# Exploring Hummers Approach for Graphene Oxide Synthesis and Industrial Viability

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Abstract-Graphene has taken the spotlight in the recent years in the scientific community; however, its industrial viability is yet to be fully realized. The present work aims to study the state of art of graphene production by analyzing patents deposited in Brazil which produce graphene via modified Hummers method. A brief review is made on modified Hummers method, where the reagents, mechanisms of the reaction, and process conditions are presented, as well as the characterization techniques commonly used in graphene-like materials. Graphite types, sizes and pre-treatment, reagents employed possible and substitutions, as well as graphene quality such as thickness, lateral size and O/C ratio are analyzed throughout the paper. Although all patents examined present detailed information and sought production in pilot or industrial scale, none presented the true scale produced in volume produced. Also, the possible environmental impact of gaseous emissions is emphasized in many patents and reagents substitutions are suggested to minimize or eliminate this problem in many of the patents analyzed. Despite all challenges presented in graphene production, recent publications have been showing great promised.

## *Keywords*—graphite, Graphene Oxide (GO), Hummers method

#### I. INTRODUCTION

The chemical element carbon was discovered in 1789 by the chemist Lavoisier and, since then, its multipurpose has been identified, as it is found in diamond and graphite. Years later, an allotrope of carbon was theoretically discovered and named graphene [1]. This nanomaterial functions as a building block to form fullerene and carbon nanotubes, however its isolation only occurred in 2004, through a technique developed by physicists Geim and Novosolev, which consists of the use of adhesive tapes [1, 2].

Graphene is composed by a two-dimensional monolayer, formed only by hexagonal arrangements of carbon atoms sp<sup>2</sup>. This structure ensures good thermal, electric and mechanical properties, such as high mechanical resistance and conductivity [3, 4]. Graphene properties are very attractive but since it presents a complex and economically unfeasible production processes, it has not been used in the industry. Thus, the search for economic and practical procedures that generate a high yield and purity has been increasing lately [4].

There are physical and chemical methods for obtaining graphene from graphite. In general, the chemical techniques

utilize concentrated acid and strong oxidants producing large quantities of sub-products which also compromise product quality [5, 6]. On the other hand, the physical techniques are based on the breaking of interactions between the layers showing lower yield [5].

This study analyzes the procedures and reagents used in the methodology developed by Hummers to obtain Graphite Oxide (Gr-O), as well as processes of exfoliation for Graphene Oxide (GO) and reduction for reduced Graphene Oxide (rGO), to discuss possible strategies to enable the application of this process in the industry. Although the Hummers methodology generates a product with lower structural quality than other treatments already known and promotes an impact on the environment, its application for large-scale production is the most indicated due to the shorter operation time, greater process safety, high yield and economic viability [7].

#### II. DEVELOPMENT

Graphite oxidation, using the Hummers method, is performed from the reaction between sodium nitrate (NaNO<sub>3</sub>), potassium permanganate (KMnO<sub>4</sub>) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). NaNO<sub>3</sub> promotes spacing of graphite layers and, the reaction of H<sub>2</sub>SO<sub>4</sub> with KMnO<sub>4</sub> result in the dimanganese heptoxide (Mn<sub>2</sub>O<sub>7</sub>), which is the active substance that advance the oxidation of sp<sup>2</sup> carbon to sp<sup>3</sup> and formation of oxygenated groupings [6, 8, 9].

Next, the influence of the reactants and operational conditions used in the process of obtaining Gr-O, GO and rGO will be discussed. Most of the research carried out was based on patents that portray real problems and advantages found in large and pilot scale applications.

## A. Graphite

It is of great importance to choose the type of graphite that will be used in the synthesis of Graphite Oxide (Gr-O), since the size of graphite particles directly influences the oxidation time.

Aiming at production on an industrial scale, graphite with very small size present low carbon, being that an unfavorable factor, while graphite at a relatively large size needs longer time to oxidize. Table 1 illustrates the types of graphite used in some patents and the size mentioned by the authors.

## B. Reactants

 $NaNO_3$  acts as an interlayer agent, but it may promotes the formation of toxic and polluting gases such as nitrogen dioxide (NO<sub>2</sub>), nitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>) and ammonium (NH<sub>3</sub>) when in high temperatures [10]. Thus, on an industrial

scale, it becomes more interesting to replace  $NaNO_3$  with an agent that causes less environmental impact, such as ammonium nitrate ( $NH_4NO_3$ ), which, despite generating gases of nitrogen ( $N_2$ ), oxygen ( $O_2$ ) and water ( $H_2O$ ) in greats quantities, does not show evidence of formation of any toxic gas [11].

