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Green Routes for Graphene Oxide Reduction and Self-Assembled Graphene Oxide Micro- and Nanostructures Production

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Abstract

Graphene-derived materials are currently studied because of their actual and projected applications. Among them, graphene oxide (GO) promises for outstanding applications as it can be prepared at large scale by simple, scalable, and low-cost techniques. The existent chemical methods based on the graphite exfoliation (phase solution and Hummers based) produce highly functionalized graphene, i.e., GO-like materials that converts into reduced GO (rGO) after a reduction treatment. The present work presents the current scenario on the GO green reduction methods, on the development of hierarchical carbon-based structures by the self-assembly of GO sheets at interfaces, and on rGO-based hybrid nanocomposites. It is worth noting that, to date, the production and application of graphene-related materials are the fastest-growing research areas.

Keywords: graphene oxide, reduced graphene oxide, green reduction, metal, composites, self-assemble

1. Introduction

Graphene, one-atom thick layer of densely packed carbon atoms into a honeycomb crystal lattice, is considered the key building block of graphite, carbon nanotubes, and fullerenes [1]. It is of current interest due to its remarkable physical and chemical properties, which makes it

useful for theoretical studies for several technological applications. Current applications of graphene include flexible electronics, batteries, and so on [2]. Diverse methods have been proposed to produce high-quality single and few layer graphene films. Among them, graphite micromechanical cleavage, chemical vapor deposition, and graphitization of SiC have been the most utilized methods [3]. Although these methods produce high-quality graphene in a controlled way, they suffer from mass production scaling.

In the past years, graphene-derived materials, such as graphene oxide (GO), graphane (the hydrogenated version of graphene), graphene fluoride, and so on [4, 5] have been paid special interest because of their potential applications. Particularly, GO and its reduced version, reduced-graphene oxide (rGO), have emerged as a technologically important material by its their own right [6].

GO is mainly prepared through chemical methods and therefore achieves unique and useful physiochemical properties to prepare a variety of functional materials for a range of advanced applications, such as rGO self-assembled microstructures [7, 8] and, rGO-based composites with inorganic nanoparticles (metals, semiconductors, metal oxides). These GO-derived materials have successfully been tested in the technological areas of nanomedicine, electronics, environmental remediation, energy conversion, and others [7–9].

The chemical methods to prepare single-layer GO use graphite as the raw material, which is exfoliated either using strong oxidants in aqueous medium (based on Hummers' method) or using organic solvents (based on the solution-phase technique), among others [10]. During the graphite oxidation process, oxidative species intercalate into graphite galleries provoking the partial disruption of the graphene sp^2 -hybridization and the covalent attachment of oxygen-rich species. This results on the weakening of the interlayer attractive force, so that single-layer GO sheets are easily obtained upon application of low power sonication in water [8].

From a structural point of view, GO is considered as a graphene sheet comprising in-plane undisturbed π -conjugated domains, and functionalized ones with covalently attached hydroxyl and epoxy groups, and additional carboxyl and carbonyl groups located at the sheet edge [11]. This chemical structure gives GO an amphiphilic character and then makes it dispersible in polar or nonpolar solvents [12]. This amphiphilic character preserves in rGO because it is obtained after the partial remotion of these functional groups by a reduction process.

Interestingly, rich oxygenated groups attached to the graphene structure makes GO and rGO highly hydrophilic and susceptible for further functionalization. Therefore, pristine or reduced GO can conveniently be functionalized to facilitate the interfacial interaction between GO and other materials including polymers, metal oxides, and inorganic nanoparticles to form GO-based composite materials, or to link the sheets together and then lead to macroscopic GO-based materials [13, 14].

Due to its multiple applications, GO is produced at an industrial level. Nowadays, worldwide research groups are looking for ways to find cost-effective and environment-friendly methods for graphene-derived materials' mass production. These include electrochemical, mechanical, and chemical exfoliation of graphite [15]. In general, these methods produce GO-like materials,

i.e., functionalized graphene, and they may be further processed to produce rGO with multiple functionalities. To date, the phase solution graphite exfoliation-based methods have demonstrated their high versatility to fabricate bulk amounts of graphene-derived materials at relatively low cost [16].

There are diverse methods for GO reduction, such as thermal reduction, chemical reduction using toxic or green reductive reagents, and multistep reduction (either by combining chemical and thermal processes or by combining green and toxic reducers to get an effective reduction). Dangerous and toxic reagents such as hydrazine, oxalic acid, sodium hydrosulfite, and sodium borohydride were reported to reduce GO efficiently. On the other hand, GO environment-friendly reduction routes include flash photo reduction, hydrothermal dehydration, solvothermal reduction, catalytic reduction, and photocatalytic reduction. Furthermore, green reductants have also been essayed including vitamin C, alcohols, bovine serum albumin, gingseng, bacteriorhodopsin, bacteria, and polyphenols (present in green tea and caffeic acid, among others) [17, 18].

This work presents an overview on the environmental-friendly methods to reduce GO and produce GO-based nanocomposites. A survey of their applications is also presented.

In addition, we present the mechanistic aspects on GO-based nanocomposites, as well as those associated in the formation of GO nano- and microstructures by self-assembly process.

2. Green methods to reduce GO

For applications where the exceptional electrical conductivity and transparency of graphene are demanded, GO can be subjected to an additional chemical treatment to detach the covalently oxygenated groups on graphene basal plane and restoring the sp^2 -hybridization. As previously mentioned, the detected drawbacks for the chemical reductants, such as hydrazine, hydroquinone, and sodium borohydride [19], have fuelled the search for both environment-friendly methods and chemicals for GO reduction. The so-called “green technologies” satisfy both criteria, and the most reported green technologies may be classified, selected reducing agent, into four groups, as indicated in **Table 1**.

