the addition of positively charged materials results in GO flocculation. In addition, we can use GO electrostatic assembly to coat positively charged surfaces or in layer-by-layer film preparations. Thus, GO dispersions and batches must be carefully characterized according to their sheet size, oxidation degree, pH, and viscosity, in order to achieve reproducibility on the processing methods developed. In this review, we will discuss the most recent literature on the use of GO and RGO as functional nanomaterials for the preparation of nanostructured films, fibers, and membranes.

2 GO films

Films have been linked to human technological processes for several thousand years. Cellulose film, better known as paper, was and perhaps still is, the most used media to store information quickly, permanently, in a mobile device, using a limited space. Nowadays, however, the applications of films have extended to many other fields, such as packaging, construction, industry, and flexible electronics. The discovery that GO can form freestanding films has been long known, because the filtration of GO aqueous dispersions leads to the deposition of a very thin film attached to the filter that, after drying, can be peeled as a freestanding film. Thus, filtration became the most straightforward method to prepare GO freestanding films. After the breakthrough publication of Dikin et al. [20], discussing the outstanding mechanical properties of this material, many groups worldwide have shown interest for developing GO and nanocomposite GO papers, and these reports have been reviewed elsewhere [21, 22].

The filtration method is depicted in Figure 1A. Basically, a GO aqueous dispersion is forced through a filter, using either vacuum or high pressure, and while the water passes through the filter, the sheets are deposited on the surface forming a compact layer with a high degree or sheet orientation. The mechanism for GO sheet ordering and film formation [25], and the relation between structure, hydrogen bonding, and mechanical properties, has

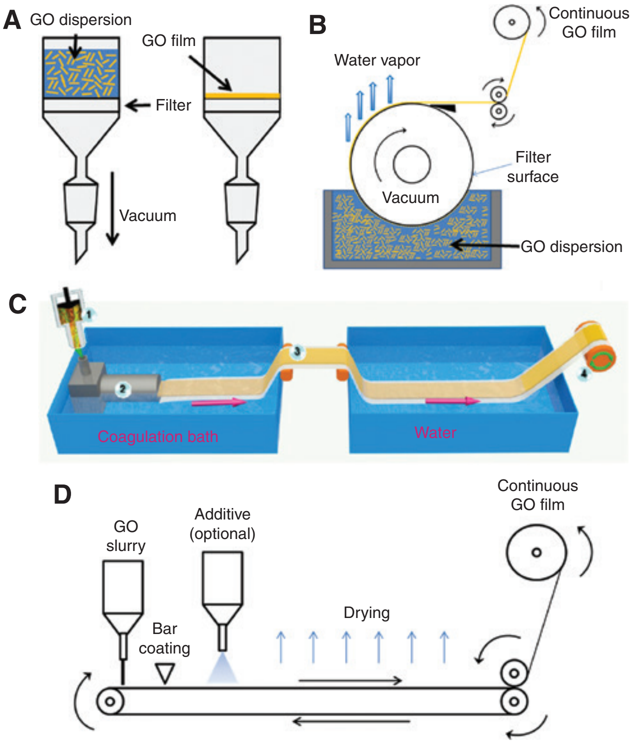

Figure 1: Schematic diagrams depicting the methods for preparing GO films. (A) Vacuum filtration (batch), (B) continuous vacuum filtration or casting, (C) continuous slit-die wet spinning [23], and (D) continuous blade coating [24].

been studied using techniques such as high-resolution scanning electron microscopy and X-ray diffraction. A typical problem is the adherence of the film to the filter, but this can be easily resolved by using non-sticky or rigid filters, such as those made of fluorinated polymer or anodized alumina, or by applying a positive pressure at the end of the filtration process. However, although alumina is probably the most used type of filter for preparing GO films, recently, Yeh et al. [26] found that alumina ions released from anodized alumina filters might react with GO following a mechanism that has been long known and used to strengthen the mechanical resistance of GO films [27]. Theoretically, the filtration method can be applied in a continuous process such as that shown in Figure 1B, but there are no experimental reports on samples prepared in this way. Indeed, an important limitation of the filtration method is the production of limited size samples, and the high amount of energy and time required during fabrication. The colloidal nature of GO prevents the use of standard film production methods, and few continuous processes have been reported. In this context, Liu et al. [23] have shown that slit-die extrusion of concentrated GO dispersions can result in the continuous formation of GO films with thicknesses ranging from 1.5 to 10 µm. This process takes advantage of the colloidal instability and cross-linking of GO dispersions. Figure 1C shows the typical arrangement, whereby the GO concentrated dispersion is extruded into coagulation bath containing an ethanol/water/calcium chloride bath, and then continuously transferred to a washing bath. The film is then dried and rolled up with a production speed up to 1 m/min. Using a different approach, large-area film production can be achieved using blade coating of GO dispersions onto non-adherent surfaces such as Teflon. In principle, this process can be continuous, as shown in Figure 1D. Blade coating of a GO aqueous dispersion with liquid crystalline order (Figure 2A) and large sheet size (Figure 2B) resulted in large-area films (900 cm^2; see Figure 2C) with thicknesses in the range 500 nm to 20 µm. These films were dried in a low relative humidity environment at temperatures between room temperature and 60°C. The drying mechanism is shown in Figure 2D, and fractured images of the films revealed the formation of a stronger and ordered skin on top and bottom of the films (Figure 2F). This skin imparts a thickness-dependent mechanical behavior that is a result of a different degree of ordering, as reported by