Table 1. Types of graphite used in some patents						
Patent	Graphite	Size (µm)				
BR1120200230294 [10]	Electrode scrap	100-150				
BR1120200217450 [11]	Kish	$\geq 50$				
BR1020160149967 [7]	Lamellar	*				
BR1020200209787 [12]	Mineral	*				
BR1020160289386 [13]	Natural	$\pm 10$				
WO2015075455 [14]	Nanoparticles	>100				
WO2017027731 [15]	Mineral	100-150				
WO2015044478 [16]	Synthetic	<20				
CA3097307 [17]	Kish	<420				
CA3057958 [18]	Kish	<420				
CA3031731 [19]	Natural	*				
EP3059209 [20]	Natural flakes	*				
US20160311688 [21]	Dust	>200				
US20160347617 [22]	Anthracite	>200				
ES2779151 [23]	Single crystals	2-50				
ES2507415 [24]	Pre-graphitic material	*				
ES2534575 [25]	Dust	<20				
AU2015252756 [26]	Expandable	*				
EP3050844A [27]	Powder	<20				

<sup>\*</sup> The authors did not mention the size of graphite used.

 $H_2SO_4$ , in addition to exercising the function of activator and media of the oxidizing agent, it also acts as on intercalation agent [12]. The use of highly concentrated acid is not attractive due to the generation of a residue that is difficult to recover. In addition, it is necessary to pay attention to the amount of acid used in process, as its scarcity in the face of a high concentration of oxidant can cause an explosion [13, 14]. On an industrial scale, it may be feasible to carry out a recycling of this solution before the washing process in order to recover and reutilize some reactants [14].

 $KMnO_4$  is used as oxidizing agent due to its high solubility in sulfuric acid [15]. The presence of excess permanganate may cause product contamination, therefore it is necessary to treat it with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and wash it with H<sub>2</sub>O [16]. Furthermore, it is common to use hydrochloric acid (HCl) during the washing process to eliminate low solubility substances, such as manganese dioxide (MnO<sub>2</sub>) and sulfates [4, 17].

The interruption of the oxidizing process can be performed by the addition of an interrupting agent. To enhance this process, it is a widely adopted approach to use two interrupting agents in conjunction. In most cases,  $H_2O$  and  $H_2O_2$  are the preferred substances used [9].

The Gr-O production is not limited to only the Hummers method, other methodologies are also applied, utilizing the reactants cited on Table 2 [10–17].

Table 2. Reactants used in Gr-O production					
Intercalating Agents	NaNO <sub>3</sub> ; NH <sub>4</sub> NO <sub>3</sub> ; KNO <sub>3</sub> ; Ni(NO <sub>3</sub> ) <sub>2</sub> ; Cu(NO <sub>3</sub> ) <sub>2</sub> ; Zn(NO <sub>3</sub> ) <sub>2</sub> ; Al(NO <sub>3</sub> ) <sub>3</sub>				
Acid	H <sub>2</sub> SO <sub>4</sub> ; HCl; HNO <sub>3</sub> ; H <sub>3</sub> PO <sub>4</sub> ; C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> O <sub>2</sub> ; HSO <sub>2</sub> OH				
Oxidizing Agents	KMnO <sub>4</sub> ; H <sub>2</sub> O <sub>2</sub> ; O <sub>3</sub> ; H <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ; H <sub>2</sub> SO <sub>5</sub> ; KNO <sub>3</sub> ; NaClO				
Interrupting Agents	Deionized H <sub>2</sub> O; H <sub>2</sub> O <sub>2</sub>				

## C. Operation Conditions

System temperature must be controlled throughout oxidation process, for the purpose of preventing the formation of gases such as carbon dioxide (CO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>) and nitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>) [7]. Although higher temperatures favor graphite oxidation, at high temperatures a large amount of CO<sub>2</sub> is generated, promoting reduction of carbon in Gr-O structure and forming holes of different sizes in the graphite structure [4, 28]. Temperature oscillations can cause an increase in the oxidation rate, compromising the structure of Gr-O [7]. Moreover, variable control is important to avoid occurrence of basal plane super-oxidation phenomenon and to also preserve product structure, since once damaged, it is unrepairable [10, 18, 19].

Throughout oxidation, the system is kept under mechanical or magnetic stirring. However, magnetic stirring promotes the reduction of graphite oxide layers' dimensions, this being an unfavorable factor when compared to layers formed by mechanical stirring [8]. The product formed in oxidation reaction is variable, for this reason properties are controlled according to operating conditions [8, 17].

