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RESEARCH ARTICLE

Evolution of Graphene, Graphene Oxide, Reduced Graphene Oxide: An Exploratory Study Using Citation Network Analysis

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ABSTRACT - Graphene and its synthesis, along with its derivatives, have been at the forefront of materials' research since its discovery in 2004. An analysis done during Dec 2023 using the keywords "graphene" and "synthesis" revealed nearly 40,000 research papers including journal articles, conference proceedings, reviews, books and book chapters; analysis of this vast data is beyond human abilities and requires computational intelligence. One of the research methodologies employed in analysing such vast data is Citation Network Analysis (CNA). Choosing the threshold citation to be two, the CNA constituted a cluster containing 294,680 papers. Using CNA, this study categorises this extensive literature into 12 clusters, unveiling their main paths of evolution. Notably, the most active research area focuses on the development of electrode materials for electrochemical applications. Additional focal points include advanced photocatalysts, electrocatalytic nitrogen fixation, wideband electromagnetic wave absorption materials, catalysts for formic acid oxidation, and flame retardancy in epoxy resin. The preference for the modified Hummers' method for synthesising graphene oxide emerges prominently due to its scalability. The implications of these findings are profound, paving the way for advancements in graphene synthesis with widespread impacts in industrial applications. By examining the historical trajectory of graphene research, this study offers critical insights, guiding future research endeavours in advanced materials science.

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1. INTRODUCTION

Since its discovery in 2004, the carbon allotrope Graphene - the wonder material of the 21st century - has found applications in numerous fields, from energy to electronics to drugs, to name a few. It is one of the most researched/ being researched substances because of its remarkable electrical, thermal and mechanical properties. Even though it has huge potential to replace different materials in the technological field, the challenges in the large-scale production of graphene such as its high production cost, high energy consumption, resource intensive, difficulty in getting pure form etc., hinder its wide usage. To advance synthesis methods for graphene, a review of the existing literature is essential. A search using the keyword "graphene" AND "synthesis" in the Web of Science database on 04 December 2023 gave nearly 40,000 search results, showing the enormity of the science and engineering literature devoted to graphene synthesis. Analysing and learning from this enormous literature are tedious and often beyond human abilities. In that context, the use of software/computer-based learning approaches is preferred for reducing the burden on researchers.

This study attempts to explore different research studies on graphene and its derivatives to find the evolution of the synthesis processes using computational methods such as Citation Network Analysis (CNA). CNA is one of the most important and beneficial analysis methods for researchers to study the relationship among academic publications, discover new knowledge, use the collected knowledge, and manage it. In CNA, the relative importance of a research paper is displayed via the number of citations it receives in subsequent research publications. Although the number of citations in a research paper increases with time, their relative weight remains constant. In its history of over a decade, CNA provides a tool for analysing the relative impact of research contributions. Such an exploration of the vast number of studies will be beneficial in discovering the evolution of the methods of synthesis of the material which can then potentially lead to improved production technologies.

1.1 Historical Background and Related Work

The first step in the history of graphene can be attributed to the discovery of a suspension of tiny crystals, when British chemist Benjamin Brodie exposed graphite to strong acids and named it carbonic acid /graphone. These crystals were later identified as graphene oxide (GO). Before the official discovery of graphene in 2004, many researchers have already published their works on graphene. For example, Ruess and Vogt observed very thin to a few nm in thickness flakes of graphene [1] and Ulrich Hofmann, Hanns-Peter Boehm and co-workers were able to find monolayers, and later coined the term 'graphene'[2]. In the 90s, the research on graphene was further taken up by Heinrich Kurz (1990), Thomas Ebbesen and Hidefumi Hiura (1995) and Rod Ruoff and his colleagues (1999) and described their respective findings as

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'optically thin layers', 'nm-thick origami' and 'thin graphite platelets' [3][4][5]. Despite several attempts at graphene synthesis, no one had figured out how to extract it from graphite until two researchers at the University of Manchester, Professor Andre Geim and Professor Konstantin Novoselov, separated graphene in 2004 by stripping off graphite with sticky tape, which earned them the Nobel Prize [6]. A million times thinner than human hair, graphene is the thinnest substance ever produced which is also 200 times stronger than steel. Graphene is made up of a single layer of covalently bonded sp^2 hybridized carbon atoms arranged in a hexagonal structure. It is a zero-overlap semi-metal with electrons and holes as charge carriers, resulting in higher electrical conductivity which led to its description as the most conducting material in the world. A single-layer purest form of graphene has 70% higher electrical conductivity than copper.