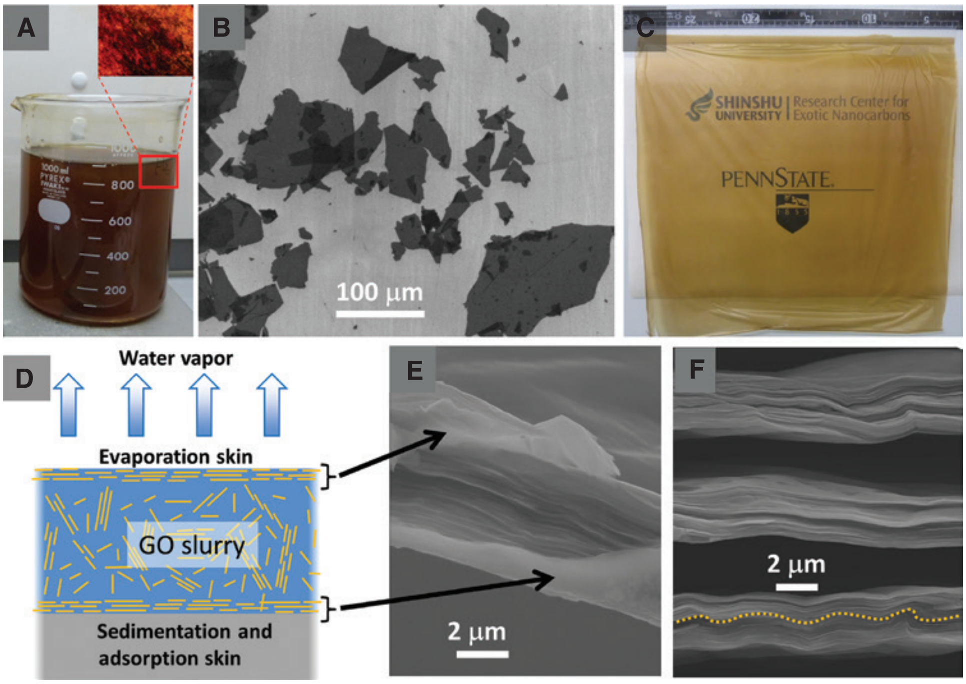

Figure 2: Graphene oxide films can be prepared by blade coating. (A) A 1-l beaker containing the GO slurry. The inset shows the dispersion under cross-polarizers. The red and green birefringences indicate the presence of liquid crystalline order in the dispersion. (B) The sheet size can be measured by SEM after drying the diluted GO dispersion. Sheets up to 100 µm in lateral size can be observed. (C) Large-area freestanding GO film with a density of about 0.4 mg/cm^2 and average thickness of 1.4 µm. The films do not tear easily and can be manipulated in ambient conditions. (D) Mechanism of drying of the GO film. (E) SEM cross-sectional image showing the formation of a “stronger” skin on both surfaces of a 4.7-µm-thick film. The arrangement of the GO sheets parallel to film surface can be seen, and (F) shows the cross section of a GO film prepared by blade coating. The yellow line is added as a guide to show the waviness of the sheets.

us and others [24, 28]. Similarly to films made by filtration, thicker films produced using blade coating possess lower ordering when compared to thin films made by the same technique, and the waviness of thick films is evident on the cross sections (see Figure 2E). Comparatively, films of the same thickness made by blade coating exhibit lower order when compared to those made by filtration, thus resulting in films with lower moduli but dramatically higher elongation to fracture and toughness. Several methods have also been used to increase the mechanical properties of graphene papers, being cross-linking the more common. Both metallic ions such as calcium, magnesium [27], or aluminum [26] and organic compounds [29] result in GO films with higher Young's modulus and improved water resistance. The main methods and their general features to prepare GO films are summarized in Table 1.

3 Electrically conductive RGO films

One of the most attractive features of GO is that it can be used to prepare electrically conductive RGO papers. The preparation of RGO papers can be done either by chemical or thermal reduction of GO papers [32, 35], or by filtration of stabilized RGO dispersions [30, 36]. Chemical reduction of GO films is relatively easy, and a wide range of reducing agents can be used. In spite of its toxicity, hydrazine is one of the most common and effective reducing agents for GO films, which provides good deoxygenation and good electrical conductivity [37]. It is low cost, has a strong reducing power, quickly reduces the GO, is water soluble, and decomposes thermally into gases; thus, it can be eliminated by washing or by thermal treatments. Concentrated hydrazine solutions can also behave as a stabilizer due to the strong alkaline nature of the hydrazine solutions [38]. For the thermal reduction, low temperature [35] and slow heating [32] need to be used in order to avoid the formation of pores, film cracking, or weakening due to fast gas evolution. Some of the applications of these electrically conducting films are in the preparation of energy storage devices such as capacitors and batteries. Wang et al. [39] used electrically conducting RGO paper to electrochemically deposit polyaniline. The combination of its high electrical conductivity with its layered structure and high surface area makes it an ideal support for the pseudocapacitive polyaniline. The resulting supercapacitor had great volumetric and gravimetric capacitance, combined with a convenient flat and flexible shape. This approach has also been used to prepare RGO paper-supported capacitors containing metal oxide nanoparticles such as manganese dioxide [40, 41] and conducting polymer-manganese dioxide mixtures [42]. In the field of batteries, RGO papers containing silicon nanoparticles [43] have been used as electrodes. In this case, the graphene sheets not only worked as efficient current collectors, but also limited the degradation of silicon nanoparticles after lithium intercalation. This is most likely due to the wrapping effect of the graphene sheets, providing mechanical support to the individual silicon nanoparticles increasing their cycling stability.

4 GO fibers

In the past, fibers were used to make yarns for making clothes, in order to insulate and protect people against the environment. Fibers were soon used for other applications. For instance, they were twisted into ropes, the simplest flexible device to transfer a mechanical load, thus enabling the first mechanical machines and also weapons. In the XIX century, electrically conducting single filaments made of metal were developed to transfer electricity, and this resulted in the invention of the electrical wire. To date, wires are still used to transfer power electricity, either in a small device or in the worldwide transmission network, and have been always made of metals; however, recently, after developing electrically conductive fibers made of carbon nanotubes [44, 45] and RGO [23], these

Table 1: Methods of preparation of graphene oxide films.

