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Sustainable Synthesis of Graphene Oxide from Tyre-Char and Its Applications in Cement

Submitted by

Weeraddhana Chethana Himeshani Silva

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Abstract

Increasing demand for sustainable materials and the pressing need to manage waste efficiently have driven researchers to explore the potential of waste-derived materials in various applications. This thesis investigates the synthesis of graphene oxide (GO) from waste tyres using microwave-assisted pyrolysis and its application in cement mortar. GO is a two-dimensional carbon material that has many oxygenated functional groups on its surface. This material has gained much attention due to its unique properties such as its hydrophilic nature, ability to functionalisation, and high mechanical strength. However, traditional methods including Hummer's methods for producing GO are energy-intensive and costly. This research provides a novel approach to synthesising tyre char-based graphene oxide (TC-GO), utilising waste tyres as a carbon source, thereby addressing both environmental and economic concerns. Given the rapid development of the automotive and transportation industries, the annual output of waste tyres has significantly increased, necessitating the exploration of alternative disposal methods to prevent environmental contamination caused by waste tyres.

The primary objective of this research is to develop a sustainable and cost-effective method to produce GO by using a two-step microwave-assisted pyrolysis process. This method involves the breakdown of waste tyre rubber into tyre char (TC), which is further chemically treated to obtain GO. Microwave irradiation offers several advantages, including rapid, energy-efficient heating, making it a more cost-effective and environmentally friendly alternative to conventional methods. The resultant TC and TC-GO were characterised using advanced techniques, such as X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM), to confirm their structural and chemical properties.

The second phase of the research focuses on the application of TC-GO in cement mortar to enhance its mechanical properties. Nanomaterials like GO can enhance cement properties including its strength, life span, and microstructure. Cement mortar samples were prepared with varying concentrations of TC-GO and TC (0.01%, 0.03%, and 0.05% by weight of cement) for comparison. The compressive and flexural strengths of these samples were evaluated at 7 and 28 days, with particular emphasis on understanding the mechanisms by which TC-GO improves the mechanical performance of cementitious materials. Microstructural analysis was also conducted to investigate the surface morphology and distribution of TC-GO within the cement matrix.

The experimental results demonstrated that the incorporation of TC-GO significantly improves both the compressive and flexural strength of cement mortar compared to control samples as well as those containing only TC. The most notable improvement was observed with the addition of 0.03% TC-GO, which led to a 15% increase in mechanical strength. The

enhancement in mechanical properties is attributed to the high surface area and functional groups of GO, which contribute to better bonding and load transfer within the cement matrix. Furthermore, the microstructural analysis revealed that 0.03% TC-GO improves homogeneity and reduces porosity in the cement mortar, contributing to its overall performance. However, the flow table test results indicated a reduction in workability for both TC and TC-GO cement mixtures, likely due to the differences in their surface properties.

This research introduces a sustainable and efficient method for synthesising GO from waste tyres and highlights its potential as a performance-enhancing additive in construction materials. The use of waste tyres not only reduces environmental impacts but also offers a low-cost alternative to traditional carbon sources used in GO synthesis. Additionally, the findings from this study suggest that TC-GO can be a valuable addition to cementitious materials, improving their mechanical properties and microstructure, which makes it highly appealing to the construction industry. Importantly, by enhancing the strength of cement mortar with TC-GO, there is potential to reduce the overall percentage of cement required in the mix. This reduction in cement usage directly contributes to lowering CO₂ emissions, addressing a critical challenge for the construction industry as it moves towards achieving net-zero emissions by 2050. Since cement production is a major global contributor to CO₂ emissions, reducing its usage could have a substantial environmental impact. The ability of TC-GO to decrease cement content while enhancing performance supports the goals of decarbonisation and resource efficiency. This advancement supports the construction industry in its transition toward greener and more sustainable practices.

