Review

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Chemical synthesis of reduced graphene oxide: a review

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Abstract

Due to its exceptional and distinct features, graphene has become a prominent two-dimensional material. According to the raw materials and synthetic procedures, there are two categories of graphene synthesis techniques: "bottom-up" and "top-down" methods. Reduction of graphene oxide (GO) is one of the "top-down" techniques that use graphite as the starting material. This approach is now regarded as the most potential way to produce graphene on a large scale and is particularly well-suited for chemical modification and subsequent processing. This review summarizes the synthesis procedure of reduced GO (RGO) and presents the preparation methods of it and its precursors, such as graphite oxide and GO. In addition, the possible approaches for reducing the defects in RGO have been discussed.

Keywords: Graphite oxide, graphene oxide, reduced graphene oxide, graphene oxide structure, graphene structure

INTRODUCTION

Graphene is a two-dimensional layer of sp2-hybridized carbon that is atomically thick and is organized in a lattice-like honeycomb. With a thickness of just 0.335 nm and a band gap close to zero, graphene possesses inherent ultra-high carrier mobility, which gives it the potential to replace silicon as an ideal material for nanocircuits. The advantages of low thermal conductivity, high specific surface area, strong toughness, and high hardness make graphene have good exploitable value in the fields of electronics, materials, energy, and

communication. Due to its outstanding properties, there has been a tremendous driving force to find methods of synthesizing scalable, reproducible, and high-quality graphene, such as micromechanical exfoliation, chemical vapor deposition (CVD), nanotube slicing, and solvent exfoliation[1]. All these methods can produce high-quality graphene but are accompanied by high cost and low output. To solve these problems, an old carbon family member, graphite oxide (GrO), was brought back on stage; its single layer is called graphene oxide (GO). The method involving GO, namely reducing GO, is now regarded as the most potential way to produce graphene on a large scale and is particularly well-suited for chemical modification and subsequent processing.

Reduction of GO promises an alternative pathway to graphene[2]. In chemical conversion methods, graphite flakes are first oxidized and then peeled off to obtain GO; it may be thought of as a single layer of GrO or as several layered layers. The functional groups are then removed from the GO sheets in order to produce reduced GO (RGO). As the derivative material of this method, GrO is cheap and easy to synthesize in bulk quantities[3,4]. The exfoliation of GrO is convenient due to its good dispersibility in many common solvents, such as water. GO sheets can be further functionalized because of the numerous oxygen groups on their surface and edge or reduced back to a graphene-like material[5]. The detailed introduction of this "top-down" technique was presented in this paper.

SYNTHESIS OF GRAPHITE OXIDE

In 1859, British scientist B.C. Brodie made the initial discovery of GrO through a reaction involving the introduction of $KClO_3$ to a slurry of graphite in fuming HNO_3, and this substance was known as "graphic acid". Forty years later, L. Staudenmaier enhanced Brodie's $KClO_3$-fuming HNO_3 technique by adding chlorate in numerous aliquots during the course and introducing concentrated sulfuric acid to elevate the acidity level of the mixture. These enhancements made the process simpler and more practically applicable. After another 60 years, an alternate oxidation method was developed by Hummers and Offeman[6] by mixing graphite with $KMnO_4$, $NaNO_3$, and concentrated H_2SO_4. This method is still widely used in current studies and experiments and is called "Hummers' method". In recent years, some improved versions of the Hummers' method have emerged, which improved oxidation efficiency by increasing the amount of $KMnO_4$ and adding a mixed acid of H_2SO_4/H_3PO_4[1]. In the following sections, these recipes for GrO preparation will be introduced in detail.

Brodie's oxidation method
Brodie was the first to employ $KClO_3$ in severe fuming HNO_3 to synthesize a new chemical involving carbon, oxygen, and hydrogen. This pioneering work led to an increase in flake graphite quality. He washed the batch to eliminate any salts that had developed during the process, dehydrated it at 100 °C, and subsequently returned it to the oxidizing environment. After three repetitions of that process, a material with a "light yellow color" that did not alter with subsequent oxidation treatment was developed. According to the elemental analysis of his product, he gave the final molecular formula of the oxidized graphite as $C_{11}H_4O_5$. Furthermore, he learned that the chemical was dispersing in basic or pure water but precipitated in acidic environments, which led him to come up with the name "graphic acid" for the newly synthesized compound. As a result of heating at 220 °C, the reduction in carbonic acid and carbonic oxide caused a change in the C:H:O composition of the material to 80.13:0.58:19.29. However, although this technique may oxidize graphite, its usage is limited due to the long reaction time and hazardous gas emissions.