Method	Microstructure	Disadvantages	Energy/time input
Vacuum filtration [20, 26, 30]	Highly ordered structure	Limited size	High energy and time consuming
Casting [31]	Ordered	Time consuming	Low
Blade coating [24]	Ordered structure	Dewetting limited thickness	Low
Slit-die wet spinning [23]	Highly ordered	Limited thickness	Low
Layer-by-layer assembly [15, 32]	Highly ordered	Limited to small size sheets	Very high
Spray coating [33]	Disordered	Inhomogeneous thickness	Very low
Interfacial assembly [34]	Disordered	Mechanically weak films	Variable

materials have started to become an alternative in terms of transmitting electric power. Due to their high electrical conductivity and outstanding mechanical properties, several groups investigated the formation of GO-based fibers. However, due to processing challenges, this target has not been easily achieved. It is important to point out that polymer fibers have been reinforced with GO sheets, but in this section we will focus on fibers where GO plays a key role as the structural material.

Depending on the oxidation conditions and the graphite source, the GO oxidation degree, mechanical properties, colloidal stability, and sheet size different GO-based materials could result [11]. GO dispersions can be dispersed in water in concentrations high enough to form a solid after a phase inversion process, similar to polymer solutions. Due to the highly anisotropic shape, these highly concentrated dispersions usually self-assemble into liquid crystal phases [46–48] that have a high solid content. When these aqueous dispersions are immersed in an excess of water-miscible organic solvent, a phase inversion occurs, and GO precipitates into an elongated semisolid gel that can be winded out of the solvent (Figure 3A). After drying, this precipitate densifies and transforms into a solid GO fiber. This process is known as wet spinning and was used for the first time by Xu and Gao to prepare GO fibers from their water dispersion by precipitation into a methanol/NaOH coagulating bath using a continuous process [51]. The process is relatively easy to scale up with multiple spinnerets, as shown by Jalili et al. in Figure 3B [46, 49]. The preparation of GO fibers by wet spinning has been a prolific field in the last few years and has been recently reviewed by Xu and Gao [53]. Wet spinning can be modified also to prepare nanocomposite GO fibers by adding a second material on the GO dope. GO nanocomposite fibers can also be prepared by chemical grafting of GO with polymers followed by the above-mentioned wet-spinning process. If the amount of polymer is limited, the morphology and electrical conductivity of the RGO is maintained, while new properties such as chemical resistance or toughness can be transferred to the fiber. Poly(vinyl alcohol) (PVA) stabilized with GO was prepared by *in situ* reduction of GO in a PVA solution. These process-reduced GO sheets could then be wet spun into kilometer-long fibers [54], and able to reach Young's moduli of about 10 GPa and electrical conductivity values up to 351 S/cm after chemical reduction in hydroiodic

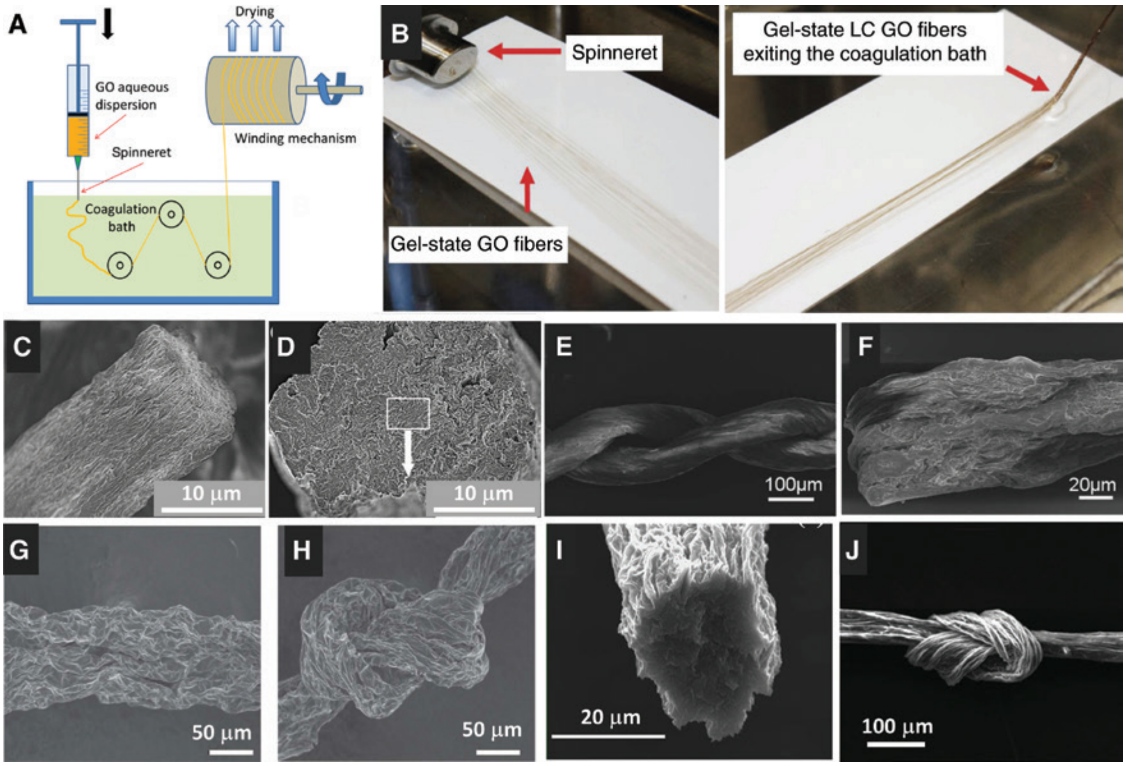

Figure 3: Wet spinning of GO dispersions and different morphologies can be obtained. (A) General scheme of the GO wet-spinning process. (B) Multiple spinneret GO fiber production [49]. Different fibers obtained by several groups: (C) and (D) GO by Jalili et al. [49], (E) and (F) chemically reduced GO by Cong et al. [50], (G) and (H) chemically reduced GO from Xu and Gao [51], (I) thermally reduced GO and (J) large flake GO from Xiang et al. [52].

acid. Similarly, polyacrylonitrile (PAN)-grafted GO [55] and poly(methyl methacrylate)-grafted GO [56] have also been wet spun into electrically conducting fibers with outstanding mechanical properties.