Green technologies	Reducer agent sources
Bioreduction	<ul style="list-style-type: none">•Bacteria•Plants•Commercial biomolecules
Photoreduction	<ul style="list-style-type: none">•Electromagnetic irradiation
Reduction by polymers	<ul style="list-style-type: none">•Polyelectrolytes
Aided-metal reduction (or reduction by metals)	<ul style="list-style-type: none">•Transition metals
Mechanochemical reduction	<ul style="list-style-type: none">•Ball milling system
Electrochemical reduction	<ul style="list-style-type: none">•Supporting electrolyte

Table 1. Representative green technologies for the GO reduction.

2.1. Green reducers and their effectiveness

2.1.1. Bacterial reducers

Bacteria are living beings capable of surviving under the most extreme conditions, i.e., in severe temperature and chemical composition. Bacteria have been found in the most warmed underwater pools, where tectonic plates emanate pernicious gasses and incandescent material or in lakes of extreme saline composition, surrounded by an environment that is highly concentrated in arsenic, such as those found in Mono Lake, California [20]. To survive, bacteria can take organic and inorganic molecules from the surrounding environment and transform them into the substance required to start the cellular process in which oxidation-reduction mechanism is employed to obtain an energy source [21, 22]. The overall redox process carried out by bacteria has been used in GO reduction by means of *Shewanella* [23], *Bacillus subtilis* [24], Extremophiles bacteria [25], *Escherichia coli* [26], and *Gluconacetobacter xylinus* [27].

Note that the involved reaction mechanisms depend on the bacteria cell structure, which determines the capacity for directly or indirectly hydrolyzing the acidic groups attached to the GO molecular structure, particularly, the groups that comprise oxygen atoms. Wang et al. [23] used *Shewanella* for reducing GO (**Figure 1**) through a mechanism that consists segregating the heme group proteins such as c-type cytochromes, through the membrane and these proteins act as electron intercessor [28].

Zhang et al. [24] reported that depending on the bacteria type, it is possible to select a process to efficiently reduce GO for specific applications of the final nanomaterial. It was also proposed that, in the bacteria-based reduction processes, the parallel action of different bacteria could increase the effectiveness of reduction process. Based on Zhang's observations, Raveendran et al. [25] achieved reducing GO using extremophiles bacteria, obtaining graphene with excellent conductive properties.

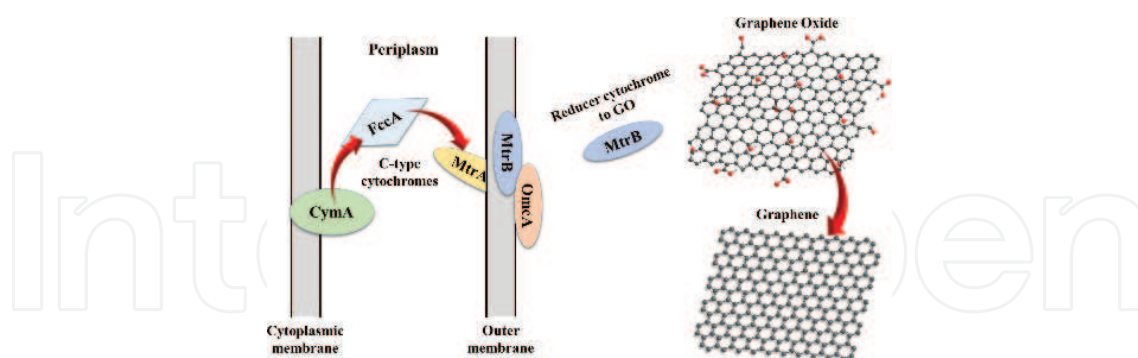


Figure 1. As bacteria, *Shewanella oneidensis* utilizes terminal electron acceptors during its respiratory metabolism. It transfers electrons from cell surface to any extracellular acceptor such as metal oxides or graphene oxide. It was proposed that GO reduction by *Shewanella* proceeds via an electron exchange among MtrB, MtrC and OmcA cytochromes to finally transfer an electron to GO and then reduce it.

2.1.2. Biological reducers

The chemical compounds naturally existing in plants (phytochemicals) have been used for years as nutrients, drugs, etc. In the past few years, phytochemicals, such as vitamins, amino

acids, saccharides, alkaloids, proteins, and enzymes [29, 30], have been studied as reductant precursors for metals and GO. The reported attempts for the GO reduction by using phytochemicals go into the employment of either laboratory-extracted (plant extracts) or commercial-purchased phytochemicals.

Herein, we present some relevant results emphasizing on the reductant chemical source.

2.1.2.1. *Plant extract reducing*

To date, the GO reduction by means of plant extract is intensively studied [31]. In this approach, the plant is chosen considering the antioxidant compound contents. For preparing the plant extract leaves, flowers, stems, and/or roots are refluxed in water, alcohol, or water-alcohol mixtures as solvents.

Green tea has proven to be an excellent source of antioxidant biomolecules. For example, it was successfully used for reduction of graphene oxide [32]. The reducing capacity of green tea is based on the antioxidant biomolecules extracted from emulsion, mainly polyphenols.

Extracts of chrysanthemum flower and lycium barbarum plants, used in the traditional Chinese medicine, were recently reported for GO reduction by Hou et al. [33, 34]. The extracts were obtained in aqueous media at boiling temperature and then filtered. Afterward, the extract was poured into the GO dispersion at the water boiling point for 24 h. The authors reported that the chemical composition of extracts, namely, chrysanthemum extract and flavonoids (diosmetin, luteolin, apigenin, and glucoside), were the predominant phytochemicals. Whereas the lycium barbarum extract comprised flavonoids, phenols, carotenoids, and polysaccharides as dominant phytochemicals.

The authors suggested that polyphenols present in chrysanthemum and lycium barbarum extracts transform to quinone releasing H^+ ions that interact with GO for reducing it. Importantly, chrysanthemum and lyceum barbarum plants hold promise to effectively reduce GO, because the C/O ratio values obtained by X-ray photoelectron spectroscopy (XPS) were 1.35, 4.96, and 6.5 for pristine GO, rGO-chrysanthemum, and rGO-lycium barbarum, respectively.