Researchers and commercial manufacturers employ a variety of pathways to synthesise graphene. The most common obstacles faced by researchers, according to A. A. Moosa and M. S. Abed, are "controlling the synthesis conditions to achieve the optimum yield, keeping the pristine structure to realise on-demand properties, minimum layers with the smallest lateral size, and minimum oxygen content" [7]. Graphite exfoliation method is considered the simplest way to produce graphene and graphene oxide. The studies of Lee [8] highlighted the importance of understanding the interactions between electrolyte ions and graphite for the electrochemical manufacturing of graphene. In contrast to chemical and mechanical peeling, Liu [9] advocated the simple, fast and efficient electrochemical method of peeling graphene. However, he emphasized that this method is more expensive and has limited application in industrial large scale graphene production. Pingale [10] advocated "the synthesis of graphene powder by ultrasonic-assisted electrochemical exfoliation using an acidic bath" in order to overcome the many drawbacks of mechanical exfoliation.

In the case of derivatives of graphene, one of the most commonly used safer, faster and more efficient methods of synthesizing graphene oxide was proposed and carried out by William S. Hummers and Richard E. Offeman way back in 1958 [11]. The 'Hummers method' involved adding graphite to a solution of concentrated acid with potassium permanganate ($KMnO_4$) as the primary oxidant. The modern variations of the method are many, mostly in the process of oxidation, leading to modified, improved and simplified versions. Kudus [12] proposed a simplified Hummers' method whereby GO is produced by oxidizing ultrasonically exfoliated water-dispersible graphene in an H_2SO_4/HNO_3 mixture. Modifying the method, Alkhouzaam varied the operating conditions; temperature, oxidation time, and reactant ratios to synthesize six different types of particles [13]. A lower than the prescribed concentration (decrease ~ 40%) of acid was proposed by Zhu et al. and they claimed that by using this improved Hummer's method, they were able to lower the production of high-concentration aqueous waste acid [14].

The disadvantages or risks associated with the synthesis of another derivative of graphene - reduced graphene oxide (rGO) - included the unwieldy experimental conditions and high cost of the thermal reduction process, harmful nature to the environment and the human body of the reducing agents like dimethyl hydrazine, metal hydride, hydroquinone etc [15]. Pumera [16] and Luo [17] pointed out that the use of ultraviolet (UV) irradiation results in poor functioning condition of the product. Owing to the very large number of research studies conducted worldwide and also with the availability of the vast majority of papers online, many researchers resorted to the help of computer-assisted technologies to gain insight into the development in the fields of research with respect to specific materials, products, processes, applications etc. related to their own field of research. Citation Network Analysis, a computer-assisted review approach that can map the scientific structure of a field of study based on citation practices, is a frequently used way to tackle the huge amount of research studies. Further analysis of the clusters of information can then be done with the help of different and appropriate software, like Gephi, Pajek etc.

Yang proposed an improved Subject-Action-Object (SAO) network-based method for analysing trends in graphene technology development [18]. Nguyen, taking graphene as a case study, extracted a dataset pertaining to the topic using 'Derwent Innovation', CrossRef, Levenshtein edit distance calculation, and data-driven modelling and simulation [19].

In this paper, an attempt is made to explore the changing aspects and the evolution of methods of synthesis of graphene and its two derivatives using social citation network analysis followed by main path analysis and cluster analysis.

2. METHODS AND MATERIAL

Citation Network Analysis (CNA) was used to sift through the vast number of research papers and select the relevant and important ones. The network obtained as a result of CNA is subjected to further analysis using the software: Gephi and Pajek. Figure 1 depicts the different steps that were adopted for the study. The various processes involved in creating a network are detailed below.

2.1 Metadata Extraction from Web of Science

Metadata is "data about the data". For the construction of a network, the first step is extracting metadata any bibliographic database using keywords. For this study, the meta data were collected from "Web of Science", one of the popular bibliographic databases, using keywords "Graphene" and "Synthesis". Bibliographic details, such as authors, title, publication year, journal, abstract and cited references, were taken from the returned search results and saved as a text file.