However, one of the challenges of wet spinning is the preparation of smooth-surface GO fibers. This is particularly important for the development of textiles, because when fabrics made with these fibers are in contact with the skin, the fabrics made with smooth-surface fibers usually have a *silky* feeling, while those made with rough-surface fibers might be felt as uncomfortable. The GO dispersions usually contain a large amount of water, and during the phase inversion process, the surface of the cylindrically extruded GO suspension turns harder faster than the core of the fiber. When these GO-containing hydrogel fibers release the rest of the water and dries, the surface deforms due to the fiber reduction volume, and similarly to a raisin, the fibers wrinkle considerably as can be seen in the scanning electron microscope (SEM) images of the fibers prepared by different groups, shown in Figure 3C–J. Wet spinning is suitable to prepare not only pure GO but also nanocomposite fibers by dispersing a second material on the GO dispersion. Using this approach, GO reinforced with electrically conductive silver nanowires [57] and nanotubes [58] have been obtained. Using the same approach, clay-reinforced GO fibers have been prepared by wet spinning, resulting in fibers with greater oxidation resistance [59]. Another modification of wet spinning is by using an annular die during the spinning process, thus resulting in the extrusion of hollow fibers [60].

Another technique used to prepare fibers is the self-assembly of polyelectrolyte-functionalized GO sheets. With this technique, Zou and Kim prepared fibers using anionic and cationic polyelectrolytes as adhesives and the liquid-water interface [61]. Dong et al. developed a different approach to make RGO fibers by reducing hydrothermally a concentrated GO dispersion within a cylindrical tube [62]. The RGO matched the container shape and reduced its size, and after drying an electrically conducting porous fibers with good flexibility was obtained [63]. Extruding concentrated GO dispersion with liquid crystalline order into liquid nitrogen followed by freeze drying constitutes another method able to obtain a highly oriented porous GO sponges, that after twisting results in a GO fibers [64]. Twisting a graphene paper is another approach that was used in our group [24] and others [65, 66], and this idea has been borrowed from the previously developed carbon nanotube fiber technology [45]. Figure 4A shows different snapshots of the twisting of a GO film into a fiber, where reduction in the length and transformation into a homogenous fiber can be seen. Figure 4B shows a SEM image where the folding process is seen in detail. The morphology of the fibers is dependent on the film thickness and fiber diameter as seen in Figure 4C–E. Interestingly, scrolled GO fibers show an almost perfect circular cross section, and smoother surface, as compared to wet-spun GO fibers. We studied the mechanism of deformation of the GO thin films, and found a thickness-dependent bending behavior that can be seen in Figure 4G,H. It can be observed that ultrathin films exhibit a more plastic behavior compared to the thick ones, most likely due to the reduced thickness. This method is also suitable for the preparation of nanocomposite fibers, two examples showing WS_2 and nylon composite fibers are shown in Figure 4I and J, respectively.

The applications of graphene fibers are promising, covering mainly smart textiles [46, 49, 67], energy devices, and actuators [65, 66]. However, the main challenge in GO fiber technology is to control the morphology of the wet-spun fibers, avoiding their mechanical fragility after reduction.

5 GO membranes

5.1 Nanocomposite reverse osmosis (RO) membranes for separation technologies

The origin of the use of carbon in purification technologies is as old as civilization itself, and the good absorption characteristics of many types of carbons have been studied for many years [68]. However, using carbon as an adsorbent results in the saturation of the pores and, consequently, the process stops and the adsorbent should be substituted. Nevertheless, carbon adsorbents are so efficient that they have been used widely as active materials in many filters for organic compounds and heavy metal ions. Nowadays, 2D carbon materials belong to a particular family of materials with large surface and atomic-scale thickness. While the GO thickness is <1 nm, their lateral dimensions could easily exceed 100 μm. These layers could be assembled into stacked structures, thus resulting in a structured material with monodisperse slit pores and superior mechanical properties. These kinds of GO film structures can be assembled using various techniques: vacuum filtration [20], casting [31], blade coating [24], spray coating [33], spin coating [69], polyelectrolyte-induced layer by layer self-assembly [70], and Langmuir-Blodgett [71]. Due to the presence of functional groups in GO, these stacked layers would not only separate substances by size exclusion but also by electrostatic repulsion [72]. Consequently, a new kind of separation

