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Current Research and Future Perspectives on Graphene Synthesis

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Abstract. Although graphitic materials are considered indispensable across many industries, practitioners and researchers have shown that graphene is still in development and its industrial implementation in mass production may save many organizations millions of dollars a year. This paper presents a comprehensive and systematic literature review of graphene synthesis methods. In our research, we noticed an increasing trend in publications for research under diverse scenarios (e.g., engineering, entrepreneurship, academy, etc.), which limits the generalizing of the findings due to the nature of graphene's synthesis. Most of these studies were conducted about electrical and mechanical properties for possible sector applications due to its structure. We found that less effort has been made to analyse the development and synthesis of methods that allow graphene manufacturing in industrial quantities. We classified the five most important synthesis methods of graphene, categorizing chemical vapor deposition (CVD), and adhesive tape exfoliation as the most implemented methods, with the latter getting better quality and greater quantity of graphene. We also identified needs for research on graphene that goes beyond its known properties, by focusing on models that encompass the innovation needed for manufacturers of materials in areas, such as electronics and energy.

1 Introduction

1.1 What is graphene?

The relevance of graphene, as building block to other graphitic materials for industrial applications, such as circuit components, elastomers, and energy storage, is still in development in literature. However, some authors show graphene as one of the most versatile materials due to its electrical and mechanical properties (i.e., electrical conductivity, elasticity, hardness, etc.) [1]. Since the beginning of its synthesis [2], graphene has been defined as a carbon sheet with the thickness of a single atom that is densely packaged in a hexagonal structure [3].

1.2 Which are graphene synthesis methods?

Currently, the synthesis of this material can be performed in five main different ways [3]: (1) ultrasonic exfoliation of graphite oxide; (2) thermal deposition of chemical vapor; (3) exfoliation with adhesive tape; (4) mechanical exfoliation; and (5) microwave plasma process using helium at low temperatures.

1.3 Why is graphene study relevant?

At present, graphene industry is limited to simple, small layers, as its synthesis on an industrial scale is still very complicated. However, synthesis methods continue to be investigated to achieve the feasibility of their large-scale production [4]. The European Union's scientific research initiative "Graphene Flagship" uses tape peeling and chemical vapor deposition to synthesize graphene for applications in areas, such as energy, electronics, biomedicine, telecommunications, etc. [5].

1.4 What are the difficulties in graphene synthesis?

Although there is extensive research on graphene, there is no systematic review of successful implementations of its production methods in industrial processes [6]. As research in this field is still in development, it would benefit significantly from a study aimed at reorganizing available knowledge. Hence, an updated systematic literature review of ways to synthesize graphene is needed. Such study also makes an important methodological contribution by applying elements of reviews, from the so-called "Medical science" to fields, such as Mechanical and Materials engineering, where concepts are often very heterogeneous, failing to provide enough help for industries to produce graphene efficient and effectively.

1.5 What are the objectives of this study and the research question?

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The lack of a review of previous literature on synthesis methods, presenting both current comparisons and future perspectives in this important field, has led us to conduct a study, that not only highlights the qualities of graphene, and its relationship to current synthesis processes [7], but also explores issues that have not yet been answered by the literature. The *research objectives* are: *(1) To consolidate existing knowledge on the main methods available for graphene synthesis; (2) to make a comparison based on quantity and quality of synthesis; and (3) to provide a starting point for researchers and practitioners looking to implement graphene in industrial applications and provide suggestions for future research*

To meet these objectives, we asked the following *research question*: *Which of the five graphene synthesis methods in question is the most efficient and feasible for industry implementation?*

The paper is structured as follows: It continues with propositions. Then, the methodology is described. Subsequently, the analysis and discussion are developed. Finally, we provide a critical conclusion of current research, with suggestions for future perspectives on graphene synthesis.

2 Related work

The discovery of graphene has prompted the scientific community to examine widely the possible applications of this material. Graphene is commonly referred to as a two-dimensional sheet of material with hybridized carbon atoms, configured in a hexagonal structure and its thickness is equivalent to the diameter of an atom [3]. The analysis between variables and factors, such as quantity and quality in synthesis processes, is explained below.