## D. Exfoliation and Reduction of Graphite Oxide

In the exfoliation step, the weakening of Van der Waals interactions of the GO occurs, promoting separation of GO layers. Agitation during the reaction period can also promote a partial exfoliation of the graphite oxide. Thus, there is a significant loss of structural stacking [29]. The carbon layers are disaggregated due to action of forces [20], these being produced from mechanical stirring [30], magnetic stirring [21], ultrasound bath [22], among others. The choice of exfoliation technique is of paramount importance as it directly affects the characteristics of the product, such as lateral size, number of defects, types of functional groups, among others [22]. According to studies carried out by Neiva and Zarbin [31], the more abrasive the exfoliation process, the smaller the lateral size of the graphene layer [31]. Therefore, the choice of exfoliation technique is of paramount importance as it directly affects the characteristics of the product. For example, for electrochemical sensing applications, it is more advantageous to use a more aggressive technique such probe ultrasound, as in this case smaller graphene layers favor sensor sensitivity.

GO obtained thorough the described methodology presents epoxy, hydroxyl, carboxylic and carbonyl groups, in its basal plane and edges, which are essential functional groups to improve the physicochemical properties of this material [32, 33]. Additionally, these functional groups allow dispersion in various polar solvents facilitating the treatment of graphene oxide layers and, also, preventing the formation of irreversible restacking [21, 23].

After the exfoliation step, the reduction process of graphene oxide is done for the purpose of restoring electrical properties, since oxygenated groups affect the materials conductivity [34]. Reduction can be performed through chemical methods, which consist of the injection of the reducing agent such as sodium borohydride (NaBH<sub>4</sub>) [6]. The poliol method can be employed and promotes a greater structural restauration of GO, however, NaBH<sub>4</sub> shows higher oxygenated groups elimination [22]. Physical models that employ fast heating of system can also be used to promote the

expansion of the perpendicular dimension of the carbon layers [20].

## E. Graphene-like Materials Characterization Methods

The Raman spectroscopy technique is widely used to characterize carbon rich compounds for being fast and nondestructive method [3]. The main bands are denominated D and G. Through band D it is possible to evaluate the level of defects and impurities of the compound, since the increase in disorder promotes the incidence of wider and intense bands. Furthermore, the band G indicates the amount of graphitic materials present in the product. Other bands are of lower relevance to graphene-like- materials produced through chemical exfoliation [24].

A destructive technique, but that allows analyzing the thermal stability of graphene through the monitoring of the mass variation as a function of the increase in temperature is the Thermogravimetric Analysis (TGA) [17]. At temperatures between 20-100 °C, it is observed a loss of mass associated with the release of water molecules, between 100-400 °C, the pyrolysis of oxygenated functional groups, between 400-540 °C, the oxidation of graphene structure and 540-800 °C the non-oxidized graphite [17, 25]. TGA is very interesting because it makes it possible to quantify the efficiency of the graphite oxidation process and the degree of GO functionalization [4].

In addition to these techniques, graphene based materials can be characterized through other different qualitative and quantitative techniques such as X-Ray Diffraction (XRD) to calculate the crystallinity index and estimate number of stacked layers, Scanning Electron Microscopy (SEM), to analyze the surface topography and the lateral size of the graphene-like materials, which can be done also by Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) to measure the number of stacked layers, among others [3, 26].

## III. ANALYSIS OF PATENTS DEPOSITED IN BRAZIL

Although there are different routes of production of graphene oxide, it is necessary to pay attention to the quality of product generated. The structural properties are an impacting factor since the ideal is a product with only one layer of carbon, but due to the difficulty of production, graphene with a few layers is acceptable.

The patent deposited by Vu, Alvarez and Sanchez [10] proposes a GO synthesis using graphite electrode electrode residue as reagent, with application directed to metallurgical industry. In these conditions, the obtained product present a thickness between 2 and 120 nm. The synthesis consists in the trituration of the electrode residue before oxidation to reduce the reaction time, since the particles will present lateral size which are inferior to the initial, between 100 to 200  $\mu$ m. A similar patent by the same author presents a synthesis by the oxidation of pre-treated Kosher graphite, with lateral size equal or superior to 50  $\mu$ m and thickness between 5 to 50 nm. Analyzing both cases, it is evident that

the graphite particle size will directly affect the lateral size of graphene-based material. Furthermore, the use of smaller graphite particles ensures a higher product homogeneous in terms of thickness.

In the patent by Duzynsk *et al.* [35], a method of exfoliation of graphite in the liquid phase is proposed. The product obtained is composed of few-layers graphene ranging from 11 to 73 stacked layers of graphene leading to thickness between 4 to 25 nm. It is observed that Brazilian patents use the Hummers method as a basis to obtain a product with low number of stacked layers, as is the case of patents written by Reis *et al.* [12], which reaches a degree of exfoliation with 2 to 3 layers and a thickness of 5 to 15 nm, and Pasquini and Morais [13], which reaches a structure with 10 layers and thickness less than 5 nm.