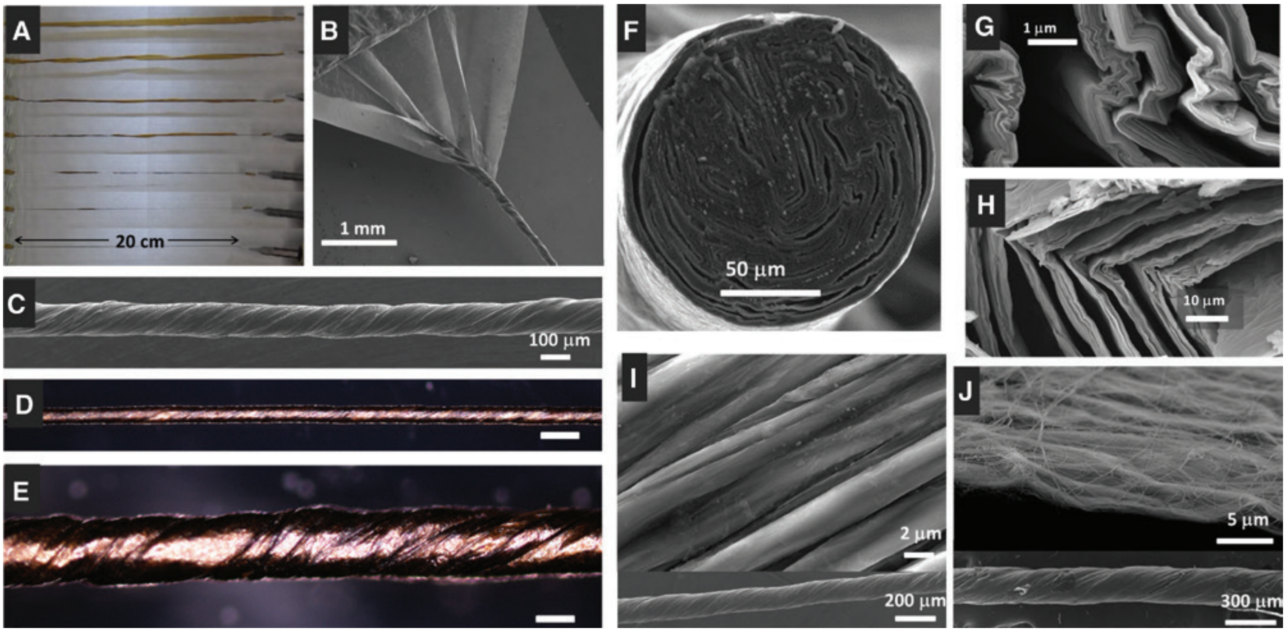

Figure 4: GO fibers prepared by scrolling GO films. (A) Snapshots of the scrolling process. (B) SEM showing a detail of the scrolling area. (C) SEM image of a typical scrolled GO fiber. (D) Optical microscopy image of a GO fiber made with very a thin film (approximately 700 nm). (E) GO fiber produced with a thicker film (2.9 µm thick). (F) SEM image of a cross section of a GO film made by scrolling after being cut using a focused ion beam. (G) Folding behavior of the 700-nm and (H) 2.9-µm-thick GO films. (I) and (J) show nanocomposite films (top) and fibers (bottom) made with tungsten disulfide and polymer nanofibers, respectively.

materials has been born with these novel 2D nanocarbons, as they take advantage of the highly monodisperse pore distribution, good mechanical properties, and tunable surface chemistry. Theoretical studies by classical molecular dynamics suggest that chemically modified GO membranes can reach high salt rejection (near 100%), and water flows up to 100 times higher than those shown in currently used membranes [73]. In another theoretical work, Sun et al. [74] studied the thermodynamics of ion transport across GO membranes using first-principles calculations based on the plane-wave-basis-set density functional theory approach. The calculations suggest that the separation mechanism is balanced between the cation-π interactions with the sp^2-hybridized clusters of GO sheets, and the desolvation effects of the ions.

Hu and Mi [75] first proposed to use layered GO films as a separation membrane. In order to avoid redispersion of the GO in aqueous media, the GO structure was cross-linked by a chemical reaction using trimesoyl chloride, which reacts with the carboxylic groups located mainly at the edges of the GO sheets. This multilayered hydrophilic structure allowed the flow of water while rejecting other compounds either by size exclusion or electrostatic repulsion. The authors realized that the separation properties of the membrane could be controlled by modifying the functionalities and spacing of the GO sheets. One of the advantages of GO is the facility to prepare ultrathin films (e.g. >500 nm). Han et al. [76] prepared nanofiltration ultrathin membranes using GO sheets by filtration and calculated that up to 1 m^2 of membrane could be prepared using only 34 mg of GO. These membranes are negatively charged and rejected >99% of organic dyes. Kim et al. [77] investigated thin film nanocomposite RO membranes with high chlorine resistance made by cross-linking GO and aminated GO sheets using trimesoyl chloride. Salt rejections were then evaluated by cross-flow filtration and were found to be as high as 98%, with considerably high chlorine resistance when compared to typical polyamide membranes.

GO has also been used as an additive to improve the performance of polymer-based RO membranes. Safarpour et al. [78] found that by adding only 0.02 wt.% of RGO/titania nanocomposite to polyamide reverse osmosis membranes, the antifouling behavior and chlorine resistance of the nanocomposite membranes could be considerably improved. Indeed, after the chlorine resistance test, the control membranes decrease their salt rejection by 30%, while the RGO/titania membranes suffered only a 3% reduction. The chlorine resistance improvement is attributed to the lower reactivity of the nanocomposite membrane against chlorine due to interaction with the functional groups of the reduced GO. Kim et al. [79] prepared an aromatic polyamide/GO/CNT nanocomposite membrane with enhanced chlorine resistance, water flux, and mechanical behavior when compared to pure PA membranes. In this case, the GO helps disperse the CNTs due to their surfactant properties [80]. Bano et al. [81] also prepared GO/PA nanocomposite membranes, and found that flow increased in 1200% without affecting the salt rejection. The increased hydrophilicity of the membrane also resulted in a moderate improvement in antifouling property.

Gahlot et al. [82] prepared cellulose-supported membranes with a nanocomposite active layer made of GO and titania by filtration. These membranes were further photocatalytically reduced, in order to increase their hydrophobicity and salt rejection (e.g. up to 95% of salt rejection). The authors concluded that the hydrophilic TiO_2 nanoparticles intercalated between RGO sheets might be the reason while the water permeation did not decrease considerably. Similarly, GO membranes were deposited on the surface of hollow ceramic fibers [83] showing good filtration performance for organic solvents such as acetone and methanol, and a sharp cutoff of about 300 Da with higher flux than most commercial membranes. Joshi et al. [84] studied the permeation of ions across graphene membranes in the wet state, and found an atypical transport behavior. The monodisperse pore size provides this material with molecular sieve properties in which the pores size increased considerably if wet, thus allowing only ions with radii lower than 4.5 Å. The diffusion of small ions along these capillaries is several orders of magnitude higher than expected from single diffusion. The behavior is attributed to the well-defined slit pores of GO membranes that offer strong capillary forces, also known as super pressure effects.