Staudenmaier method
To improve the technique of Brodie, Staudenmaier added copious amounts of sulfuric acid and an overabundance of oxidizing agents. Multiple aliquots of concentrated sulfuric acid (H_2SO_4) were added, and

to raise the oxidation ability of Brodie's $KClO_3$-fuming HNO_3 formulation, potassium chlorate solution was introduced to the reaction mixture throughout the method. These changes enabled the creation of a heavily oxidized GrO product in a single reaction vessel, considerably simplifying the GrO synthesis technique. However, the improvement in Staudenmaeir's method did not eliminate the flaws in Brodie's method; the oxidation procedure was still time-consuming and risky. The addition of potassium chlorate can persist for more than a week, and continuous hazardous gas explosions can occur when chlorine dioxide is removed from the inert gas. More modification or development of this oxidation method is necessary in this case before it can be widely used.

Hofmann method

Considering that fuming HNO_3 acid is extremely poisonous and hazardous, Hofmann *et al.* employed concentrated sulfuric acid combined with concentrated nitric acid to make GrO in place of fuming nitric acid[7,8]. As the main oxidant, $KClO_3$ exhibited a high oxidation ability and typically serves as an in-situ source of dioxygen in acid solutions. So far, several research groups have successfully synthesized GrO using this method[9,10].

Hummers' method and its modifications

Chemists Hummers and Offeman, working at the Mellon Institution of Industrial Research, created an alternative process for creating GO about 60 years after Staudenmaier's method. For the oxidation of graphite, a water-free mixture of concentrated sulfuric acid, sodium nitrate, and potassium permanganate solution was made and kept at temperatures below 45 °C. First, 2.3 L of sulfuric acid was chilled to 0 °C in an ice bath with 100 g of graphite powder and 50 g of sodium nitrate. After that, 300 g of potassium permanganate was progressively added to the suspension. After the ice bath was withdrawn, the internal temperature of the suspension was raised to 35° and kept at that temperature for 30 min. After 20 min, the mixture turned brownish-gray pasty, and just a little amount of gas had evolved. After 30 min, 4.6 L of water was gradually incorporated into the paste, resulting in a powerful fizz and raising the temperature to 98 °C at the same time. The diluted sample became brown when this reaction was kept going at this temperature for 15 min. After the procedure, three percent H_2O_2 was added to turn the remaining permanganate and manganese dioxide into colorless soluble manganese sulfate. The watery dilute solution was filtered and continuously rinsed with warm water to get rid of the soluble salt of mellitic acid. To obtain the dry form of GrO, centrifugation was utilized first, followed by dehydration at 40 °C over phosphorous pentoxide under vacuum.

In 2004, the graphene research gold rush began, and GrO also emerged as a star material. Numerous publications have been written discussing its preparation, reduction, and structure. A more effective way to prepare GrO was disclosed in 2010 by Marcano *et al.* [Figure 1][11]. In this new process, they excluded $NaNO_3$ and increased the dosage of $KMnO_4$. Additionally, they further added H_3PO_4 as a replacement acid to the reaction container. This enhanced technique generates no harmful gas and avoids a significant exotherm. The yield and oxidation degree of GrO prepared with this method are higher than that of GrO prepared with Hummers' method.

Additionally, they discovered that the improved approach disturbs the basal plane of graphite less than Hummers' method. They believe this may be due to the development of five-membered cyclic phosphate groups between the phosphoric acid and two vicinal diols on the graphite basal plane[12]. The oxidation process of graphite in C-H_2SO_4-[O] systems ([O] = $KMnO_4$) can be described by the following formula[13,14]:
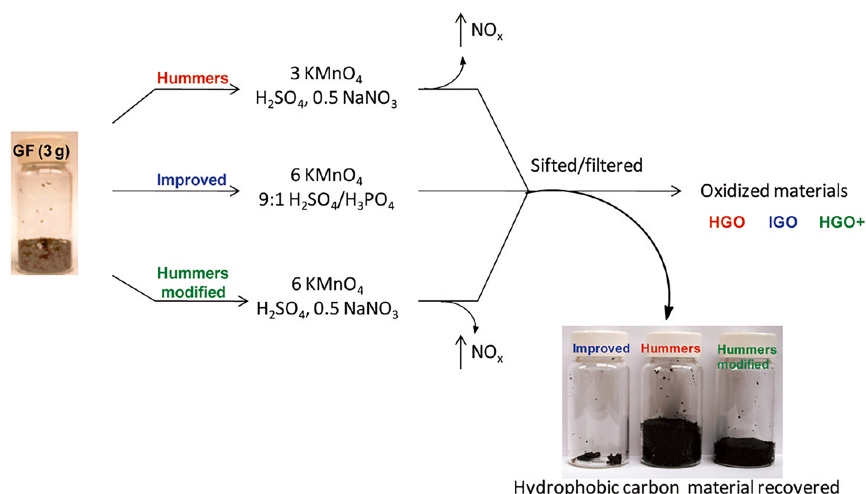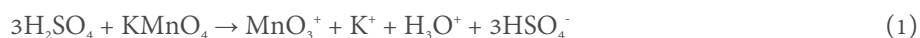
Figure 1. Depiction of the steps used to create GO beginning from graphite particles[11]. GO: Graphene oxide; HGO: graphite oxide prepared by Hummers' method; HGO+: graphite oxide prepared by modified Hummers' method; IGO: graphite oxide prepared by improved Hummers' method.