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List of abbreviations

(Abbreviations are listed alphabetically)

BET	Brunauer Emmett Teller
FESEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier Transform – Infrared Spectroscopy
GO	Graphene oxide
MW	Microwave
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
TC	Tyre char
TC-GO	Tyre char-derived graphene oxide
TEM	Transmission Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction

List of publications

Candidate prepared the following publications during the course of this thesis:

- Silva WCH, Zafar MA, Allende S, Jacob MV, Tuladhar R. *Sustainable Synthesis of Graphene Oxide from Waste Sources: A Comprehensive Review of Methods and Applications. Materials Circular Economy. 2024;6(1):23.*

Chapter 1

Introduction

1.1 Rational

Novel materials are key drivers of scientific and technological advancements, leading researchers to explore materials with exceptional properties. Graphene oxide (GO) and its related materials have garnered significant attention and have become some of the most extensively researched. GO is a two-dimensional carbon material characterised by oxygen-containing functional groups, including carbonyl ($=O$), hydroxyl ($-OH$), epoxy ($-O-$), and carboxyl ($-COOH$), distributed across its basal planes and edges. This functionalisation gives a hybrid system of both sp^2 and sp^3 hybridised carbon atoms [1]. GO is hydrophilic, making it relatively easy to prepare in water or organic solvent-based suspensions [2]. Additionally, GO has a large surface area and its ability to undergo functionalisation enhances its versatility [3]. It also exhibits high mechanical strength and greater chemical activity [4]. These unique physical and chemical properties make GO suitable for a wide range of applications such as biomedicine [5], energy storage [6], environment [7], and the construction industry [8].

Over the years, various chemical methods based on oxidative exfoliation have been developed for the synthesis of GO. These include early techniques, such as Brodie (1859) [9], Staudenmaier (1898) [10], and Hofmann (1937) [11], as well as more recent approaches, like Hummers (1958) [12] and its versions: Modified Hummers (2004) [13] and Improved Hummers (2010) [14]. However, these methods have notable limitations, including the use of strong oxidising agents, lengthy reaction times, the emission of toxic gases, and the generation of hazardous byproducts and pose significant safety risks [15]. Graphite, commonly used as the precursor for GO synthesis, is scarce and expensive. The production of synthetic graphite further complicates the process, as it requires extremely high temperatures ($\geq 2500^\circ C$), driving up costs [16]. In Australia, the challenges are even more pronounced due to the minimal graphite mining and production, making it difficult to source locally and exacerbating the cost and availability issues [17, 18].

Considering the limitations of traditional methods, biomass and carbon wastes offer viable alternatives for producing nanostructured carbon materials. This is due to their high carbon content, environmental-friendly, lower processing temperatures, widespread availability and cost-effectiveness [19]. Recently, several studies have reported the successful synthesis of GO from biomass sources such as coconut shells [20], sugarcane bagasse [21], tea [22], and pine leaves [23], as well as from industrial waste materials including bio-shoot [24], and tyre wastes [25]. Waste-derived GO has shown potential for applications in areas such as energy storage, water treatment, catalysis, and adsorption [20, 26]. While most researchers have utilised carbonisation

and the Modified Hummers method, only a few have explored alternative approaches such as pyrolysis and catalytic processes for GO synthesis [15].

Among the various pyrolysis methods, microwave-assisted pyrolysis has emerged as one of the most efficient, cost-effective, and environmentally friendly options compared to conventional techniques [27]. This innovative technique utilises microwave energy, which is absorbed by materials and converted into heat, allowing for rapid and uniform heating of wastes [28]. This leads to improved yield and quality of the resulting carbon materials. The effectiveness of this method is influenced by the dielectric properties of the feedstock, often necessitating the use of a microwave susceptor to enhance energy absorption [28]. Operating at lower temperatures and shorter reaction times than traditional methods, microwave-assisted pyrolysis reduces energy consumption and minimises undesirable byproducts [27]. Furthermore, it can be scaled up for industrial applications, making it a promising option for sustainable waste conversion with expanding potential materials science.

This study introduces the sustainable synthesis of GO from waste tyres using microwave-assisted pyrolysis and explores its application in cement composites. The microwave pyrolysis technique with chemical treatment was employed to synthesise tyre char-based graphene oxide (TC-GO). Both the synthesised tyre char (TC) and TC-GO were extensively characterised through various analytical techniques to confirm their structural and chemical properties. The TC-GO was then incorporated into cement mortar to assess its effects on the mechanical strength and microstructure. For comparison, cement samples containing only tyre char (TC) were also prepared, and all relevant tests were conducted to evaluate the performance of both TC and TC-GO modified cement. This approach highlights the potential of waste-derived graphene oxide for enhancing construction materials while promoting environmental sustainability.