Another positive outcome of incorporating GO on reverse osmosis membranes is its potential antibacterial activity [85]. Perreault et al. [86] prepared surface-functionalized aromatic polyamide RO membranes with GO by covalent bonding. The resulting GO was strongly attached to the membrane and kept its antibacterial properties. Indeed, these membranes showed bactericidal inactivation against *Escherichia coli* without affecting the transport properties. He et al. [87] added 0.12 wt.% of GO to the aromatic polyamide RO membranes, resulting in a flux increase of 80% with no negative effects on the salt rejection. The GO also enhanced the membrane hydrophilicity and shifted its surface charge to higher pH. These characteristics provided the membrane with better resistance against bacterial growth, which might result in long-term antifouling. Therefore, it is clear that GO is becoming a viable alternative to modify the surface of membranes providing properties such as antibacterial, antifouling, and separation properties. Choi et al. [88] modified the surface of PA membranes with GO sheets, improving the hydrophilicity, water flux, and chlorine resistance, while decreasing the surface roughness. Both higher hydrophilicity and lower surface roughness have been directly linked to better antifouling behavior, thus resulting in positive features of the membrane modification. Similarly, Wang et al. [89] functionalized the surface of carboxymethyl cellulose/quitosan nanocomposite nanofiltration membranes with modified GO. In these cases, the improved performance results from the formation of a functional layer with size exclusion properties and high electrostatic water repulsion. GO has the advantage of not only possessing various functional groups, but also electrostatic charge. Due to this rich chemistry, several methods have been developed to modify the surface of membranes with GO, and some of them are shown in Figure 5. Covalent modification of GO to optimize its electrostatic assembly (Figure 5A) or covalent bonding (Figure 5B) has been carried out through the carboxylic acid groups on the edges. Another technique has been the electrostatic surface adsorption (Figure 5D) or the layer-by-layer assembly (Figure 5D).

5.2 Proton conducting and forward osmosis GO-based membranes

Recently, Paneri and Moghaddam investigated the transport of GO membranes as a function of sheet size and GO synthetic method [90]. They found that GO membranes prepared using the modified Hummer's method exhibit lower permeation properties, fewer number of ion exchange sites, smaller interlayer spacing, and a shortened transport path, when compared to those membranes made with GO obtained by Marcano et al. [16], and explained most likely due to the lower oxidation degree. Sulfonated GO has been used as additive of sulfonated polyethersulfone (SPE) for proton-conducting membranes, thus increasing their proton conductivity to almost twice of that of pure SPE, and increasing the water retention while keeping constant its swelling ratio [82].

5.3 Gas and pervaporation separation membranes

Nair et al. [91] found a very interesting permeation behavior on GO membranes made by filtration (Figure 6A) that consists of several hundred of GO sheets assembled parallel to the film (Figure 6B). The authors found that water could evaporate freely across the GO membrane while