$$3H_2SO_4 + KMnO_4 \rightarrow MnO_3^+ + K^+ + H_3O^+ + 3HSO_4^- \tag{1}$$

$$MnO_4^- + MnO_3^+ \rightarrow Mn_2O_7 \tag{2}$$

$$H_2SO_4 + 5C_{24S}^+ + [O] \rightarrow H_2O + 5C_{24S}^+HSO_4^- \cdot 2H_2SO_4 \tag{3}$$

$$5C_{24S}^+HSO_4^- \cdot 2H_2SO_4 + Mn_2O_7 \rightarrow 5C_{24S}O_y + MnO_2 + H_2O + SO_x \tag{4}$$

where C_{24S} represents the graphite, and $C_{24S}^+HSO_4^- \cdot 2H_2SO_4$ is a graphite bisulfate formation.

PREPARATION GRAPHENE OXIDE FROM GRAPHITE OXIDE

GO can be considered as a single layer of GrO. Besides being applied as the precursor for macroscale and high-quality graphene production, GO also has important uses in its own right. Because of its unique structure, GO has solution processability, amphiphilicity, and high surface area. These properties make it ideal for a wide range of applications, including sensors, energy storage, electronic, and biomedical fields. As we know, the zero-band gap of graphene will limit its potential for opto-electronic applications. However, unique optical properties can be obtained when the surface of graphene sheets is functionalized[15]. In this case, GO can be regarded as a kind of chemically modified graphene material that exhibits such versatile chemistry and tunable fluorescence. In recent years, the photoluminescence of GO has already been used for various applications, including sensors, drug delivery, catalysis, and low-cost opto-electronic devices.

Structure of GO

As mentioned above, the structure of GO should be the same as the structure of a GrO layer. Although GO has been extensively studied by different characterization methods, its exact chemical structure is still ambiguous. The difficulty in structure analysis of GO can be attributed to three points: (i) depending on the synthesis circumstances, GO is a molecule with a wide range of compositions that are not stoichiometric; (ii) it immensely attracts moisture; and (iii) it gradually decomposes when the temperature exceeds 60 to 80 °C.

Regular lattices composed of discrete repetition units were widely indicated by early structural models of GO [Figure 2]. The initial hypothesis of Hofmann and Holst proposed that epoxy (1,2-ether) connections with a suitable combination C_2O were used to connect the oxygen to the carbon atoms of the hexagon layer planes. In addition to corrugating the basal plane and adding hydroxyl groups to the lattice, Ruess improved this model in 1946[17]. According to the Ruess model, in 1,3 positions, the axial OH groups and ether oxygens are tied to the fourth valencies of carbon atoms. This model postulates a wrinkly carbon sheet composed of chairs built of trans-linked cyclohexane. Mermoux[18] supported Ruess' idea by pointing out the structural parallels to poly (carbon monofluoride), $(CF)_n$, a structure that demands the formation of C-F bonds by the full rehybridization of graphite's sp2 planes to sp3 cyclohexyl structures. More than a decade later[19], Scholz and Boehm proposed a model that entirely removed the epoxide and ether groups while introducing hydroxyl groups on the fourth position of 1,2 oxidized cyclohexane rings. Nakajima and Matsuo developed a noteworthy model based on the Ruess model in 1988, proposing a stage 2 type $(C_2F)_n$ model through fluorination of GO[20].

The majority of the models mentioned above have been replaced by the two most current models designated by Lerf-Klinowski[21] and Décány[16], respectively, due to the evolution of the means of characterization. The periodicity of the structure was rejected in the Lerf-Klinowski model and replaced with a nonstoichiometric amorphous option. Based on solid-state nuclear magnetic resonance (NMR) information, the GO layer was described as a random distribution of flat aromatic portions with unoxidized benzene rings and wrinkled regions with alicyclic six-membered rings carrying C=C, C–OH, and ether groups (reassigned to 1,2 positions). The GO sheets are terminated by the C–OH and COOH groups. Based on the Lerf-Klinowski model, Sinclair and Coveney[22] consider that graphene is an inhomogeneous double system composed of oxidizing and non-oxidizing regions. The oxidation process of graphene is mostly based on the outward diffusion of reaction sites, the overall appearance of irregular islands, and the oxidation diffusion rings seen at different sites will affect each other, which will be an important factor in the uncontrolled functional groups in the graphene system. Mouhat *et al.* conducted research on the improved theory based on the graphene double system and found that the functional groups of the highly functional regions are close to each other, and it is easier to form a large number of hydrogen bonds than the discrete functional groups, so it shows that semi-ordered GO is more stable than irregular GO[23]. Another popular GO structure was the Decany model, which combined the Scholz-Boehm and Ruess models while maintaining the corrugated topology of the carbon network. While expanding the trans-linked cyclohexyl networks and including 1,3-ethers into the structure, the fundamental structure of this model is comparable to that of the Scholz-Boehm model. Based on these findings, the Dekany model consists of two separate domains: a corrugated network of ketones and quinones and a trans-linked cyclohexyl domain with tertiary alcohols and 1,3-ethers scattered throughout.