1.2 Research Objectives

The main aim of this research project is to develop a sustainable method for synthesising GO from waste tyres using microwave-assisted pyrolysis, combined with chemical treatment, and to explore its applications in cement. The following objectives have been defined to achieve this goal:

- Produce tyre char (TC) from waste tyres using a microwave pyrolysis system.
- Synthesise tyre char-based graphene oxide (TC-GO) through microwave pyrolysis and chemical treatment
- Characterise the produced TC and TC-GO to confirm their properties.
- Apply the synthesised TC and TC-GO to cement mortar and investigate their effects on strength and microstructural properties.

Achieving these objectives will significantly contribute to the sustainable and environmentally friendly production of GO, while also advancing the development of cement mortar with improved properties.

1.3 Thesis Organisation

This thesis is organised into five chapters, including an introduction, a literature review, two data chapters, and a conclusion. A brief overview of each chapter is provided below:

- **Chapter 1** introduces the motivation behind the study, identifies the research gaps, and outlines the objectives of the thesis.
- **Chapter 2** presents a literature review discussing the relevant research on the production of GO from various waste materials. It details the synthesis of GO from different waste sources and their potential applications. This chapter was published as: Silva WCH, Zafar MA, Allende S, Jacob MV, Tuladhar R. *Sustainable Synthesis of Graphene Oxide from Waste Sources: A Comprehensive Review of Methods and Applications. Materials Circular Economy*. 2024;6(1):23.
- **Chapter 3** focuses on the microwave pyrolysis of tyre waste to produce tyre char (TC) and the subsequent synthesis of GO from TC. The synthesis involves a microwave pyrolysis process combined with chemical treatments. The produced TC and TC-GO are characterised and compared using various methods, including Raman spectroscopy, XRD, XPS, SEM and TEM. The findings of this chapter are currently under review in a journal as: *Sustainable Synthesis and Characterisation of Tyre Char-based Graphene Oxide via Microwave-Assisted Pyrolysis* in a journal.
- **Chapter 4** investigates the application of the synthesised TC and TC-GO in cement mortar, incorporating it at ratios of 0.01%, 0.03%, and 0.05% by cement weight. This chapter examines the compressive and flexural strength, along with the microstructural properties of the cement mortars of TC and TC-GO. The results are currently under review in a journal as: *Tyre-Char Derived Graphene Oxide Impact on Cement Mortar: A Study of Mechanical and Microstructural Characteristics* in a journal.
- **Chapter 5** provides the overall conclusions of the thesis and offers several recommendations for future research.

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Chapter 2

Literature review

This chapter provides an in-depth review of the literature on the synthesis of GO from various waste sources and biomasses, emphasising agricultural and industrial waste. It highlights the structural properties of GO, traditional synthesis methods, and key characterisation techniques used. The review also identifies existing research gaps in the field. Special attention is given to waste-derived GO and its potential applications, such as in tissue engineering, energy storage, and environmental remediation, offering insight into the versatility of GO across different sectors.

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Abstract

Graphene-based materials have gained significant attention due to their unique mechanical, chemical, thermal, and optical properties. Among these, Graphene oxide (GO) is one of the promising materials extensively studied. Unlike other graphene derivatives, GO is chemically modified with diverse oxygenated functional groups, rendering it more hydrophilic. It serves as a precursor for graphene synthesis. Notably, recent researchers have focused on synthesising GO using alternative low-cost carbon-rich materials such as coconut shells, sugarcane bagasse, tea, pine leaves and scrap tyres instead of graphite. These non-conventional carbon sources decrease the demand for costly, non-renewable graphite, increase reliability, and offer an eco-friendly approach to waste management. This comprehensive review aims to explore accessible methods for synthesising graphene oxide and highlight various alternative feedstocks utilising agricultural, industrial, and plastic waste as precursors. Furthermore, a comparative assessment of various production methods and their performance in different applications is outlined to provide insights for the commercialisation of GO in future applications.