2.1 Graphite oxide ultrasonic exfoliation (GO)

Graphite powder undergoes an oxidation process, where graphite oxide is obtained, required to be processed, using the improved Hummer method, in which oxidizing agents (e.g. potassium permanganate, sodium nitrate and sulfuric acid) are used, which ensure a simple, high-productivity and low-cost process [8]. Graphene synthesis is validated through IR, XRD, Raman and XPS analyses. The electrochemical behavior of GO and graphene can be evaluated by electrochemical impedance spectroscopy and linear sweep [9]. This synthesis is capable of producing graphene films, whose thicknesses ranges from 40 nm to 80 nm, with densities up to 1350 kg/cm3 and porosity [10]. Thus, the following proposition is presented:

> *Proposition 1: GO is a direct method of obtaining mass scale and low-quality graphene.*

2.2 Chemical vapor deposition process (CVD)

Since it was first reported in 2008, CVD literature has resulted in the development of various procedures for obtaining graphene as shown next [11].

2.2.1 Graphene growth on hexagonal boron nitride

In the chemical deposition of graphene vapor in combination of perfect lattice, graphene is more energetically favored in h-BN, under the conditions of this process, also obtaining few layers of graphene. Layer numbers may increase as the growth time and the rate of methane flow increase [12]. In each intermediate layer, each carbon atom binds together with the surrounding carbon atoms by hybridization, contributing from an unlinked electron to a large bond, allowing electrons to move freely between layers [13].

2.2.2 Graphene bilayer growth on copper (Cu)

The mechanisms that determine the growth of high-quality monolayer and bilayer graphene in Cu use chemical vapor deposition (CVD). While Cu's surface micro topography affects strongly the uniformity of the grown graphene, the purity of Cu's film determines the number of graphene layers, synthesized under low pressure conditions [14]. This sublayer mechanism can facilitate the synthesis of uniform single-layer films but presents challenges for growing uniform CVD bilayer films [15].

2.2.3 Growth of graphene monolayer in nickel (Ni).

In contrast, the deposition of chemical vapor at high temperatures leads to the formation of multilayer graphene by thick carbon segregation; the growth of graphene is limited below 600 °C; on gets optimal growth at 550 °C, established as the right temperature for the high quality graphene growth; and the formation of graphene is prevented at below 500 °C, limiting its growth [16]. Some experimental research show that Ni is better for graphene growth than Cu [17]. To check the quality of the CVD method, the surface analysis is performed using an optical microscope and Raman microscopy, for the analysis of graphene layers. Therefore, we formulate the following proposition:

> *Proposition 2: The CVD method provides high quality graphene, but with reduced production.*

2.3 Adhesive tape exfoliation method and CVD

Adhesive tape is remarkably effective in controlling residues on graphene surfaces that produces the thickness of graphene grown, improving the transmittance and uniformity of graphene, because the thickness is reduced by the repetition of the adhesive tape [18]. The film is inspected and coated with a Ni layer and dried at room temperature, before being placed in the CVD camera for direct graphene growth. To confirm the quality of the adhesive tape exfoliation method, Ni is used as a catalyst and carbon source, where exfoliation directly improves the quality of cultured graphene [19]. So, we suggest the next proposition:

> *Proposition 3: The adhesive tape exfoliation method is effective at reducing impurities and generating large amounts of graphene.*

2.4 Mechanical exfoliation

Mechanical exfoliation can be classified based on directional paths (i.e., normal and cutting force vectors). One study on the normal strength synthesis route is graphite peeling, using advanced ultra-sharp single wedge glass wedge machinery [20]. This method eliminates the need for manual operation, thus saving time and costs. Another technique uses a machine three-roller mill, to produce 1.13–1.41 nm graphene [21]. It facilitates the exfoliation and fragmentation of graphite to nano-sized graphene, as well as the mixture between graphene and composite materials, and even graphene functionalization [22]. The quality of graphene produced is controlled by the synthesis of ball grinding by process parameters, such as grinding media type, time, matrix, velocity and initial size of the precursor [23]. The following proposition is stated:

> *Proposition 4: The graphene mechanical exfoliation method is a process that improves graphene quality by regulating extraction parameters process (i.e., speed, time, matrix, size).*

2.5 Microwave plasma process with helium at low temperatures

By pretreating Cu sheet substrate, the synthesis of graphene with microwave plasma is generated, using a mixture of helium and hydrogen gas [24]. Using X-ray photoelectron spectroscopy, one can verify removal of contaminants on the surface of Cu's oxide [25]. We set out the following proposition:

> *Proposition 5: Plasma process improves graphene quality using a mixture of helium and hydrogen for impurity removal.*

3 Methodology

The paper considers the following three steps from the Systematic Literature Review (SLR) methodology [26].