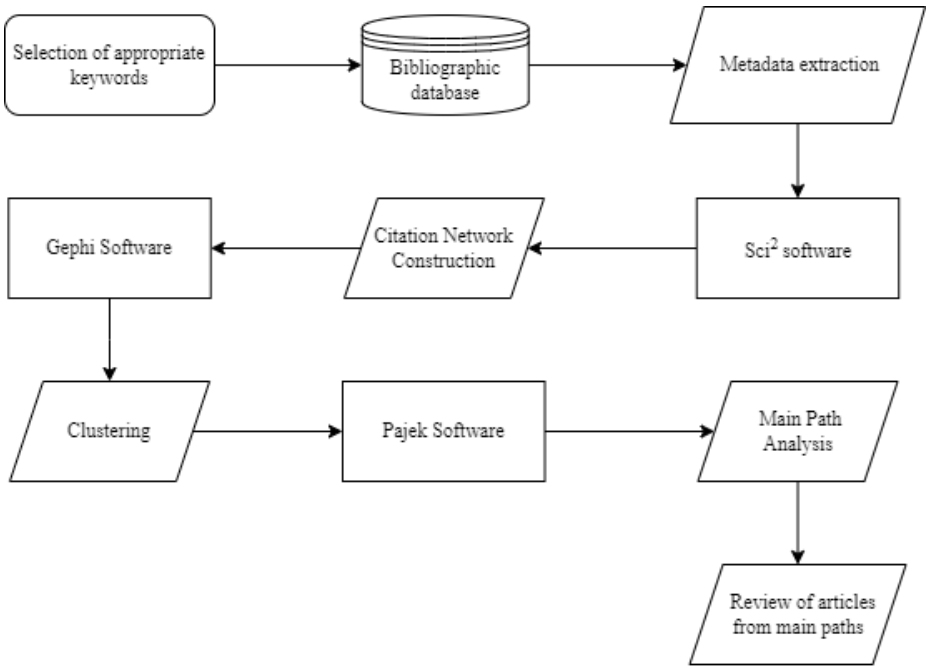

Figure 1. Design of the study

2.2 Network Creation in Science of Science Tool

A citation network is constructed from the bibliographic metadata collected from the database using the Science of Science (Sci[2)] software (Network = Total Number of Articles + Total Number of its References). This network showcases the relationship between research papers and cited references. The extracted file will show the total number of articles in the network, depicted as vertices. The network can further be assessed using Gephi and Pajek software.

2.3 Clustering using Gephi Software

Gephi is an open-source software and is the "leading visualisation and exploration software for all kinds of graphs and networks". From the network file created using Sci[2], the papers that have been cited at least two times are taken to get relevant papers, leading to the creation of a new network. From the new network, the giant component is taken for content analysis (main cluster, island). For this research, modularity-based clustering is considered (modularity is a measure of the structure of networks or graphs). Each cluster is extracted from the data based on modularity, and the Main Paths of the different communities are analysed using the Pajek software.

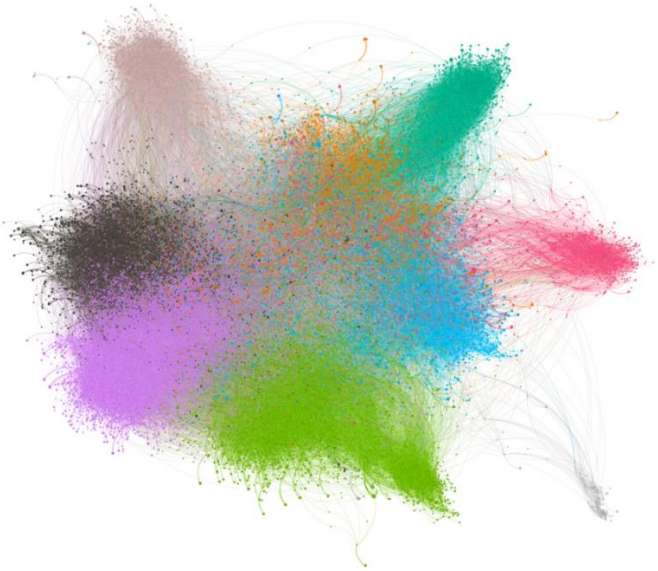

Figure 2. Clustering in Gephi software

2.4 Main Path Analysis using Pajek Software

Pajek provides various tools and algorithms for network analysis. The main paths of clusters developed from the aforementioned network are considered here, and the papers that show the evolution of research are identified. Examining these papers will demonstrate how the research began and how it is developing into new areas, approaches, and strategies.