Keywords

Graphene oxide, Synthesis methods, Waste materials, Biomass, Characterisation, Applications

2.1 Introduction

Novel materials are key drivers of scientific and technological advancements, leading researchers to explore materials with exceptional properties. Graphene and related materials have garnered extensive attention and emerged as highly researched materials in the global. Graphene is often called a “material of the future”, because of its exceptional properties [1]. Since it was first separated from graphite through a simple mechanical peeling method in 2004 by Novoselov and Geim [2], graphene has significantly impacted various industries, including transparent conductive films [3], flexible electronics [4], energy storage [5], optoelectronics [6], robotics [7], biosensing [8], water purification [9], textile industry [10] and more. Graphene comprises a two-dimensional hexagonal skeleton made of a single layer of sp^2 hybridised carbon atoms with exceptional electrical, mechanical, thermal, and physicochemical properties [11]. Despite its numerous unique characteristics, graphene has several drawbacks, including low electrochemical activity, easy agglomeration and complex and expensive processing, which significantly limit its application in certain fields including medical and biological [12]. To overcome these limitations, researchers have employed functional modifications to transform graphene into graphene oxide, expanding its potential applications.

Graphene oxide (GO) is a layered carbon structure with oxygen-containing functional groups distributed across its basal planes and edges. This configuration gives a hybrid system comprising a mixture of sp^3 and sp^2 hybridised carbon atoms [13]. GO can exist as a mono- or multi-layer stacked structure, with a monolayer referred to as graphene oxide, two layers known as two-layered GO, and GO possessing more than two layers but fewer than five layers referred to as a few-layered GO. Multilayered GO comprises five to ten layers, while material with eleven or more stacked layers is denoted as graphite oxide [14, 15]. GO has outstanding properties, notably its hydrophilic nature, which allows it to disperse in numerous solvents, especially water [16]. Additionally, graphene-based composites can be synthesised by modifying the oxygen-functionalised groups of GO [17]. GO has found applications in diverse fields such as desalination [18], drug delivery [19], oil-water separation [20], immobilisation catalysis [21], solar cells [22], energy storage [23], healthcare [24] and construction materials [25]. The production of graphene has seen development in numerous ways recently. The methods reported for graphene synthesis can be categorised into top-down and bottom-up approaches [26]. In the top-down approach, graphite is separated to yield graphene, whereas the bottom-up approach involves synthesising graphene from a carbon precursor [27, 28]. The predominant method for producing GO is the top-down approach, which involves obtaining GO by exfoliating graphite oxide [29]. To promote environmental sustainability, researchers have explored novel production methods for synthesising GO, offering economic and environmental benefits [30, 31]. By using waste-based carbon and transforming it into graphene and GO, numerous applications can be realised [31-33].

The latest review authored by Torres et al. (2021) concentrated on examining the production, performance, and diverse applications of graphene-derived nanomaterials sources from waste biomass. However, it is worth noting that the study did not sufficiently concentrate on the production of GO from waste sources. The synthesis of GO from waste sources remains a persistent challenge, necessitating further research and improvement. These challenges include optimising synthesis parameters, managing variable carbon content, addressing contaminations, assessing environmental impact, and considering factors such as cost, scalability, and reproducibility [32, 34]. Therefore, it is crucial to focus on the development of novel methods that enable cost-effective, environmentally friendly, and scalable production of GO, while also exploring its diverse applications. This comprehensive review article aims to provide an extensive overview of the existing methods employed in synthesising GO from waste materials and investigates its wide-ranging applications. By addressing these challenges and exploring new avenues, this review aims to contribute to advancing GO synthesis and its utilisation in sustainable applications.