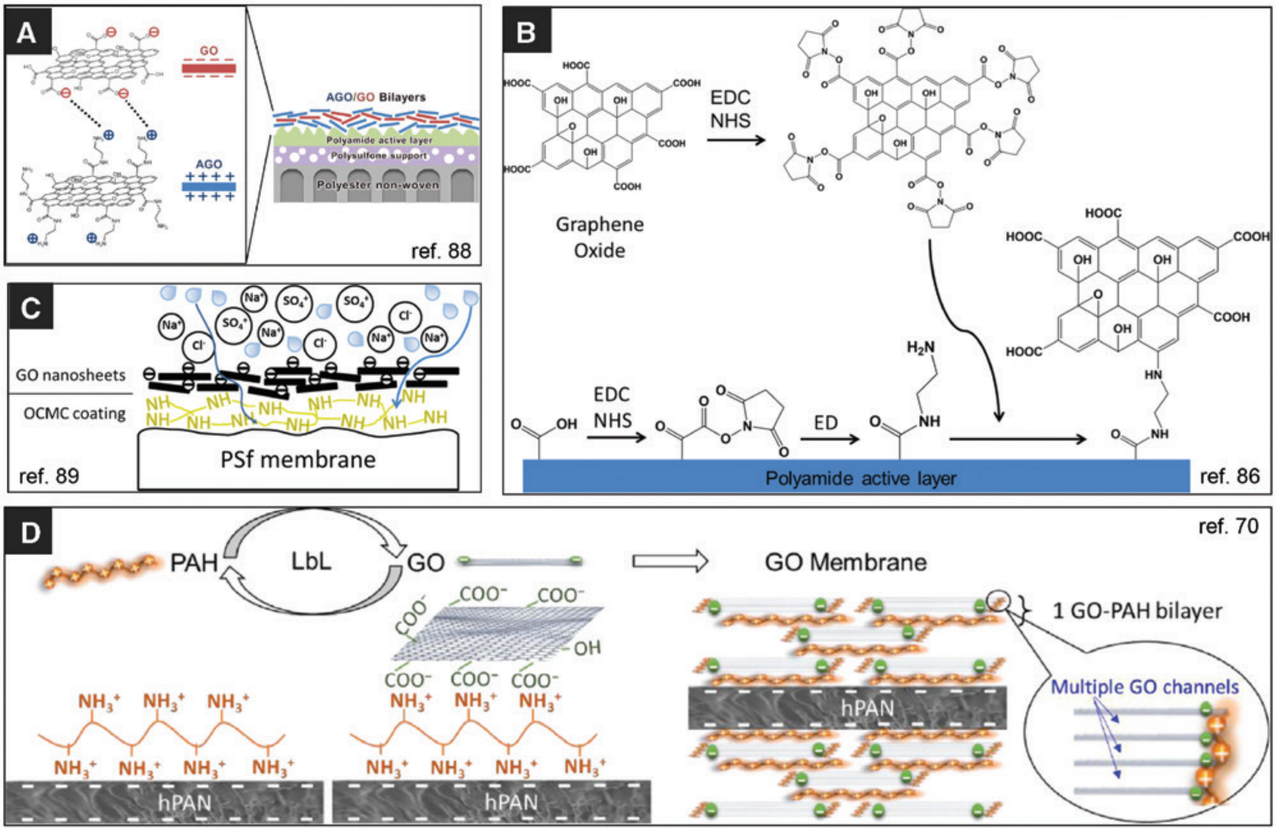

Figure 5: Surface functionalization of membranes with GO proposed by several authors. (A) Electrostatic assembly of oppositely charge functionalized GO. (B) Amino coupling of N-hydroxysuccinimide functionalized GO. (C) Electrostatic adsorption of GO. (D) Polyelectrolyte-aided layer-by-layer assembly of GO.

other substances such as ethanol, acetone, or hexane could not permeate through. In spite of the high water vapor permeability, not even small gas molecules such as helium could pass through the membrane (Figure 6D,E). The superpermeability of water across the GO is explained by the almost friction-free flow of a water monolayer molecules between the graphitic domains within the GO sheets, similar to the superfluidity of water inside carbon nanotubes [92]. The reason for this contrasting behavior between the permeation of water and other molecules is explained by the blocking of the slit pores of GO due either to contraction in low-humidity environments or by clogging with water molecules. Li et al. [93] prepared ultrathin GO membranes with molecular sieving properties by simple filtration over anodized alumina supports. These membranes were highly permeable to hydrogen as compared to carbon dioxide and nitrogen, with selectivity ratios considerably higher than those of silica-based molecular sieves. Kim et al. [94] prepared GO membranes using two different methods, spin coating and air/liquid interfacial deposition. The membranes showed high O_2/N_2 selectivity, and the permeation could be improved by thermal treatment at moderate temperatures (140°C). They also found that the membrane behavior could change from a molecular sieve to a nanoporous membrane when they change the preparation method from spin coating to interfacial deposition. This confirms the importance of the GO sheets stacking and arrangement.

The mechanism of gas separation through GO membranes has also been studied by molecular dynamics simulation [95]. This theoretical study shows a strong dependence of gas separation properties with interlayer spacing and the surface chemistry of the membrane. GO has many polarized groups such as carbonyl, hydroxyl, and carboxylic groups, particularly when it is fully oxidized. However, it can also be easily functionalized with amino groups in many ways, thus offering an effective material for CO_2 separation. Polymer/GO nanocomposite membranes can also show improved performance. Polyether block amide filled with a small amount of GO exhibited improved performance against the separation of CO_2 from N_2. The membranes showed high selectivity (91 CO_2 to N_2) and high permeability, with improved operational stability. Using a similar polymer matrix,

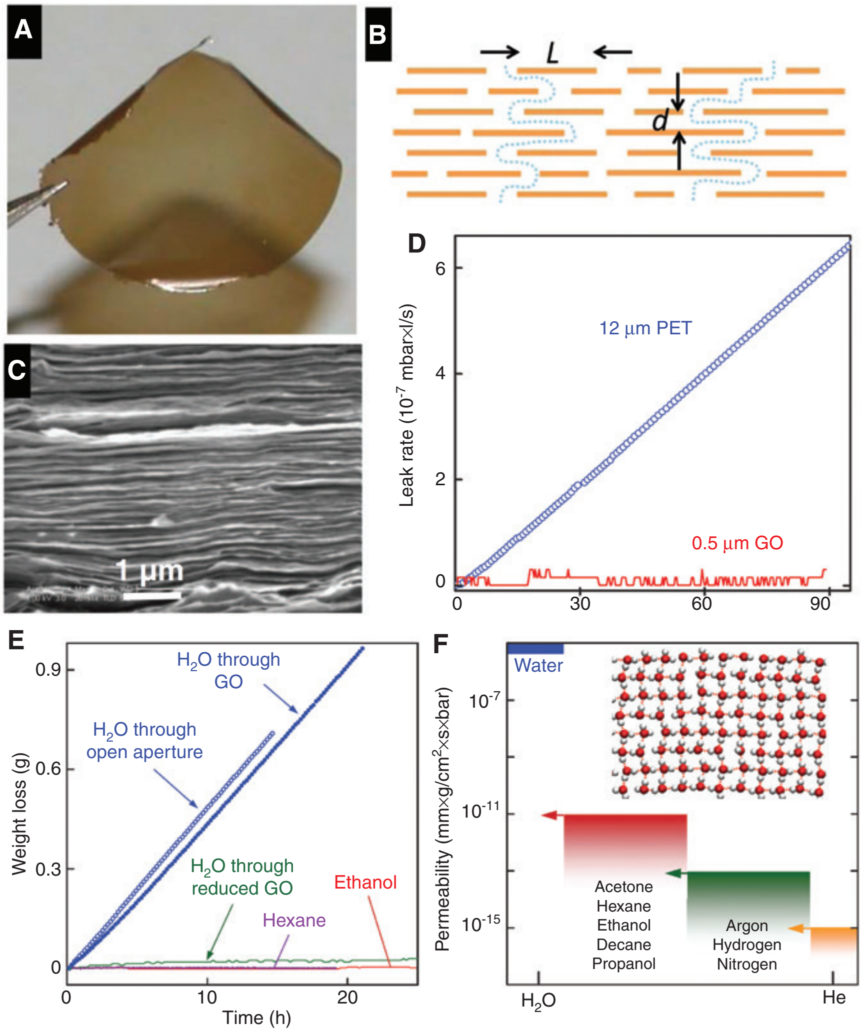

Figure 6: Image of a typical freestanding GO membrane prepared by vacuum filtration. Adapted from Nair et al. [91]. (A) Optical photograph of a film. (B) SEM cross-sectional image showing the structure of the film. (C) Model of permeation through the GO film. (D) Leak rate of helium across a polyethylentherephtalate film and GO. (E) Evaporation of water, hexane, and ethanol across the GO membrane. (F) Comparison of different gas and liquid permeabilities against water.