Unfortunately, the precise structure of GO is still unknown because of the starting materials or the oxidation technique; the extent of oxidation might vary dramatically, which can significantly alter the structure and properties of the material. Recent research matched exploratory data to density functional predictions and found that partial oxidation is thermodynamically preferable to total oxidation[24]. Until the usual structure of GO is known, the phrase "graphite oxide" may indicate a class of many compounds that differ only slightly in functional group arrangement and relative content.

Exfoliation of GrO

The Van der Waals force between GrO layers is usually broken to prepare GO. Because of its strong dispersibility, GrO may be scattered in an extensive selection of solvents, which facilitates the application of different forces on the exfoliation of GrO. Based on the species of outer force applied in the synthesis process of GO, the main exfoliation methods can be divided into sonication exfoliation, stirring and shaking exfoliation, and thermal exfoliation.
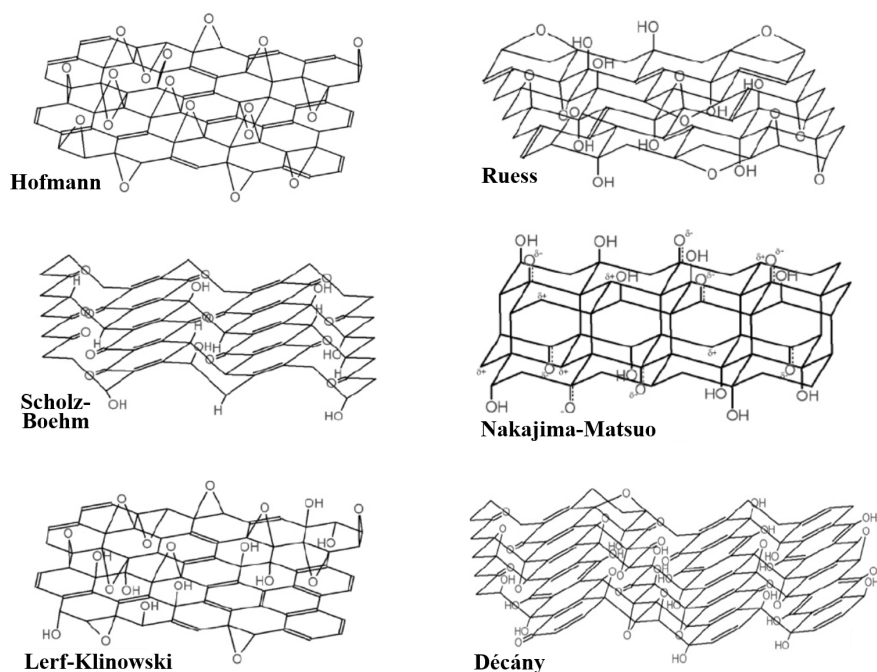
Figure 2. Proposed structure models for GO[16]. GO: Graphene oxide.

Because of its larger d-spacing and polar functional groups, GrO may be readily exfoliated in water by sonication. In recent studies that involved the preparation of GO, most of them exfoliated GrO in water to obtain GO and achieved exfoliation degrees ranging from 50% to nearly 100%, depending on the oxidation degree of GrO[25-28]. However, for many applications, such as the preparation of GO-based polymer nanocomposites[29,30], organic solvents should be used to dissolve GO sheets. According to reports, GrO has already been directly exfoliated with moderate sonication in dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), and ethylene glycol[31]. Additionally, surfactants, such as didodecyldimethylammonium bromide (DDAB), have also been used to distribute GO in chloroform and achieve a concentration of 1 mg/mL[32]. Generally, stable GO dispersions prepared in organic solvents can reach a concentration of 1 mg/mL, while in water, the dispersions can go up to 7 mg/mL[33]. It is worth noting that practically all of the sheets have diameters on the order of one meter.

Aside from the powerful cavitation caused by sonication, stirring or shaking GrO can also exfoliate the GrO layers while keeping their lateral size. As reported by Ionov *et al.*, laterally stirred GO with a lateral dimension of 50 μm can obtain GO monolayers with diameters up to 40 μm[34]. Using 300 m graphite flakes as a starting point, oxidation and shaking produced GO monolayers with an average lateral size of 100 m and a maximum lateral size of 200 m[35]. Cai *et al.* have prepared micron-scale GO by a high shear method, which has less crushing damage to graphene without significant difference in functional groups[36]. GO sheets with lateral diameters of roughly 15 μm may be manufactured using the same technique and a starting material of 25 μm. In contrast to relatively mechanical exfoliation methods, thermal exfoliation of GrO can occur within just seconds[37,38], and most thermal exfoliation can prepare GO without the use of liquids. Because of the use of high temperature, thermal exfoliation occurs in synchronous graphene exfoliation and reduction in most cases. The oxygen groups on GrO layers dissolved and released gases during the heating process, creating pressure between neighboring graphitic layers. GrO can be exfoliated

into GO monolayers when this pressure surpasses the van der Waals interlayer attractions between GrO layers. Schniepp *et al.* initially swiftly heated GrO to 1,050 °C, and then exfoliation of GrO occurred within 30 s[25]. According to McAllister *et al.*, thermal exfoliation only took place when the rate of GrO functional group breakdown exceeded the rate of gas diffusion, creating high enough stress to break the van der Waals contact between graphene layers[38]. They also discovered that a temperature of 550 degrees Celsius is necessary for quick exfoliation. Moreover, by increasing the heating time to five minutes, GrO may also be thermally exfoliated at lower temperatures, such as 250, 300, and 400 °C.