2.2 Structure and Properties of GO

GO represents the oxidised counterpart of graphene, a concept dating back to the pioneering work of the English chemist Brodie in 1859, who first documented graphite oxidation. The term “graphene” was officially coined about thirty years ago to describe the single atom-thin carbon layer of graphite [35]. Graphene is a material composed of carbon atoms bonded to each other in a repeating pattern of hexagons, as depicted in Fig. 2.1 (a). Graphene is recognised as a fundamental building block for all two-dimensional material made of sp^2 graphitic structures, which includes graphite oxide [2]. Compared to graphene, graphite oxide possesses a more complicated structure due to numerous oxygenated functional groups. Studying the structure of graphite oxide is fundamental to comprehending GO. Despite the production of graphite oxide in the mid-1800s, ongoing debate persists regarding its composition and structure due to its non-stoichiometric composition, complexity, and sensitivity to preparation methods [36, 37]. GO comprises a monolayer of graphite with carboxyl, hydroxyl, and epoxy oxygen functionalities distributed across its basal plane and edges, leading to a combination of sp^2 and sp^3 hybridised carbon atoms, as depicted in Fig. 2.1 (b) [38].

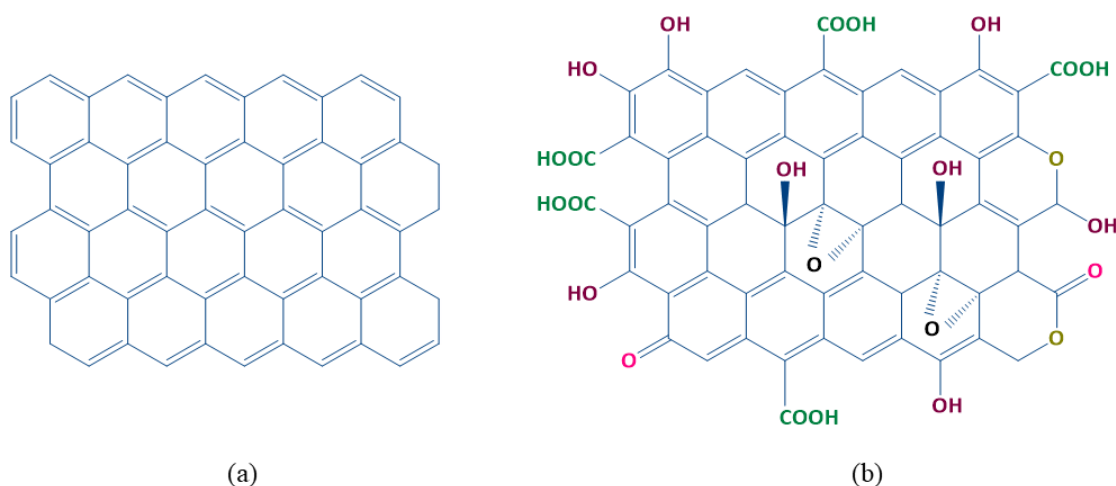


Figure 2.1 The schematic illustrations of a) the hexagonal arrangement of sp^2 hybridised carbon atoms in graphene, and b) GO, where oxygen and hydrogen atoms are incorporated into the hexagonal network [39].

Graphene exhibits remarkable mechanical, electrical, thermal and optical properties attributed to its distinct structural and morphological characteristics [11]. Despite these properties, the practical applications of purely single-layer graphene are hindered by its hydrophobic nature and the challenges associated with mass scale production [40, 41]. However, the precursor GO has advanced much in large-scale production by exfoliating bulk graphite oxide. Consequently, the proportion of defects in the graphene structure significantly impacts its physical and mechanical properties [42]. Conversely, GO exhibits higher chemical activity than pristine graphene due to the abundance of oxygen-containing functional groups and structural defects [14]. GO can undergo reduction processes to yield graphene, which can be achieved through different methods such as treatment with reducing agents [43], thermal annealing [44], or electrochemical techniques [45]. Furthermore, GO has exhibited strong oxidising properties that can be used for a diverse set of reactions such as oxidation of olefins, methyl benzenes, and various dehydrogenations [46]. Another reactivity of GO is its ability for chemical functionalisation. The functionalisation involves introducing carboxylic acid, hydroxyl, and epoxy groups to GO through chemical reactions [14]. In addition, GO can be functionalised by activating it with specially selected polymers or small molecules [47]. This functionalisation has a notable effect on enhancing the dispersibility of GO in organic solvents, such as N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), and dimethyl sulfoxide (DMSO) [48]. In contrary to graphene, GO exhibits hydrophilicity. This hydrophilicity facilitates the incorporation of GO into aqueous systems and improves its compatibility with other materials, enabling diverse applications in fields such as nanocomposite, drug delivery, and biosensing [40, 49]. These unique features of GO unlock a broad range of applications in different industries,

offering enhanced performance and improved functionality in numerous technological and scientific endeavours.