3.1 Search strategy

For the collection of the most relevant publications, we relied on the source of information, ScienceDirect, and Google Academic as support. These publications have undergone a SLR, whose data was validated by Scopus.

3.2 Publication selection

The selection process for documents was done in three phases, as follows:

3.2.1 Search restrictions

It consists of collecting published papers such as papers from scientific journals, conference papers, journal-related papers, doctoral dissertation, and books. Publications included were in English or Spanish, with their field of study based on graphene, within the timeline of 2010-2020. 176 documents were collected in the field of study of graphene.

3.2.2 Inclusion and exclusion criteria

All the information obtained from the keywords [(1) graphene, (2) method, (3) synthesis, (4) production, (5) quality] were included, but also combinations close to them or where only one of the terms that summarizes the focus and nature of the topic. Example of Boolean operators for the keywords were: "synthesis AND graphene", "method OR synthesis", "graphene and synthesis OR production", "quality AND graphene". All information that does not belong to the study area is excluded (i.e., publications that did not meet the inclusion requirements previously mentioned and established for the search), but publications that are not written in the English or Spanish languages are also excluded, and/or that they were from the period covered. Duplicates were removed using Mendeley. Those that were gray literature were eliminated. A total of 110 documents were included. A total of 66 documents were excluded.

3.2.3 Final publications

We focused on both the title and the summary, selecting the documents that have a clear approach with graphene synthesis and its methods. Papers should be classified as part of the quartiles (Q1, Q2, Q3, Q4) ranked in Scopus and/or WoS. It resulted in the inclusion of 15 publications.

3.3 Extraction of information

The 15 papers were studied to determine the research carried out on graphene synthesis methods, focusing on the amount and quality of graphene production.

4 Analysis and discussion of results

4.1 Analysis of the main journals

Studies based on graphene synthesis methods have been published in a wide range of journals, considering methods and ways of synthesis. The selected research papers belong to 12 academic journals: Carbon, Materials Chemistry and Physics, Small, Accounts of Chemical Research, ACS Nano, Applied Physics Letters, Journal of the American Chemical Society, Journal of

Materials Chemistry A, Current Opinion in Chemical Engineering, Japanese Journal of Applied Physics, Physical Review Letter, and IEEE International Nanoelectronics Conference. Carbon is the main one on the number of publications of the main topic.

4.2 Citation and data validity

The value for a research paper citation is determined by how many times it has been cited by other papers. The 15 final publications were validated, by cross-comparing and reviewing the papers between four of the authors, who resolved the differences. Table 1 supports the quality of the data by the level of impact shown, using Scopus which shows that all journals are Q1, except for one that is Q2, but of high impact. In fact, three of these Q1s are of 10% highest impact.

Table 1. Citation and data quality.

Source	Year	Citation	H Index	SJR	Level	CiteScore
[8]	2010	6123	310	6.21	Q1	14.29
[9]	2018	13	132	0.65	Q2	2.74
[10]	2010	662	195	3.55	Q1	9.9
[11]	2013	715	354	9.47	Q1	14.75
[12]	2011	111	247	2.12	Q1	7.42
[14]	2011	219	247	2.12	Q1	7.42
[16]	2010	131	401	1.33	Q1	3.58
[27]	2009	7900	1058	13.25	Q1	8.64
[18]	2020	10	247	2.12	Q1	7.42
[19]	2011	358	542	7.47	Q1	7.42
[20]	2015	436	264	0.15	Q1	14.75
[21]	2016	27	35	1.21	10%	10.66
[22]	2017	99	80	0.84	Q1	4.33
[24]	2016	7	1	0.11	Q1	7.42
[25]	2014	77	120	0.15	10%	6.33