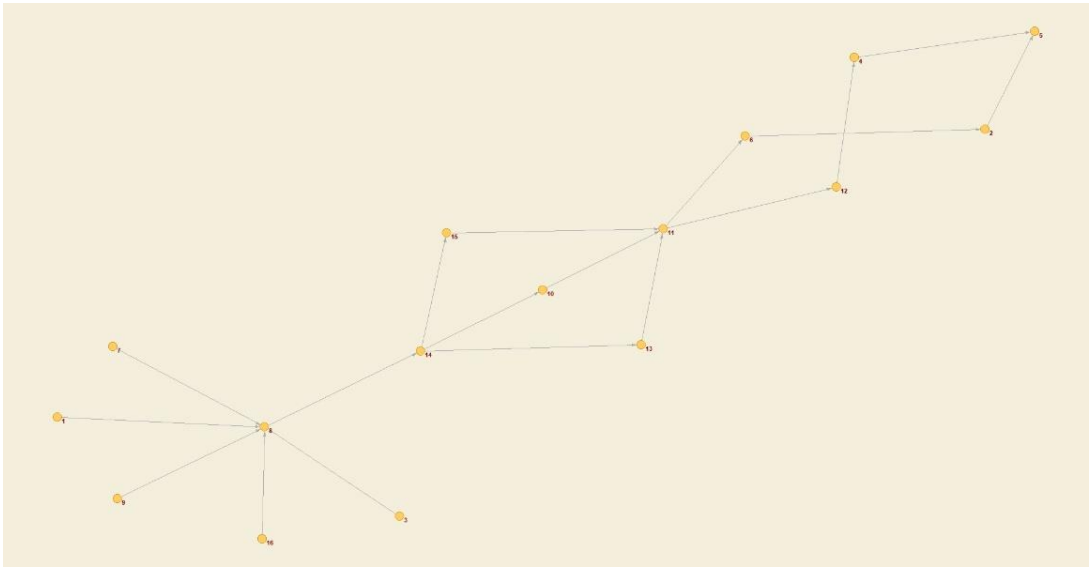

Figure 3. Main path of a cluster created using Pajek software

2.5 Review of the Main Paths of Clusters

The review process includes the comprehensive analysis of the key research articles identified through the main path, constructed using Pajek software, which shows the pivotal pathways in the evolution of graphene, graphene oxide, and reduced graphene oxide. The primary focus lies in extracting crucial information related to synthesis, properties and applications of the material from the identified articles. Through an exhaustive literature review, each selected article is examined for gaining valuable insights into the materials' developmental trajectories.

The whole process of investigation encompasses an in-depth examination of material synthesis methodologies, interpreting the diverse routes employed in the fabrication of graphene-based materials.

3. RESULTS AND DISCUSSION

The CNA was conducted on the research papers published from 2018 to 2023 to create a network that involves every article and their cited papers on the synthesis methods of graphene and its derivatives. The details of publications on graphene in the Web of Science platform on 25 October 2023 using the keywords “graphene synthesis” are given in Table 1.

Table 1. Details of publications on graphene

Type	Number
Publications in Web of Science	43,583
Articles in Web of Science indexed journals	38,542

Examining the trend for the last 20 years, it was found that the number of publications on the topic has increased significantly since 2018. The highest number of publications was found in the year 2020. The Citation Network Analysis was carried out using the Sci^2 tool, Gephi and Pajek software. A total of 12 clusters were obtained through network analysis. Cluster 0 focuses on the design and synthesis of advanced materials for wideband electromagnetic wave absorption. Graphene is described as a crucial component in the design and synthesis of the materials for electromagnetic wave absorption. Cluster 1 articles discuss the high-performance heteroatom-doped carbon anode for alkali-ion batteries. Graphene-based materials are extensively utilised in various energy storage applications like Li-ion, Na-ion and K-ion batteries. Cluster 2 focuses primarily on the synthesis and applications of nitrogen-doped carbon dots derived from various biomass sources. Cluster 3 generally discusses the preparation of nanocomposites involving graphene oxide nanoparticles through innovative microwave-based methods. Cluster 4 explores various aspects of electrocatalytic nitrogen fixation and N_2 reduction catalysts, and though graphene-based materials are not the sole focus of this cluster, the examples given indicate the evolving trend of incorporating graphene and graphene-related materials in electrocatalytic nitrogen fixation research for improved catalytic activity and efficiency. Cluster 5 concentrates on cutting edge research in graphene nanostructure engineering and explores various on-surface synthesis methods to create unique structures with specific properties. Cluster 6 articles focus on the synthesis and application of innovative nano catalysts for formic acid oxidation. These catalysts are various combinations of metals supported on materials like graphene. Cluster 7 focuses on advanced materials and nanocomposites designed for use in supercapacitor electrodes. There is a clear trend in exploring different forms of graphene and its derivatives ranging from graphene oxide to reduced graphene oxide and nitrogen-doped graphene oxide. Cluster 8 discusses the innovative flame-retardant materials for epoxy resin and Cluster 9 discusses the advanced nanostructures for energy storage and catalytic applications and the articles cover a range of materials, including