2.1.2.2. *Commercial reductants*

2.1.2.2.1. *Vitamins*

Vitamin C (L-ascorbic acid) has been widely used in GO reduction because of its reducing effectivity and is comparable to that of hydrazine, besides promoting highly stabilized dispersions of rGO sheets in water. It has been observed that oxidized L-ascorbic acid is unreactive and stable and does not provoke damage to living cells [31].

In some GO reduction reactions, L-tryptophan (an aromatic amino acid) has been considered as a stabilizing agent to prepare highly stable rGO aqueous dispersions [35]. It effectively prevents against agglomeration of the rGO sheets because it readily adsorbs on undisturbed π - π domains at the basal plane of the rGO chain, which minimizes the attractive π - π interaction. Furthermore, the remaining terminal carboxylate anion of L-tryptophan has provided an electrostatic repulsion between the individual graphene sheets.

The L-tryptophan-stabilized rGO dispersion prepared with vitamin C exhibited good electrical conductivity of 14.1 S/m (pristine GO: 5.72×10^{-10} S/m). The mechanistic aspects for the GO chemical reduction remains unknown, but a plausible reduction mechanism was proposed as comprising two-step S_N2 nucleophilic reactions. That is, L-ascorbic acid oxidizes into the dehydroascorbic anion releasing electrons and protons, which react with oxygenated groups on the GO sheet to reduce it.

The free-stabilizing agents including vitamin C-reduced rGO dispersions were also prepared by Zhang, who reported high stability for all the prepared samples. The electrical conductivity with a value of 800 S/m was obtained in the sample prepared for 48 h [36]. Fernandez-Merino et al. [37] reported that the reduction capability of vitamin C could be improved by increasing the alkali concentration into reducing solution; using this approach the reduction time was shortened to 15 min. Furthermore, rGO showed good dispersibility in polar organic solvents, with high C/O ratio (~12.5) as well as high electrical conductivity (7700 S/m). In addition, riboflavin (vitamin B2), phosphate salt of vitamin B2, and pyridoxine (vitamin B6) were used to reduce GO. These bioreductants have also been proven to successfully reduce GO [38].

2.1.2.2.2. *Saccharides*

Saccharides are nutrients that may be used as reducing agents; these are classified into four chemical groups: mono/di/oligo/polysaccharides. Monosaccharides, glucose, and fructose have demonstrated mild reductive ability and nontoxic property in GO reduction experiments. In general, their potential for reduction is closely related to the ease to form open-chained structures [31]. In the GO reduction, it was found that their oxidized products play an important role to stabilize rGO sheets in aqueous dispersions, i.e., they may act as capping agents. Both saccharides and their oxidized products are environmental friendly. Zhu et al. [39] used glucose, fructose, and sucrose in aqueous ammonia solution for the reduction of GO. They determined that the ammonia solution is useful for both completion and enhancement of the GO deoxygenation reaction rate. In addition, they found that the reduction capability of sucrose was weaker than that for the glucose and fructose, under similar reaction conditions. The resulting rGO powder was biocompatible and highly dispersible in water. Likewise, Akhavan et al. [40] found that glucose increases its power to reduce GO in the presence of an iron catalyst under neutral condition.

On the other hand, dextran (a polysaccharide) was tested as a GO reducer in aqueous ammonia [41]. However, the as-reduced rGO exhibited a rather low electrical conductivity (1.1 S/m) that can be notably improved (10,000 S/m) upon thermal annealing (500°C under Ar atmosphere).

2.1.2.2.3. *Amino acids*

L-Cysteine is a thiol-containing amino acid that is liable to oxidate to cystine. It inhibits oxidative properties because thiol groups can suffer redox reactions. Chen et al. [42] synthesized rGO using L-cysteine as reducing agent under mild conditions. They proposed the reduction pathway for GO by L-Cysteine might be like that observed in the GO reduction by vitamin C. That is, at first, the reactions comprehend nucleophilic attack by thiol groups, which develop upon proton releasing during the L-Cysteine oxidation process. Afterward, the released protons react with the oxygenated groups producing water and byproducts, inducing the GO reduction. The rGO suspension conductivity increases by about 10^6 times in

comparison to that of pristine GO. Bose et al. [43] used other amino acid such as glycine for reducing GO. They found that glycine not only reduces the GO but also functionalized it, as a result amine group can covalently bound to a GO network. In other work, L-Lysine was successfully used for reduction of graphene oxide in the presence of carboxymethyl starch (CMS) as stabilizing agent. The rGO suspension exhibited good dispersion stability in water [44]. Furthermore, L-aspartic acid has been employed for synthesizing rGO, the product obtained by this process also presents uniform separation in water as well as good electrical conductivity of ~ 700 S/m [45]. Other studies have revealed that some amino acids such as tryptophan, arginine, and histidine reduce the GO and also augmented the consolidation of rGO-metal nanoparticles [46]

2.1.2.2.4. Gallic and citric acids

Gallic and citric acids are natural organic acids that have been tested as GO reductants. It was found that both acids could play the dual role as a reducing agent and a surfactant. Li et al. [47] found that the GO can be significantly reduced by gallic acid in aqueous ammonia, either at room temperature or under heating condition. Although, the reduction mechanism of GO by gallic acid has not been explored, it is expected that its three adjacent hydroxyl groups (pyrogallol moieties) interact with the GO in-plane oxygenated groups. The prepared rGO suspensions displayed excellent dispersibility in various solvents such as H₂O, N-Methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), dimethylformamide (DMF), and methanol, probably due to adsorbed oxidized gallic acid.

On the other hand, citric acid has extensively been studied for the synthesis of silver and gold nanoparticles. Recently, Ortega-Amaya et al. [18] used the one pot approach to produce highly dispersible functionalized rGO by using citric acid. This process was made in aqueous medium at room temperature, under Ar atmosphere. To explain the dual role of citric acid as a reducer and a stabilizer, the authors assumed that protons released by the citric acid dissociation bind to epoxy or hydroxyl groups to form water molecules and an active carbocation at the GO network. Afterward, a di-ionized citrate HCit²⁻ anion covalently binds to the carbocation to stabilize it. The whole effect was one of reduction by protons, and functionalization by HCit²⁻ anion. Last one being the predominant specie in the aqueous solution at pH 4.