2.3 Synthesis Methods of Graphene Oxide

There are several conventional and modern methods to prepare graphite oxide. Table 2.1 provides a concise summary highlighting the key differences among these methods.

Table 2.1 The comparison of different GO synthesis methods [50].

Method	Oxidants /description	Toxicity	Advantages	Disadvantages	Ref.
Brodie Method	HNO ₃ , KClO ₃	Yes	-	Weak acidity, small size, limited thickness, contributing to structural imperfections	[51]
Staudenmaier Method	HNO ₃ , H ₂ SO ₄ , KClO ₃ (NaClO ₃),	Yes	-	Time-consuming, risk of explosions,	[52]
Hofmann Method	KClO ₃ , non-fuming HNO ₃	Yes	A powerful oxidative method	Lower level of oxidation, Time-consuming	[53]
Hummers Method	H ₂ SO ₄ , NaNO ₃ , KMnO ₄ ,	No (NO _x is released)	Higher oxidation degree than previous methods	Still incomplete oxidation, highly time-consuming, complex purification, and separation steps	[54]
Modified Hummers Method	H ₂ SO ₄ , NaNO ₃ , KMnO ₄ ,	No (NO _x is released)	Improved oxidation level	Highly time-consuming, complex separation and purification steps	[55, 56]
Improved Hummers Method	KMnO ₄ , H ₂ SO ₄ , H ₃ PO ₄	No	High yield, more organised GO structure, reduction of defects in the basal plane, environmentally friendly,	Highly time-consuming, complex separation and purification steps	[57]
Electrochemical method	Use of aqueous electrolytes, no oxidising agents	No	High quality, environmentally friendly, reuse of the electrolytes	High cost when scaling up	[58, 59]

The initial endeavour to synthesise graphite oxide was undertaken by British chemist B. C. Brodie, who explored the chemical reactivity of flake graphite. The GO synthesis generally

involves two main steps: oxidation by an oxidising agent and subsequent exfoliation of the sheets. In his experiment, Brodie introduced a mixture of KClO_3 into a graphite slurry in fuming HNO_3 acid and maintained it at a constant temperature of $60\text{ }^\circ\text{C}$ for four days. This process led to the formation of Brodie's graphene oxide (BR-GO). The composition of the resulting material was determined as $\text{C}_{11}\text{H}_4\text{O}_5$ (C/O ratio 2.2).

This product exhibited solubility in distilled H_2O and tended to clump in more acidic environments. Staudenmaier (1898) modified Brodie's procedure using conc. H_2SO_4 acid, fuming HNO_3 acid, and the gradual addition of KClO_3 during the reaction, leading to Staudenmaier's graphene oxide (ST-GO). The increased acidity in this modified process resulted in a reduced reaction time, while maintaining similar properties to BR-GO. In 1937, Hofmann [53] synthesised Hofmann's graphene oxide (HO-GO) employing KClO_3 and non-fuming HNO_3 acid, resulting in a lower oxygen content with a C/O ratio 2.5. Their investigation revealed that the conc. HNO_3 acid played a significantly impacted the extent of oxidation during the synthesis process, with lower concentrations leading to higher levels of graphene oxide oxidation.