REDUCTION OF GRAPHENE OXIDE

Reducing GO is a good way to produce huge amounts of graphene (RGO). The recently used reduction methods include chemical reduction, thermal and hydrothermal reduction, electrochemical reduction, and photocatalyst reduction.

Chemical reduction

Normally, the chemical reduction of GO occurs at a low temperature, resulting in RGO that is similar to graphene but contains residual oxygen, other heteroatoms, and structural flaws. Most oxygen groups on the GO sheet were removed by the reduction procedure, and electron conjugation within the aromatic system of graphite was largely restored. If no dispersion agent was added, the RGO generated from the process medium restored graphite domains and improved hydrophobicity and stacking interaction[39]. The typical schematic diagram for preparing RGO with this kind of chemical method from graphite is shown in Figure 3.

Hydrazine monohydrate (N_2H_4) is an extensively used reducing agent, as first reported by Stankovich *et al.*[27]. One of its main benefits is its resistance to water, which is used as a dispersing solvent in GO reduction processes. It is asserted that the reduction of GO is equivalent to the reduction of alkenes with hydrazine since many academics have thoroughly studied the reaction mechanism of hydrazine with GO. Figure 4 depicts a potential approach to epoxy group reduction[40].

Except for the decrease of epoxy, the decrease of other oxygen groups by hydrazine was found to leave a residual C-N bond, which was difficult to remove in one step[41]. Due to the toxicity of hydrazine, GO has been reduced using a variety of very effective and ecologically safe reductants [Table 1]. Some of these reductants include ascorbic acid, glucose, hydroxylamine, hydroquinone, pyrrole, amino acids, extremely alkaline solutions, reducing sugar, hydroiodic acid, reducing metal powder, urea, sodium borohydride, and others.

Thermal reduction of GO

Since it is a nonchemical process, thermal and hydrothermal reduction of GrO is also an excellent option for the creation of RGO and may not leave harmful residue. As discussed above, exfoliating GrO to GO or RGO was often accomplished by fast heating (> 2,000 °C/min)[55-57]. In a vacuum, inert, or reducing atmosphere, the annealing reduction for thermal reduction of GO is commonly carried out. The breakdown of oxygen-containing functional groups linked to the carbon plane into CO or CO_2 gases significantly increases the pressure between the carbon layers. Because of this behavior, fast heating not only exfoliates GrO but also lowers the prepared GO, making the thermal expansion of GrO a promising technique to manufacture large quantities of graphene[58]. The rupture of graphene sheets, on the other hand, may be linked to the removal of carbon atoms on the carbon plane during the breakdown of oxygen-containing groups. However, it is also discovered that this technique only produces minuscule and wrinkled graphene sheets.

Table 1. Comparison of different reduction methods of GO

Reducing agent	C/O ratio	Doping	Conditions[c]	Ref.
$NaBH_4$	8.6[a]	-	RT, 2 h	[42]
NH_3BH_3	14.2[a]	B/N-doped	80 °C, 12 h	[43]
$LiAlH_4$	12[a]	-	THF, 70 °C, 24 h	[44]
HI	12[a]	I-doped	100 °C, 1 h	[45]
Hydrazine	10.3[b]	N-doped	100 °C, 24 h	[27]
Phenyl hydrazine	9.5[b]	N-doped	RT, 24 h	[46]
Hydroxylamine	1.5[a]	N-doped	80 °C, 30 h	[47]
Urea	4.5[a]	Adsorbed	95 °C, 30 h	[48]
Hydroquinone	-	-	RT, 20 h	[49]
Glucose/NH_3	-	Absorbed	95 °C, 1 h	[50]
Al/HCl	18.6[a]	-	RT, 30 min	[51]
Fe/HCl	7.9[a]	Fe-doped	RT, 6 h	[52]
Zn/HCl	33.5[a]	-	RT, 1 min	[53]
Ascorbic acid	12.5[a]	-	95 °C, 15 min	[54]