2.1.3. Irradiation as reducer

UV, microwave, or ultrasound irradiation have been used for transforming colloidal GO to graphene with a similar quality as that produced by means of hydrazine. In acidic GO colloids, Lu et al. [48] obtained free contaminants rGO by microwave heating. First, an acidic GO colloid at pH 1, 3, or 5 was separately prepared by dropping a NaOH solution. Afterwards, each mixture was heated at 150°C under microwave irradiation, employing a power of 80 W, for 10 min. They monitored the GO reduction advance by visual observation of the color changes from brownish-yellow to black [49, 50].

A different method for the GO reduction based on electromagnetic irradiation was reported by Ding et al. [51]. The authors reported clean reduction of colloidal GO using the strong UV absorption property of water [52]. The UV radiation dissociates the water molecule into three radicals (hydrogen H₂, hydroperoxyl HO₂, and hydrated electrons e⁻), each one retaining one

of the earlier bounded electrons [53]. Then, hydrated electrons behave as a reducer to form rGO (**Figure 2**). Although the reduction process takes a long reaction time, it is possible to monitor the formation of rGO dispersions through UV-vis spectroscopy [54].

Another green processing by irradiation was published by Nyangiwe et al. [53], which is a very simple method and is described for the reduction of GO solution. By irradiating a GO sample dispersed in water with sunlight, the most oxygenic functional groups in GO were removed. The authors considered that photoreduction of GO by sunlight can be explained by a model proposed by Ji et al. [55], where the absorbed UV radiation in solvent excites the water molecule near its photoionization threshold (6.5 eV), generating solvated electrons, which will act like reducers. The complete process is described by the following equations [56]:



2.1.4. Polymers as reducers

There are scarce reports on the GO reduction by polymers. Zang et al. [57] reported the GO reduction using poly(diallyldimethylammonium chloride) (PDDA) polyelectrolyte [57]. It has been reported that the addition of PDDA to a GO aqueous dispersion triggers a chemical reaction that promotes a color change in the GO dispersion, indicating that GO transforms to rGO. Although the mechanistic aspects of the GO reduction were not clearly explained, the PDDA-functionalized rGO exhibited an excellent dispersion in water. Therefore, polyelectrolyte might be used as a reducing agent as well as a stabilizer to prepare a colloidal suspension of graphene. This method is based on the Yang et al. report [56], where PDDA was adsorbed on the external surface of carbon nanotubes through π - π and electrostatic interactions [56, 58]. It was assumed that repulsive electrostatic interaction dominates to produce well dispersed PDDA-functionalized carbon nanotubes in water.

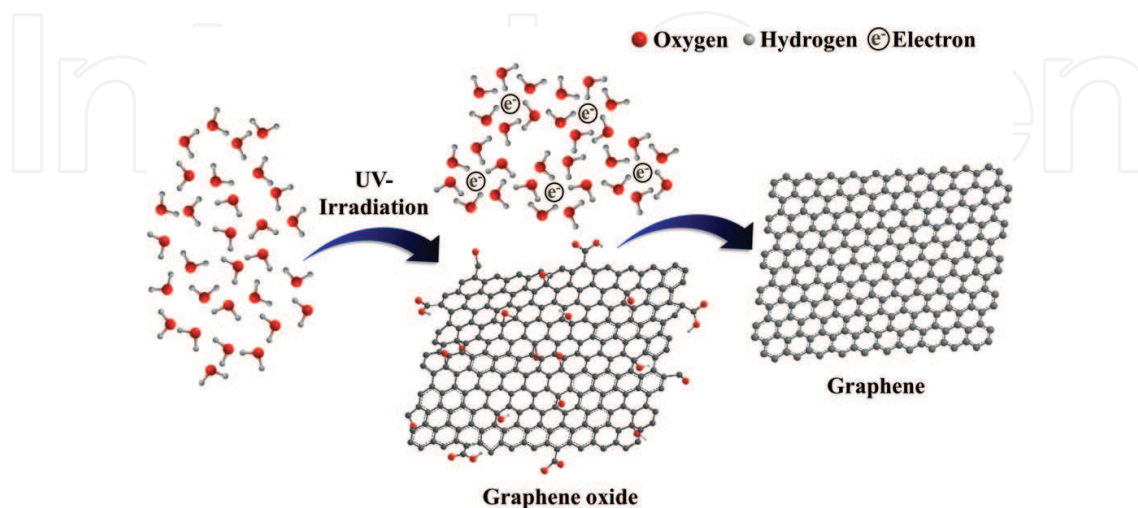


Figure 2. Schematic representation of the reduction of GO under UV irradiation.

2.1.5. Transition metals as reducers

An interestingly eco-friendly approach toward the GO reduction consists of using transition metals (e.g., Fe, Zn, Cu, and Co) as GO reducing agents. In this case, the reduction mechanism strongly depends on the experimental conditions (mainly pH and temperature) and it follows a frequently complex pathway. Some examples are described below.

GO was reduced by iron in aqueous medium by Fan et al. [59]. They studied the GO reduction by powdered iron (10 μm average size) in an acidic HCl-water mixture at room temperature. They proposed that H^+ interacts with the iron surface particle to bring forth the Fe/Fe²⁺ core/shell structure (iron particle with a thin sheet of charged Fe²⁺ ions). These positively charged Fe/Fe²⁺ species interacts with the functional groups on the GO sheets and after electron transport from Fe/Fe²⁺ to GO, the reduction of GO was achieved.

Experiments on GO reduction using Zn powder were essayed by Yang et al. [60]. To evaluate the Zn reduction capability and how it is affected by the solution pH and temperature, they prepared aqueous GO colloids with and without sodium hydroxide at room temperature and 100°C. They obtained lower reduction levels for all cases other than alkaline in 100°C conditions. The proposed reduction mechanism consists of an electron exchanging between Zn and GO to produce rGO and by products. The GO reduction using Zn powder were also carried out by Mei and Ouyang [61] and Liu et al. [62] under acidic conditions.