graphene. Cluster 10 revolves around the development and application of advanced photocatalysts for various environmental and water treatment purposes. This cluster shifts from the early use of graphene in photocatalytic materials to more advanced and innovative combinations with other materials for improved photocatalytic activity. Cluster 11 discusses the synthesis and applications of the advanced nanomaterials for various purposes, including electrochemical detection, photoelectric performance, and sensing applications. The clusters, topics and methods of synthesis generally discussed in the articles are summarised in Table 2.

Table 2. Clusters, topics and corresponding synthesis methods discussed in the selected papers

Clusters	Topic	Methods of synthesis of graphene and its derivatives
Cluster 7	Advanced Electrode Materials for Supercapacitors based on Graphene Oxide and Metal Oxides	Modified Hummers' method In-situ polymerisation Electropolymerization
Cluster 4	Electrocatalytic Nitrogen Fixation and N2 Reduction Catalysts	DFT calculations
Cluster 10	Advanced Photocatalysts for Water Treatment and Degradation of Organic Compounds	Modified Hummers' method
Cluster 1	Advanced Carbon-based Materials for High-Performance Alkali Metal Ion Batteries	Functionalized graphene
Cluster 3	Microwave-Assisted Synthesis of Advanced Nanomaterials for Energy Storage and Conversion Applications	Staudenmaier method, Modified Staudenmaier method, Heteroatom doped graphene
Cluster 5	Advanced Graphene Nanostructure Engineering and Magnetic Properties	On-surface synthesis of nanographene
Cluster 2	Green Synthesis and Multifunctional Applications of Nitrogen-Doped Carbon Dots from Biomass	Hydrothermal synthesis
Cluster 0	Advanced Materials for Wideband Electromagnetic Wave Absorption	Hummers' method
Cluster 6	Innovative Catalysts for Formic Acid Oxidation in Fuel Cells	In-situ synthesis, Modified Hummers' method
Cluster 11	Advanced Nanomaterials for Sensing and Photocatalysis Applications	Hummers' method, Functionalization by hydrothermal method
Cluster 9	Advanced Nanostructured Materials for Energy Storage and Catalysis	Modified Hummers' method, Co-precipitation method
Cluster 8	Innovative Approaches to Enhancing Flame Retardancy in Epoxy Resin	Phosphorus-nitrogen, Functionalized graphene oxide

4. CONCLUSION

In conclusion, this research has successfully undertaken the task of unravelling the evolution of synthesis processes for graphene and its derivatives using Citation Network Analysis (CNA). The vast amount of literature published on graphene and its derivatives presents a daunting challenge for researchers attempting to derive meaningful insights. The application of CNA proves to be useful in navigating this complex landscape, providing a systematic and efficient approach to elucidating the evolution of material synthesis. The resulting network of literature was grouped into 12 clusters based on the count of citations within the network. The most prominent research topic is the development of electrode materials for electrochemical applications. The most preferred method for synthesising GO is the modified Hummers' method. At its core, this research serves as a stepping stone towards unlocking the full potential of graphene and its derivatives in the field of advanced materials science.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

AUTHORS CONTRIBUTION

Aman Sheji (Methodology; Investigation; Visualisation; Formal analysis; Writing - original draft)

Dawn Sivan (Data curation; Validation; Writing - review & editing)

Rajan Jose (Conceptualisation; Supervision; Writing - review & editing)

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