[a]X-ray photoelectron spectroscopy; [b]Elemental analysis; [c]Reduction carried out in an aqueous medium or a pure solution of the reducing agent unless stated otherwise. GO: Graphene oxide; HI: chemicla formula of hydrogen iodide; THF: tetrahydrofuran.
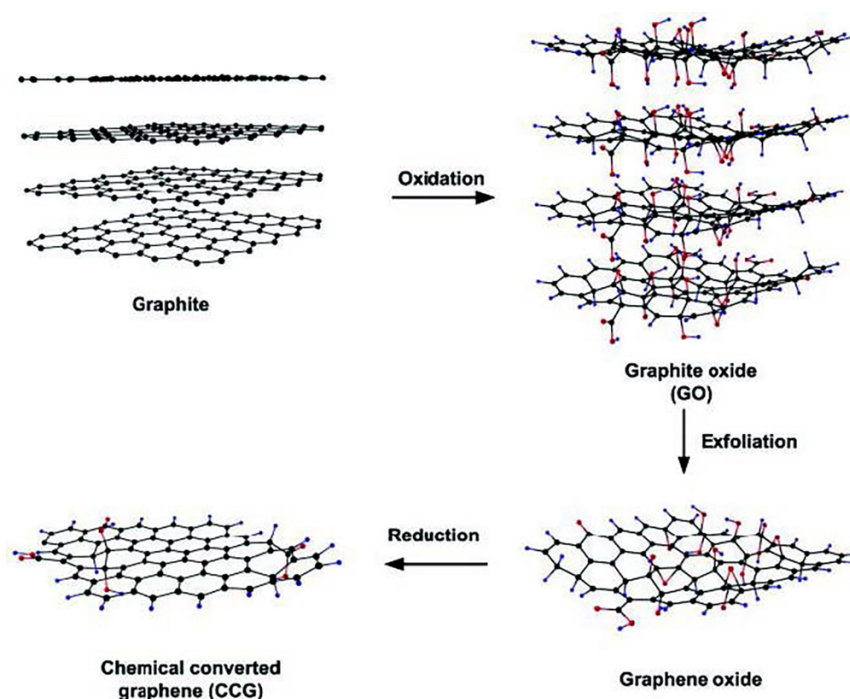

Figure 3. Preparation of reduced graphene oxide from graphite with a chemical oxidation and reduction method[39].

The decrease of GO via the solvothermal or hydrothermal method was proposed because it may be executed at ambient temperature and high pressure since the annealing reduction of GO requires a very high temperature[57-59]. Before the hydrothermal reduction was applied in the reduction of GO, it has already been utilized to convert carbohydrate molecules into homogenous carbon nanospheres and nanotubes. Compared with solvothermal reduction, hydrothermal reduction offers a green chemical route for preparing RGO, as the supercritical water performs a reducing agent function under hydrothermal circumstances[60]. According to the reports of Zhou *et al.*, the functional groups bound to the GO may be
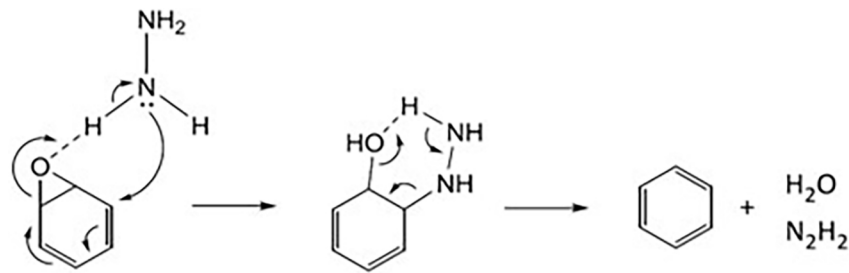
Figure 4. Potential hydrazine reduction mechanism of the epoxy groups on GO[40]. GO: Graphene oxide.

removed by the supercritical water, and the aromatic carbon lattice structures may also be recovered[61]. The solvothermal approach was used by Wang *et al.* to reduce GO in N, N-dimethylformamide[59]. After solvothermal methods processing (180 °C for 12 h), RGO has a higher C/O ratio than hydrazine reduction at standard pressure. The improved solvothermal reduction method proposed by Dubin *et al.* employed N-methyl-2-purrolidinone (NMP) as the solvent, but it was not taken out in a sealed container, and the heating temperature was below the boiling point of NMP[62]. A low C/O ratio (5.15) in the obtained RGO indicates a moderate drop in GO.

Electrochemical reduction of GO
The electrochemical elimination of oxygen functions is a different approach with promise for reducing GO[63]. GO sheets or films can be electrochemically reduced at room temperature using a buffered aqueous solution in a conventional electrochemical apparatus. In contrast to chemical reduction, electrochemical reduction often requires no particular chemical agent; instead, the reduction is accomplished by the exchange of electrons between the electrodes and the GO. In this situation, it could be possible to avoid using harmful reductants, such as hydrazine. According to Ramesha and Sampath[64], the drop of GO started at -0.6 V and peaked at -0.87 V. The reduction may be completed in a single scan at this scanning voltage range, and it is an electrochemically permanent reaction. Electrophoretic deposition (EPD) was employed by An *et al.* to create GO films[65]. Contrary to popular opinion, which holds that oxidation takes place at the anode in an electrolysis cell, they discovered that GO sheets may also be reduced on the anode surface during EPD.