Graphite pre-treatment is present in most Brazilian patents, as is the case of the patent conceived by Terence, Carrió and Nascimento [18], which proposes the intercalation of a polymer between the lamellar graphite previously to the oxidation reaction. The oxidation time took approximately 30 hours and the final product had lateral dimensions between 10 to 15 µm with yield superior to 90%. The patent created by Vu and Sanchez [10] also employs the intercalation of kish graphite with ammonium persulfate  $((NH_4)_2S_2O_8)$  and sulfuric acid  $(H_2SO_4)$  before the oxidation. In this case, the reaction time was of 10 minutes and the product presented lateral dimensions up to 100 µm. By comparing the processes described, it is noted a considerable difference of the reaction time. Regarding the proportion of oxygenated groups, Vu and Sanchez [10] described that periods superior to 10 minutes in the graphite oxidation process did not increase oxygen content than 45% of mass ratio. The short period of reaction led to an expressive reduction in energy consumption.

The invention proposed by Zaterra et al. [36] suggests that the use of micronized graphite instead of graphite flakes reduces the production time of GO and promotes a higher homogeneity and product yield. The micronized graphite is obtained from graphite ore and its size varies between 3 to  $60 \,\mu\text{m}$ , and the graphite flake may vary between 50 to 800  $\mu\text{m}$ . Commonly, the GO obtained from graphite flakes is usually found in the supernatant due to the variance in the size of decanted particles, this does not occur when micronized graphite is used, since in this case, the desired product is found in the decanted material, this occurs because this graphite undergoes a size reduction process in a mill with high air pressure favoring the exfoliation stage. Thus, it is notorious that the graphite source influences directly the process yield, since the graphite oxide sedimented makes easier their use.

All patents presented above aim at large-scale production, but there is a lack of information about the quantities of materials used and if produced. On the other hand, all processes and reactants chosen for synthesis are clearly described and detailed. In summary, Table 3 shows the Brazilian patents that use Hummers method as a base to industrial and pilot scale production.

Table 3. Resume of Brazilian patents								
Patent	Steps	Components	Graphite type	Graphene Layers	Lateral Size (nm)	O/C Ratio (%)		
BR 102020025525-8 A2 [36]	Oxidation, washing, drying, exfoliation and reduction	$\begin{array}{c} H_2SO_4,KMnO_4,NaNO_3,H_2O,\\ H_2O_2\:e\:NaBH_4 \end{array}$	Micronized Graphite	7-11		40%		
BR 112020023029-4 A2 [10]	Graphite electrode residue trituration, oxidation, filtration, exfoliation and reduction	Graphite, Nitrate salts, Oxidation interrupting acid, reducing acid	Graphite electrode residue		2-120	>20%		
BR 112020021745-0 A2 [11]	Graphite pre-treatment, oxidation, filtration, exfoliation	Graphite, Nitrate salts, Oxidation interrupting acid			5-50	<45%		
BR 102016014996-7 A2 [7]	Graphite intercalation, oxidation, washing e filtration	Graphite, NaNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , KMnO <sub>4</sub> , deionized H <sub>2</sub> O, H <sub>2</sub> O <sub>2</sub> e HCl	Laminar graphite					
BR 102016028938-6 B1 [13]	Balls mill oxidation, centrifugation, washing and exfoliation	Graphite, LiCl, (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , H <sub>2</sub> SO <sub>4</sub> KMnO <sub>4</sub> , H <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> O e NaOH		<10	1-15	11,35%		

#### IV. FINAL REMARKS

This study sought to analyze graphite lateral size and thickness, procedures and reactants used in the methodology developed by Hummers to produce graphene, to discuss possible strategies to enable the application of this process in the industry. Results reveal that the lateral size and thickness of the graphite used to obtain graphene influences the oxidation reaction time. Therefore, it is important to determine the ideal graphite shape to optimize the process. Moreover, with the substitution of some reactants there is a decrease in the emission of pollutant gases, promoting less environmental impact. Despite the numerous challenges encountered in industry, recent studies have been showing great promise.

In general, the analyzed patents aim at the invention of a GO production that can be reproduced both on a pilot and industrial scale. Therefore, the use of more technological resources that generate less environmental impacts are frequently cited topics, but the lack of statistical data that confirms the environmental and economic viability of the applied techniques is notorious.

#### CONFLICT OF INTEREST

The authors declare no conflict of interest.

#### AUTHOR CONTRIBUTIONS

Alicia Ribeiro Carvalho conducted the patent and literature research and wrote the paper alongside Bruno Eduardo Piske. Vinicyus Rodolfo Wiggers and Eduardo Guilherme Cividini Neiva idealized and reviewed the paper. All authors approved the final version.

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