The formation of Cu₂O/rGO nanostructures during the GO reduction by Cu nanoparticles was described by Wu et al. [63]. They mixed polydisperse Cu nanoparticles with water-dispersed GO under neutral conditions. After sonication and heating at 95°C a composite comprising of rGO sheet decorated by Cu₂O nanoparticles was observed. Authors claimed that GO was reduced through a redox reaction between Cu and GO, in which Cu nanoparticles transformed to nano-sized Cu₂O and GO was reduced. In addition, they reported that the GO reduction strongly depended on the Cu particle size, because experiments involving fine grained Cu powder was unable to effectively reduce GO.

GO reduction experiments using metal foils as a substrate were done by Cao et al. [64]. A number of metal foils (Cu, Ni, Co, Fe, and Zn) were separately immersed in a GO aqueous dispersion at pH = 6. After taking out and drying at ambient temperature, the metal foil was coated with a rGO film. It was assumed that the rGO film was developed by a self-assembly process of rGO nanosheets and that the GO was spontaneously reduced by direct transfer of electrons from metal ions to GO. Some metal ions were found in the GO layers' galleries.

Hu et al. [65] used a GO dispersion at pH = 4 to immerse metallic foils (Cu, Fe, Zn, Co, and Al) and also a nonmetallic (carbon) film supported by Cu, and after (1–12 h) immersion, the metal foil was covered by self-assembled rGO multilayers and was dried at ambient conditions or freeze dried. They found that there had been electron transfer between the metal and GO propitiated for the acid condition (**Figure 3**). A significant difference is that they found metal oxide nanoparticles decorating the rGO; another important result was that the electron exchange to reduce GO had taken place even when a conductive layer (carbon or Au, Pt, Ag) covers the Cu substrate.

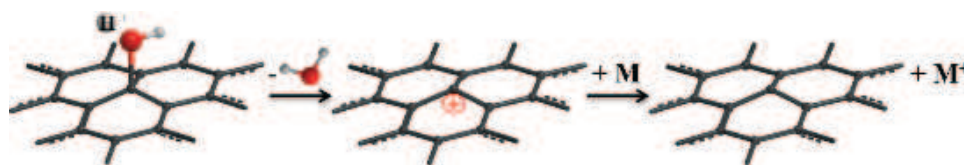


Figure 3. Scheme of GO reduction and metal oxidation. A hydroxyl group present at GO was protonated in acid conditions and then an electron transfer between metal GO took place, rGO was obtained, and oxidized metal.

2.1.6. Mechanochemical reducer: ball milling system

The mechanical reduction of GO into graphene was tested by a hydrogen-assisted ball-milling process [66]. The ball-milling process was carried out in a planetary micro ball-milling machine with a stainless steel chamber and stainless steel 5 mm diameter balls. First, 2.0 g of previously prepared GO powder by a modified Hummers' method [67] was loaded into the ball-milling chamber, and then filled with hydrogen gas. The chamber was rotated at 900 rpm for different times in the 30- to 240-min interval, to obtain a variety of ball-milled rGO samples. The GO reduction process with the milling time was visually verified by observing the GO color change from a brownish-yellow to black. The final powder, as analyzed by transmission electron microscopy, XPS, and infrared absorbance spectroscopy, consisted of well-exfoliated oxygen-free single-layer graphene [68, 69].

2.1.7. Electrochemical reduction

The electrochemical technique is widely used in thin film deposition on conductive substrates. The electrochemical reduction of GO develops either during the film deposition process or a preformed film as described in the comprehensive review [70]. The one-step and two-step approaches are usually employed to produce GO, and the reduction level can be controlled by varying the processing time, electrode material, on-off cycles, electrolyte type, and potential values. A variety of nontoxic electrolytes, such as NaCl, KCl, NaHPO₄, Na₂SO₄, KNO₃, and phosphate buffer solution (PSB), have been used. Furthermore, glass carbon, Au, Pt, Ag, and 3-aminopropyltriethoxysilane (APTES) have been tested as electrode materials [70].

In the one-step approach, GO sheets are dispersed into a mixture of electrolyte and buffer solution, and the power source is turned on and the GO thin film deposition and reduction occur simultaneously at the cathode surface material.

In the two-step approach, a thin film is deposited by some technique (drop-casting, spray pyrolysis, layer-by-layer, etc.) on an electrode of a three-electrode system (reference, working, and auxiliary electrodes), and then immersed into the electrolyte solution. Under controlled conditions of electrolyte temperature and composition, as well as electrodes potential, a rGO thin film is obtained. Recently, Fang et al. [71] used the two-step system to produce large area rGO and rGO/silk fibroin composites. They used a reference electrode of Ag/AgCl, auxiliary electrodes of ITO, Ag wire, and titanium and were tested individually and the working electrode GO materials, electrolytes of NH₄Cl, KCl, or [dmin][BF₄] were used. After the reduction process, the large area GO were tested for electrical properties, having 28,200 S/m conductivity after the reduction.

2.2. Summary of green reducing methods

A summary of the above-mentioned green reducing methods and its reduction rate is presented in **Table 2**.

Reducing agent of GO	Reducing grade reported, based on XPS measurements	References
<i>Shewanella</i>	C–C bonds increased from 28% in GO to 90–95% in rGO	[23]
<i>Gluconacetobacter xylinus</i>	C/O ratio increased from 1.8 in GO to 3.1 in rGO	[27]
<i>Camellia sinensis</i> (green tea)	C–C bonds increased from 58.9% in GO to 74.0% in rGO	[32]
Vitamin C	C/O ratio increased from 2.3 for GO to 12.5 for rGO. Samples reduced with (hydrazine was 5.5)	[37]
Microwave irradiation	C/O ratio is ~9.12, closed to value for rGO obtained by conventional hydrazine reduction ~10	[48]
UV irradiation	Functional groups that contain oxygen in the GO nanosheets were successfully removed. However, complete elimination of oxygen groups must be due to longer UV irradiation	[51]
Poly (diallyldimethylammonium chloride) (PDDA)	C–C bonds increased from 24.5% in GO to 52.7% in rGO	[57]
Metallic zinc	C/O atomic ratio increased from 1.19 in GO to 7.19 in rGO	[60]
Ball milling	In the presence of H ₂ , a dramatic decrease in the oxygen-bonded carbon components is observed	[66]

Table 2. Summary of reductive green methods.