polyethyleneimine-modified GO, Li et al. [96] also improved the CO_2/N_2 selectivity of the polymer membranes. The mechanism is caused by an increase in the effective path of gaseous molecules across the membrane due to the high aspect ratio of the graphene nanosheets. In addition, the abundance of nitrogen groups in the polyethyleneimine can improve the molecular interactions, thus promoting the CO_2 transport. In another work [97], using a low amount of GO, 1.0 wt.%, as a filler in polyimide membranes, both the selectivity and permeability performance for CO_2/N_2 mixtures was improved. In this case, it is believed that polar groups of GO can interact with the CO_2 molecule, promoting its transport across the membrane. GO modified with amino groups from polydopamine and cysteine has also shown reliable properties for CO_2 separation, with selectivities as high as 82 and 115 for CO_2/CH_4 and CO_2/N_2, respectively [98]. Ultrathin membranes of <5 nm were prepared by Kim et al., showing excellent separation of CO_2/H_2, CO_2/N_2, and CO_2/CH_4 mixtures, with good permeability but only under humidified streams [99]. It was found that water-swollen channels of GO were necessary to allow the necessary interspace needed. In this context, Koolivand et al. [100] used pristine, polyethylene glycol-modified GO, and aminated GO as fillers in polyetherimide membranes to study CO_2/CH_4 separation. The chemical modification of GO had a strong effect on the performance of the membranes, due to the formation of different free volumes around the GO nanosheets. For the aminated GO, the selectivity was as high as 142. Boutilier et al. recently examined the

Table 2: Applications of GO and graphene hybrid composite membranes in separation technologies.

Material	Membrane details	Feed	Selectivity
Pure GO [103]	Pressurized ultrafiltration deposition	Water/ethanol 15:85 wt ratio	227 Water to ethanol
GO supported on ceramic membrane [104]	Vacuum suction deposition	Dimethyl carbonate/water 97.4:2.6 wt ratio	19.8 Water to dimethyl carbonate
GO supported on silane-treated ceramic [105]	Dip coating	Water/ethanol 5:95 wt	0.67 Water/EtOh
GO/chitosan hybrid membrane [106]	Solution casting followed by GA cross-linking	Water/ethanol 10:90; water/isopropanol 10:90	1093 Water/IPA; 3220 water/ethanol
GO/alginate hybrid membrane on PAN support [107]	Spin coating followed by Ca^{2+} cross-linking	Water/ethanol 10:90	1200 Water/EtOH
Pure GO on polyacrylonitrile support [108]	Vacuum filtration-assisted assembly method	Water/sodium chloride 90:10 (direct contact distillation)	99.8% Salt rejection
Phenyldiboronic acid pillared graphene oxide/polyvinyl alcohol hybrid membrane supported on porous alumina [109]	Dip coating	Methanol/dimethoxyl methane 10:90 Methanol/dimethyl carbonate 10:90	390 Methanol/dimethoxyl methane 350 Methanol/dimethyl carbonate
Pure GO supported on PAN [110]	Pressure-, vacuum-, and evaporation-assisted self-assembly	Water/1-butanol 10:90	2241 Water/butanol
GO supported on alumina [111]	Filter-pressing deposition method	*n*-Propanol, *i*-propanol, ethyl acetate, and butanol/water	4623 Water/isopropanol

role of microstructural defects on GO membranes [101]. GO hybrid films have also been used for pervaporation studies. Zhao et al. [102] prepared hybrid GO/gelatin films by layer-by-layer assembly on top of partially hydrolyzed PAN membranes. These films showed a high flux, 2.27 l/(m^2 h), and water purity of 98.7%, when a 20:80 water/ethanol was fed. It is clear from these results that GO membranes have great potential in the field. However, the results between different research groups sometimes differ. We believe the differences in GO size and oxidation degree, and the methods of membrane preparation, are the reasons behind these dissimilar reported results. Table 2 shows some of the promising reports recently reported for GO separation of organic solvents.

6 Future challenges

GO has shown attractive properties that enable its use as building block in the preparation of different types of functional structural materials. Besides the applications discussed in this review, GO and RGO are very interesting materials for many other applications such as energy storage [112–114], oil [115], and heavy metal [116] recovery from wastewater, electrically conductive ceramics [117], chemical sensors [118, 119], bioimaging and drug delivery [120–122], among many others. However, there are still several issues that must be solved in order to allow its application at the industrial scale. GO synthesis still involves the use of strong oxidizers that are difficult to handle, and up to date, no real large-scale method has been developed to prepare GO in kilogram quantities. Due to its highly anisotropic morphology, high viscosity in aqueous dispersions, and the tedious purification and removal of synthesis by-products, efficient methods to purify large quantities of GO must be developed. GO dispersions can differ considerably due to the nature of the pristine graphite used, the oxidation degree, and the processing conditions. These affect the sheet size, and consequently its viscosity. GO is known to be an energetic material and chemical additives and storage protocols must be found to make it safe when industrially processing. In addition, the long-time environmental stability of GO is still under investigation, as GO seems to be quite reactive and could have an environmental impact when degrading. Nevertheless, due to the fascinating and unique properties of both GO and RGO, a large number of applications within these fields will most likely be developed in the coming years.

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