Photocatalyst reduction of GO
Additionally, GO can be reduced using photochemical processes with the assistance of a photocatalyst. The introduction of the review article by Pei *et al.* states that by using a photocatalyst such as TiO_2, linked functional groups on GO surfaces can be eliminated, lowering the amount of GO[5]. Williams and Kamat also detailed how TiO_2 particles helped reduce GO in a colloid condition while being exposed to ultraviolet (UV) light[66]. They showed that a color shift from light brown to deep brown and ultimately to black may be used to detect the fall of GO. The reduction of GO in a colloidal form with the aid of TiO_2 nanoparticles under UV irradiation was shown by Kamat [67]. When GO suspended in ethanol absorbs electrons from suspensions of UV-irradiated TiO_2 nanoparticles, a reduction process takes place. The hybrid between the TiO_2 nanoparticles and the GO sheets may be created prior to reduction through charge transfer interactions between the carboxyl groups in the GO sheets and the hydroxyl groups on the TiO_2 surface. Then, during reduction, this structure can be kept. GO has apparently also been reduced using photocatalytically active materials other than TiO_2, such as ZnO and $BiVO_4$[68].

METHODS TO DECREASE THE DEFECTS OF RGOS

Although the reduction of GO can remove most of the oxygen groups in GO, abundant defects, such as Stone-wales defects (nonhexagonal rings), vacancies, impurity atoms, and edges, were produced after reduction. According to the findings put out by Bagri *et al.*, reduction may be accomplished by choosing the appropriate reduction technique if there are no lattice flaws and just functional groups covering the carbon plane of GO[13]. After reduction, lattice defects in the carbon plane are more prone to occur during oxidation. These flaws are unfavorable because they can greatly reduce the quality of graphene, including its mechanical rigidity and electrical conductivity. Therefore, it is necessary to decrease the defects in RGO to improve its quality. According to recent reports, the main methods to decrease the defects of RGO include direct healing of defects in RGO and the synthesis of highly reducible GO.

Healing of defects in RGO

Generally, the healing of defects in RGO was directly executed on RGO or during the reduction of GO. The goal of conducting several experiments in this regard is to significantly increase the conductivity of GO. By using CVD, Lopez *et al.* suggested repairing GO[69]. With the exception of the presence of metal catalysts in the latter instance, the circumstances for the CVD employing ethylene as a carbon source were surprisingly similar to those used in the CVD synthesis of single-wall carbon nanotubes on SiO_2 substrates. The RGO generated after the CVD using traditional reduction procedures has an electrical conductivity that is more than 50 times lower than that of the CVD-GO. A method for real-time repair of the newly created voids using carbon radicals created by the thermal breakdown of precursors was reported by Dai *et al.*[70]. With a transparency of more than 96%, the sheet conductivity of monolayer graphene increased by more than six times to 350-410 S/cm.

Except for the protection during reduction, many researchers also tried to repair the RGO that has already been fully reduced. According to a technique described by Wang and Pantelides, vacancies can be healed by successively exposing them to CO and NO molecules[71]. At a vacancy site, a CO molecule is adsorbed, and a NO molecule eliminates the additional O by producing NO_2 later. By first creating vacancies (with an electron beam, for example) and then exposing the materials to NO molecules at room temperature, controllable N-doping may be accomplished. The healing procedure is summarized in Figure 5, and it is suggested that no extra defects will be produced during this process. Shi *et al.* concurrently enhance the reinforcing effect of graphene and address the shortcomings of RGO by ray irradiation in a polyvinyl alcohol (PVA) matrix[72]. The G-ray irradiation activated the surfaces of RGO and created free radicals in the PVA chains. The reactive groups around the margins of the RGO flaws will combine with the random chain scissions of the PVA main chain when the radiation doses are high enough to cause the repair of the crystalline graphene. PVA/RGO hydrogel composites provide an improvement in the reinforcing action of RGO. Tensile strengths of PVA/RGO hydrogel composites produced with 100 kGy and 150 kGy were 44% and 171%, respectively, higher than those of nonirradiated composites. A chemical defect repair of RGO was established by Park *et al.* using intramolecular cross-dehydrogenative coupling (ICDC) with $FeCl_3$ at room temperature[73]. Following the ICDC reaction, the Raman intensity ratio of the RGO G-band to D-band, or IG=ID ratio, increased from 0.77 to 1.64. Peak intensity was compared at a greater ratio of 3.79 to 2.88 between C=C and C–C. The increase in the proportion of sp2-hybridized carbon atoms is due to the ICDC reaction, and the healing process is shown in Figure 6. The electrical conductivity of RGO was raised to 71 S·cm^{-1} once the flaws were fixed, a 14-fold improvement over its initial electrical conductivity of 5 S·cm^{-1}.