3. Self-assembly of micro- and nanostructures

Due to their amphiphilic character GO sheets are valuable building blocks for preparing a variety of carbon-based nano- and microsized nanostructures by a self-assembly process. Because GO sheets are few nanometers in size, their self-assembly hierarchy proceeds to develop 1D, 2D, and 3D nano- and microsized materials. It thus enables to use templates for directing the self-assembly of GO sheets into complex structures with the specific shape and morphology for a given application.

It is noteworthy that the GO sheets' self-assembly was observed to occur at interfaces such as solid-liquid and air-liquid [12], and hence some hybrid metal- or metal oxide-GO nanocomposites comprise GO-coated inorganic nanoparticles.

Regarding GO self-assembled micro- and nanostructures, the presence of functional groups on the GO sheet surface promotes the assembly of nanoscale GO sheets into macroscopic 2D structures (films or fibers) and 3D bulk graphene by GO solution filtration or hydrothermal treatment. The forces that drive the self-assembly process are quite like those forces that participate in the self-assembly process of colloidal nanocrystals. Potential applications for these emergent structures are flexible fiber-type actuators, robots, motors, photovoltaic cells, and supercapacitors.

3.1. Metal-rGO hybrid nanocomposites

3.1.1. Broad classification of nanocomposites

Graphene and derivative materials are widely used to develop novel nanocomposites when combined with polymers and/or nanoparticles (semiconductors, metals, or metal oxides) [72]. These materials display superior physicochemical properties than those of their individual components and are currently essayed for water remediation, sensing, catalysis, photovoltaic films, materials reinforcement, and biomedical applications.

At present, a number of nanocomposites have been prepared by diverse methods and with specific physicochemical properties for biomedical [73], energy conversion, environmental and electrochemical storage [12], and miscellaneous [9] applications, as reported in recent review articles.

Among the variety of chemical and physical synthesis methods reported in the literature, we just include representative examples of the four classes of nanocomposites as described below.

According to their final morphology, rGO hybrid nanocomposites are broadly classified as supported, encapsulated, incorporated, and multilayered composites [7, 13]. Schematic representation of nanocomposites is presented in **Figure 4**.

3.1.2. Processing methods

The primary nanostructure GO sheets and nanoparticles (metal, metal oxide, or semiconductor) to develop nanocomposite materials are mainly processed by chemical methods.

The supported-rGO nanoparticles can be prepared by either direct synthesis of inorganic nanoparticle in the rGO dispersion or by mixing of previously prepared rGO and nanoparticles colloids. In the first approach, precursors are first dissolved in a convenient solvent, and then poured into the rGO dispersion. For preparing rGO-metal or rGO-metal oxide nanocomposites, the preferred method consists in adding the metal precursors (chlorides, nitrates, etc.) and a reducing agent (vitamin C, citric acid, L-lauric acid, etc.) into a previously pristine GO colloid. The whole processing can be performed using a range of synthesis systems such as microwave oven, hydrothermal, electrodeposition, sonication, and so on.

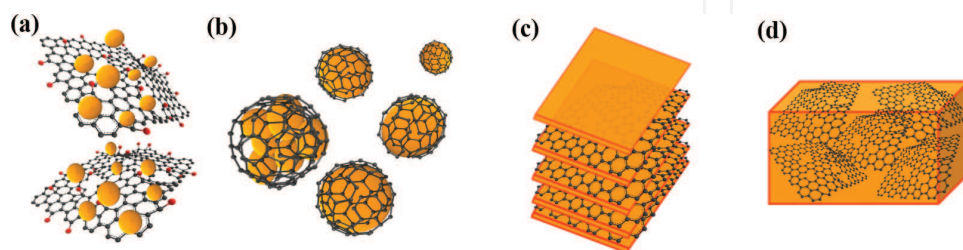


Figure 4. Kinds of metal-rGO nanocomposites. (a) Supported rGO surface is decorated by metal nanoparticles. (b) Encapsulated nanocomposites, few or multilayers of rGO are wrapping individual or clusters of MNP. (c) Incorporated layers of rGO are intercalated by metal layers. (d) rGO sheets are present in a metal matrix.

For instance, Kim et al. [74] used ascorbic acid to simultaneously reduce GO, Pd, Pt, Au, and Ag. An aqueous GO dispersion was kept at 100°C, then metal precursor and ascorbic acid solution were sequentially added. The final product consisted of rGO-supported nanosized noble metals. They used the rGO/Pd nanocomposite as catalytic material for Suzuki coupling reaction and observed that the nanocomposite catalytic activity was almost fully restored after five cycles.

An interesting version of supported-rGO nanoparticles approach is one in which rGO wraps the nanoparticle. In some cases, rGO sheets conformally enwrap the nanoparticle developing a hermetically sealed multilayer coating. The resultant composite comprises GO sheets decorated with a number of nanoparticle/rGO structures. These core/shell nanostructures are of current interest, since they are protected against oxidation or degradation. Chemical methods in solution and chemical vapor deposition have successfully been used to prepare such nanocomposites. They are used as lithium storage electrodes, high performance anodes, and biomedical applications.

Other interesting approach to obtain coated-rGO nanoparticles is the aerosol encapsulation technique reported by Chen et al. [75], to coat citric acid-stabilized Ag nanoparticles. These workers used an ultrasonic system to generate an aerosol composed of GO and Ag nanostructures, which was transported into a furnace at 600°C by using N₂ as the carrier gas. After drying, the individual drops transformed into a sample composed of Ag/rGO microstructures. This composite could be of interest for applications in tissue engineering, magnetic resonance imaging, X-ray computed tomography, and bioimaging contrast agent.