The well-established "Hummers method", pioneered by William S. Hummers Jr. and Richard E. Offeman in 1958, involved oxidising graphite to graphitic oxide through a process employing a mixture of H_2SO_4 , NaNO_3 and KMnO_4 (Fig. 2.2). Notably, this method substantially decreased the reaction time from several days, as observed in previous methods to only a few hours, ranging from 8 and 12 hours. The replacement of KClO_3 with KMnO_4 enhanced the safety of the reaction by eliminating the use of explosive chlorate compounds. At the same time, the inclusion of NaNO_3 helped to eliminate the release of toxic fumes from HNO_3 . The initial step in the synthesis of graphitic oxide involved mixing 100 g of graphite powder with 50 g of NaNO_3 in 2.3 L of H_2SO_4 . To ensure safety, the mixture was then chilled to $0\text{ }^\circ\text{C}$ in an ice bath. With continuous vigorous stirring, 300 g of KMnO_4 was cautiously introduced to the mixture to avoid the temperature exceeding $20\text{ }^\circ\text{C}$. Following the removing of the ice bath, the temperature was maintained at $35\text{ }^\circ\text{C}$ for 30 minutes. During this time, the mixture thickened gradually with a decreasing effervescence, forming a brownish-grey coloured paste with the release of minimal gas. After 30 minutes, 4.6 L of H_2O was added gradually to the paste, resulting vigorous effervescence, and raising the temperature to $98\text{ }^\circ\text{C}$. The resulting brown solution was then kept at this temperature for an additional 15 minutes. Following the dilution of the suspension with 14 L of warm water, a 3% H_2O_2 treatment was added to remove any remaining MnO_4^- and MnO_2 , yielding a bright yellow solution. Subsequently, the warm mixture was filtered to prevent precipitation as a secondary reaction. The resulting GO residue was dispersed to around 0.5% solids after washing the yellowish-brown filter cake three times with warm water. Resinous anion and cation exchangers were used to remove residual salt impurities. The dry form of GO was achieved through centrifugation and subsequent dehydration at $40\text{ }^\circ\text{C}$ using phosphorus pentoxide

under vacuum conditions. The resulting product from the Hummers method, known as Hummers' graphene oxide (HU-GO) displayed a comparable C/O ratio of 2.25 to that of BR-GO (2.2) [54]. Despite its promising results, the Hummers method suffers from time-consuming separation and purification, environmental concerns due to NO_x generation, scalability issues and large amounts of acid consumption.

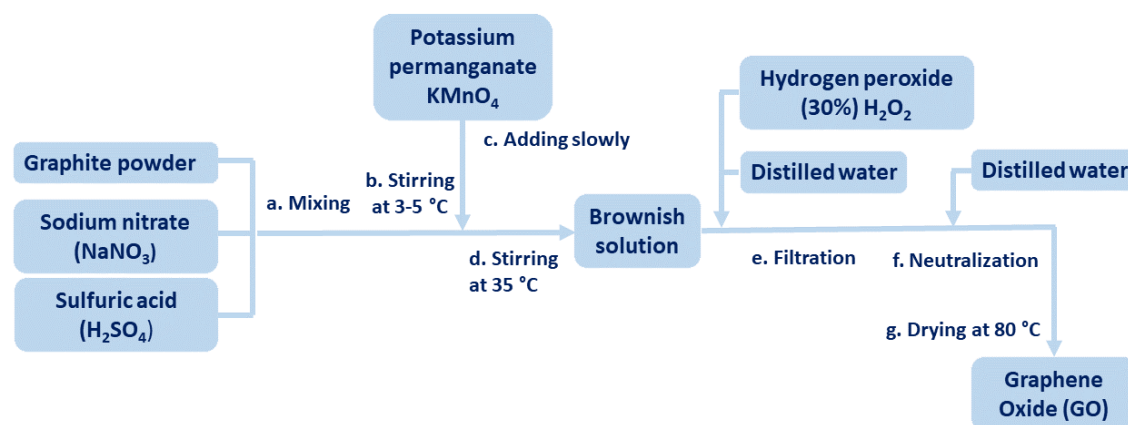


Figure 2.2 A schematic representation of Hummers method [60].