4.3 Geographical distribution of publications

By the criterion of number of citations and method of synthesis, we obtain the main five methods of graphene synthesis with their respective citations: (1) Ultrasonic exfoliation of graphene oxide = 13 citations, (2) Process by chemical deposition of steam = 691 citations, (3) Exfoliation with adhesive tape = 15 citations, (4) Mechanical Exfoliation = 409 citations, and (5) Microwave plasma process = 7 citations. The distribution of publications showed that the ultrasonic exfoliation of graphene oxide for the year 2018 was synthesized in the United States, producing 2.3 layers/nm of medium quality. The chemical vapor deposition process for 2013 was synthesized in the United States, producing 0.03 high-quality layers/nm. The adhesive tape exfoliation method for 2019 was synthesized in Asia-South Korea, producing 5 high quality layers/nm. Mechanical Exfoliation for 2015 was synthesized in South America-Argentina, producing 1.13-1.41 high quality layers/nm. The microwave plasma process for 2016 was synthesized in East Asia-Japan, producing 2 layers/nm per (11.2nm)/1, 533nm wave of medium quality.

4.4 Evaluation of proposals

4.4.1 Ultrasonic exfoliation of graphite oxide

The ultrasonic exfoliation of graphite oxide synthesizes medium quality sheets in high quantities, compared to other methods, thus *accepting Proposition 1.*

4.4.2 Chemical vapor deposition

The chemical Vapor Deposition allows to obtain high quality sheets, being convenient for example in the construction of transparent electrodes for solar panels, but the insertion of graphene in the industry is limited by the slowness of the process and low production. Thus, *Proposition 2 is accepted.*

4.4.3 Tape exfoliation technique and CVD

The tape exfoliation technique and CVD can produce graphene sheets with both high quality and production capacity, thus *confirming Proposition 3*.

4.4.4 Mechanical exfoliation of graphite

The mechanical exfoliation of graphite is a method by which the graphene produced is restricted to both medium level quality and low production. Therefore, *Proposition 4 is not accepted*.

4.4.5 Microwave plasma

The microwave plasma fails to improve the quality of graphene sheets deposited on metal substrates, at a low cost. According to this, *Proposition 5 is not accepted.*

4.5 Discussion

The study presents a systematic review of the literature on graphene synthesis methods from 176 papers published from 2010 to 2020. Trend analysis of the 16 final papers showed that there has been steady growth in the number of publications, distributed in a wide range of journals. A growing number of publications were found in Asia and North America as leading destinations based on the research domain of graphene studies. The results provide a starting point for researchers and professionals looking to implement such knowledge in organizations for a large-scale production: we classified the five main synthesis methods of graphene, categorizing chemical vapor deposition (CVD), and adhesive tape exfoliation as the most implemented methods.

5 Conclusions and future perspectives

The focus of this research was to consolidate existing knowledge on the synthesis of graphene. The results obtained show that adhesive tape exfoliation and CVD are the most used methods, presenting the best processes and providing the best mechanical and electrical characteristics to the material, because they can obtain more graphene with good quality compared to other methods.

However, of the two, adhesive tape exfoliation is the most promising method to be implemented in the industry, to produce graphene on a large scale, since it is a method derived and improved from CVD. Thus, compared to the latter, adhesive tape exfoliation has at least three advantages: (1) higher production and higher quality graphene; (2) fewer materials needed for implementation; and (3) it is a direct method for obtaining graphene, which is convenient to take advantage of industry resources.

The inherent limitations in SLR are the selection of studies and the possible imprecision in data extraction from the variable sources. However, this limitation presents an opportunity, given that the feasibility of extraction processes is a critical factor for their production in large quantities (with high quality) and their impact will be the subject of future research to determine which techniques are most conducive to successful deployment. Other synthesis methods have been proposed, such as ultrasonic exfoliation of graphite oxide, microwave plasma process using low temperature helium, mechanical exfoliation, which are still in development [4]. Because of this, there is a need to develop models that cover the methods necessary for industrial graphene mass-scale production. Hence, organizations that are about to embark on a journey of new discoveries to harness the potential of graphene, must have the right leadership to develop better models [28-29], beyond the known properties, which encompasses the innovation needed to manufacture materials, especially in areas of electronics and energy.

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