The layer-by-layer method is a thin film deposition technique in which alternating layers are successively deposited, and a film with a multilayered structure is obtained. Techniques such as immersion, spray coating, spin coating, and electrochemical are suitable ones to deposit multilayered nanocomposite films with large interfacial area. These kinds of nanocomposites are ideal for energy storage and generation.

Jang et al. [76] reported rGO/maghemite multilayered nanocomposite preparation. The GO was exfoliated by thermal expansion in vacuum at 200°C and then heated up to 300°C for 5 h. The powder of exfoliated GO, iron acetylacetonate, and oleic acid were mixed together and mechanically ground with a pestle and mortar. After heating at 600°C for 3 h, they obtained intercalated rGO-maghemite nanocomposite, and studied its performance as an anode material of Li ion batteries. In contrast with individually tested rGO and iron oxide samples, the nanocomposite displayed enhanced cycling stability and rate performance.

Incorporated nanocomposites have a low GO content (less than 1% vol) and are usually prepared by the ball-milling technique and a postsintering process. In this case, the properties to be exploited are mechanical and electrical properties, since they are applied in structural elements and implants.

Recently, the preparation of rGO incorporated in Al, Ni, Mg, and Cu matrices was reported [77]. It is expected that rGO sheets replace carbon nanotubes as a reinforcement material because rGO can be produced at large scale and at a lower cost. Zhang and Zhan [78] reported rGO-reinforced copper by ball milling and spark plasma sintering. They found that the presence of 0.1–1% vol rGO greatly enhances its mechanical properties (yield and tensile strengths) compared to those of pure Cu.

3.2. GO thin films and membrane

Currently, the GO self-assembled micro- and nanostructures are being essayed as semiconductor in thin film transistors, transparent electrode of solar cells, active material for chemical sensing, etc. These applications require paper-like and thin film of self-assembled GO nanosheets.

There are plenty of reports on the GO self-assembly into 2D and micro- and nanostructures [79, 80]. Shao et al. [14] did an exhaustive description of the mechanistic aspects of the GO self-assembly at diverse interfaces. Herein, we present the more recent findings on 2D microstructures, including thin films.

Until now several self-assembly mechanisms to form GO thin films have been proposed. The GO thin films formation frequently occurs at liquid-air-type interfaces by evaporation and Langmuir-Blodgett assembly [81, 82]. The techniques employed are simple in almost all cases and also let the assembly on the suspension surface, for instance, dip-coating, drop-casting, spin-coating, and spray-coating for mentioning some of them.

Langmuir-Blodgett assembly leads to the formation of GO very thin films and GO single layer, so when GO is obtained, it can be dispersed in a highly volatile organic solvent in the presence of little amounts of water, and then as the solvent evaporates, the GO begins to aggregate at the interface of water-air, forming a GO monolayer. The assembled material at the interfaces can be collected later by dipping a substrate [83]. The main advantage lies in the collected GO very thin films on the substrate, and they are a source to reduce the GO into graphene sheets by either chemical or thermal treatment [19, 84].

The resulting GO films have high transmittance, high surface chemical activity, and low sheet resistance. The morphology and dispersion degree can be modified by the pH of the synthesis solution; so, the pH modulates the amphiphilic nature of GO layers as evidenced by Cote et al. [85]. The self-assembled GO films are dominated by attractive forces as van der Waals forces and π - π interaction which lead to stacking of single GO layer.

In the evaporation case, the solvent is heated to accelerate its evaporation and the agglomeration of GO sheets in the interface of water-air, any solvent with relatively low evaporation point can be used to disperse and afterward evaporate it to promote the self-assembly on the solvent surface. In this way, it is possible to obtain both thin films and membranes. Similarly, the Langmuir-Blodgett assembly and evaporation induced lead to the formation of GO membranes by staking layer-by-layer (**Figure 5**). Cote and Shao [85, 86] provide examples of self-assembly using the Langmuir-Blodgett and evaporation-induced mechanisms.

As started below, the GO membrane can be considered as 2D microstructures with a morphology that depends either on the attractive or repulsive interaction among individual GO layers.

3.3. 1D and 2D microstructures (membranes and fibers) and 3D bulk structures

The GO sheet self-assembly can produce thin films and 2D membranes as aforementioned; however, this would occur at a liquid-air interface. If the interface is now liquid-solid type, a variety of microstructures of 2D and 3D can be obtained by self-assembly of single GO layers in the presence of a solid. The GO sheets' interactions with the solid surface involve π - π interaction, hydrogen bonding, electrostatic forces, and surface tension.

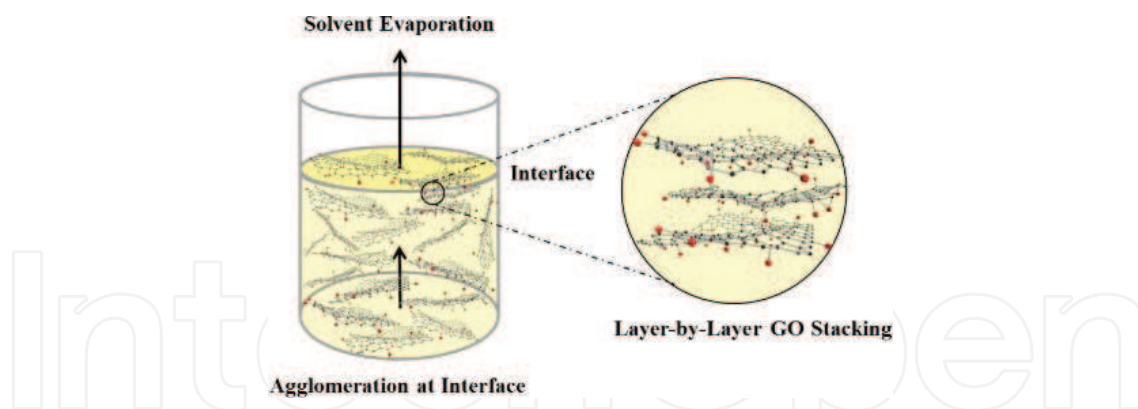


Figure 5. Self-assembly process into GO thin layers at the interface of liquid-air. The assembly is assisted by the solvent evaporation.