Synthesis of highly reducible GO

As already mentioned, both operational categories and defects can affect GO conductivity. While faults, whether they result from oxidation or reduction, tend to be simple to eliminate, treating them afterward can be more challenging. In this case, the control of oxidation degree during the oxidation procedure may
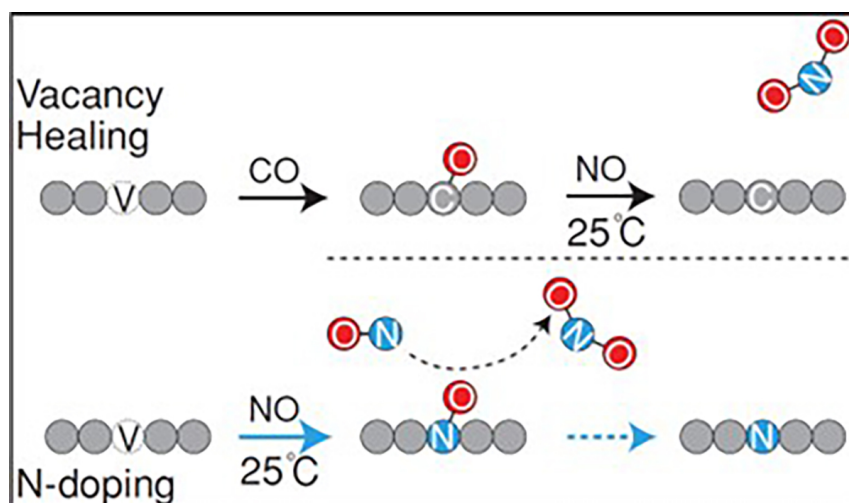
Figure 5. Diagrammatic depiction of the graphene vacancy healing and N-doping process with vacancies (V) filled by CO and NO molecules[71]. RGO: Reduced GO.
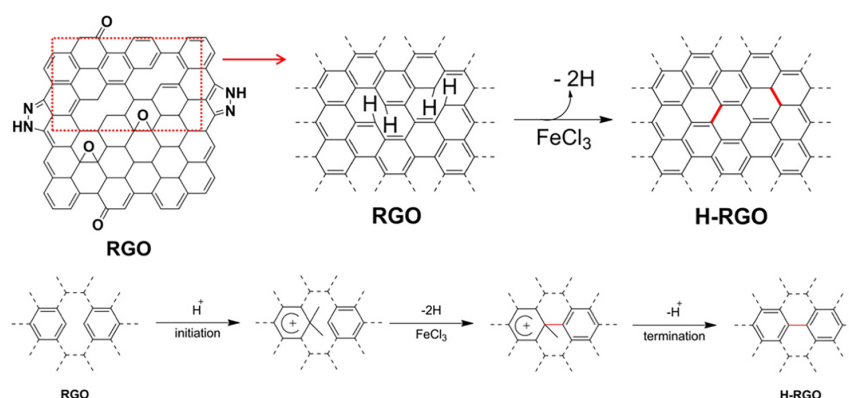

Figure 6. RGO chemical defect repair is shown schematically (top), and the intramolecular cross-dehydrogenative coupling (ICDC) with FeCl₃ is shown schematically (bottom)[73]. RGO: Reduced GO.

provide a good chance to decrease the production of defects. According to Zhao *et al.*[74] and Xu *et al.*[75], RGO was produced using minimally oxidized graphite oxide (MOGO), which was synthesized utilizing a modified Hummers technique and had a low degree of graphite oxidation. MOGO sheets have a low C/O ratio, which causes them to be heavily functionalized. However, they still maintain the structure of the conjugated carbon framework with comparatively few defects. Therefore, MOGO can be reduced to highly conductive RGO using either hydrazine or chemicla formula of hydrogen iodide (HI) reduction, both of which exhibit noticeably better reduction outcomes than the majority of previously published results and the results on GO obtained using the same reduction method but with higher degrees of oxidation. The control of the oxidation of the raw graphite should be extensively investigated in this condition in order to produce high-grade RGO through the oxidation and reduction process. This approach should be more important to assess the quality of RGO than solely focusing on selecting better strategies to minimize GO. However, most of the recent research has been concerned with the direct healing of RGO, and the preparation of RGO from mildly oxidized graphite still needs more attention.

CONCLUSION

In this paper, the brief history and synthesis procedure of chemical RGO were summarized. In this method, graphene was achieved by reducing the GO sheets, and the GO was exfoliated from the oxidized graphite. This method was one of the most potential ways to prepare graphene on an industrial scale. However, the defects in RGO, such as vacancies and residual oxygen groups, cannot be completely repaired and eliminated during reduction. Therefore, in future research, the emphasis should be on developing techniques to decrease the defect content. Healing defects in RGO after reduction may restore the graphitized structure of RGO, but the cost of this method was high, and it was challenging to produce in large-scale quantities. In this case, further development should focus on preparing RGO from mildly oxidized graphite, which could control the defect content from the source in the "GrO-GO-RGO" process and also facilitate the industrial production of RGO.

DECLARATIONS

Authors' contributions
Made substantial contributions to the conception and design of the study and performed data analysis and interpretation: Hu Y
Organize and polish the content of the article: Gao H

Availability of data and materials
Not applicable.

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

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