GO self-assembly driven by electrostatic forces produce several morphologies of 2D and 3D such as thin films, membranes, and capsules [87]. In this case, the ionization of COOH groups provides a negative charge distribution at the GO sheet edge. This charge distribution can be controlled by the pH of GO dispersion. An electric field applied in the GO solution is able to drift the negatively charged GO layers toward the positive electrode (solid element) dipped in the dispersion. GO sheets are agglomerated on the electrode surface and forced to assemble by staking. An interesting effect is presented during the GO sheets drift, since the GO layers that assemble are electrochemically reduced. So the electric field can remove the oxygen-based functional groups [88] and promote the assembly only by π - π interaction.

The presence of particles or nanoparticles in a GO dispersion can also drive the self-assembly, in this case foreign particles act as agglomeration centers, which destabilize the GO dispersion. This can be considered as a GO colloid in a disperse state [83, 89]. Therefore, attractive forces originated from particles overcome the electrostatic repulsion (colloidal stabilization) and lead to agglomeration and assembly.

Three-dimensional GO structures with polyhedral-like morphology were reported in Ref. [90]. In this case, the self-assembly process was observed at microscale. GO is synthesized by Hummers' method and the material is patterned on a silicon wafer. The patterned 2D GO membranes become the building blocks. A metallic frame is deposited around the GO membranes; it drives the folding of each membrane by surface tension forces. Considering the membrane size, the attractive forces as van der Waals are not manifested at this scale; therefore, surface tension forces are dominant here. These 3D cubes can be used as microcontainer of liquids and gases. Different assembly stages are shown in **Figure 6**, initially any material can be patterned as isolated blocks, **Figure 6(a)**, and then the metallic frame is deposited by a photolithographic process, **Figure 6(b)**. The metallic frame is constituted by two different metals, which linked the assembly blocks and allow the self-folding [91].

1D GO microfibers have been obtained by self-assembly of single GO layers; however, this is an example of microstructures' self-assembly at a liquid-air-type interface. As reported by Tian et al. [92], which these 1D fibers are formed by two forces combination, π - π interaction and van der Waals attractive forces are gradually manifested in the GO dispersion. These forces drive the single GO layers agglomeration toward the GO dispersion surface and staking layer

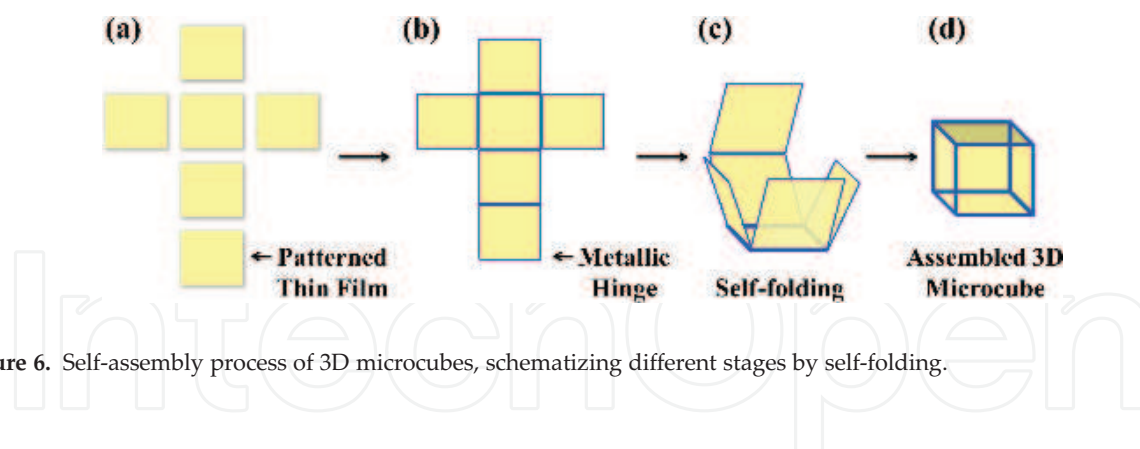


Figure 6. Self-assembly process of 3D microcubes, schematizing different stages by self-folding.

by layer. Then, progressive accumulation of GO sheets produces these 1D GO microfibers. The fibers are annealed later to obtain rGO. The authors in this case do not provide further information about the rolling up process that give place to the 1D fibers.

4. Summary

Synthesis, reduction, and advanced application of graphene oxide (GO) are fast growing research areas because there exist a great variety of preparation techniques for mass production, the chemical-based ones being the most promising. For its chemical richness, chemically obtained GO is an extraordinary product in various aspects. First, it can be obtained by means of scalable, simple, and low-cost techniques, which is important for gram- or kilogram-scale applications (e.g., rGO-metal-based composites for the lithium battery anode, rGO-based foams, water cleaning, etc.). Second, it has demonstrated to be an excellent precursor material for developing advanced materials, such as graphene, graphene when treated under hydrogen atmosphere, and Teflon-like materials when fluorinated.

This chapter presents an overview on the GO reduction by green methods, on the production methods of carbon-based structures by GO sheets self-assembly, and on preparation methods of GO-based metal nanocomposites.

The so-called green methods for GO reduction demand that both, starting chemicals and byproducts, are safe to handle and environmentally friendly. Technologies such as bioreduction, photoreduction, reduction by polymers, reduction by metals, mechanochemical reduction, and electrochemical reduction fulfill both criteria.

On the other hand, the amphiphilic character of GO sheets make them valuable as building blocks for preparing a variety of carbon-based structures produced by their self-assembly, as well as hybrid nanocomposites when combined with metal semiconductor nanoparticles. The self-assembled carbon structures and hybrid nanocomposites are currently essayed for water remediation, sensing, catalysis, photovoltaic films, materials reinforcement, and biomedical applications.

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