Over time and through further experimentation, the Hummers method underwent notable changes, leading to what is now known as the "Modified Hummers" [61]. Various modifications have been proposed, including two-step, nitrate-free, co-oxidant, and room- and low-temperature methods [56, 62]. These modifications involve adjustments to the quantities of KMnO₄ and the proportion of the reactants as recommended by different research groups. These alternations aim to optimise the synthesis procedure and increase the efficiency and properties of the resulting graphitic oxide materials [56, 62, 63]. In 2010, Marcano and his associates developed a novel approach known as the "Improved Hummers" method. This method involves mixing H₃PO₄ and H₂SO₄ in a ratio of 1:9, followed by the introduction of KMnO₄ and graphite in a ratio of 6:1 ratio within an ice bath. Subsequently, the mixture underwent heating to 50 °C and was stirred for a duration of 12 hours. To remove the excess of KMnO₄, the product was cooled and poured onto ice containing 30% H₂O₂ (3 mL). Phosphoric acid serves dual roles as a dispersing and etching agent and acts as a stabiliser throughout the oxidation process in the GO synthesis, ensuring safety. This method results in a greater yield of GO with enhanced oxidation and a more regular structure [57, 61]. However, this process is highly time-consuming with the purification and separation, large amounts of acids consumed. Modified and Improved Hummers methods have been used to synthesise carbonous waste sources into GO. Many researchers have explored various waste sources such as coconut shells [32], tea [31], rice straw [64], electronic scraps [65] and scrap tyres [66] to synthesise GO using the Hummers methods. In 2017, Nasir et al. [67] synthesised GO from carbonised oil palm including leaves, kernel shells and empty fruit bunches using the improved synthesis method. However, synthesising carbonous materials from the

Modified and Improved Hummers methods has certain limitations, including time-consuming, non-eco-friendly, complex separation, extensive purification, and low yield etc. Therefore, converting waste products sustainably to produce GO is still challenging.

The chemical routes for preparing GO often result in a structural damage due to the strongly acidic conditions and impurities. These characteristics make the material less suitable for electronic applications. Apart from the chemical methods, electrochemical synthesis offers a promising alternative for the bulk production of GO and is more suitable for electronic applications [58, 59]. This method is more eco-friendly, as it allows the reuse of the electrolyte and reduce the need for extensive washing of equipment. In contrast to standard procedures, the better quality of electrochemical GO can be attributed to using aqueous electrolytes and the absence of oxidising agents, thereby avoiding impurities [58, 59]. Furthermore, the versatility of experimental setups allows for precise modulation of the degree of oxidation and density of defects in the synthesised GO [58, 59, 68]. However, the cost of the electrolyte can increase expenses when scaling up the process. The simple electrochemical exfoliation techniques provide minimal control over the structures of the resultant materials [58].

Recently, numerous researchers [69, 70] have proposed thermochemical techniques to synthesise graphene derivatives using biomasses. Among these techniques, pyrolysis is a prominent bottom-up method to synthesise GO. The term “pyrolysis” combines “pyro”, meaning fire, and “lysis”, referring to separation, representing the process under high temperature and non-oxidising atmosphere [28]. The implementation of pyrolysis techniques on diverse waste precursors has demonstrated the successful production of graphene-based materials [71]. Mainly, carbon precursors are pyrolysed into biochar, bio-oil, gas, and other various valuable products. The pyrolysis involves various reactions, including depolymerisation, decarboxylation, dehydration, intermolecular condensation and aromatisation at different temperatures [72]. The classification of pyrolysis into two main types includes conventional pyrolysis (CP) and microwave-assisted pyrolysis (MAP), depending on the heating method utilised. Conventional pyrolysis utilises electric heating, while microwave-assisted pyrolysis relies on the microwave heating. For example, Thangaraj et al. (2023) have synthesised GO from sugarcane bagasse using ferric citrate as a catalyst in two steps of conventional pyrolysis. However, conventional pyrolysis is often inefficient and energy-intensive compared to microwave-assisted pyrolysis. Therefore, microwave pyrolysis has garnered significant attention in the research community due to its faster, more energy-efficient process and the production of more desired products than conventional pyrolysis [73, 74]. Nevertheless, a significant challenge associated with this method lies in the complexity of regulating particle size and incomplete understanding of the mechanism of microwave pyrolysis. There is insufficient study of GO synthesis using only microwave pyrolysis technique.

2.4 Characterisation of Synthesised Graphene Oxide

The characterisation of synthesised GO involves a comprehensive analysis utilising a range of analytical techniques such as X-Ray Diffraction Analysis (XRD), Raman Spectroscopy, Fourier Transform – Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS) etc.

XRD, widely used for crystalline material characterisation, reveals crucial information about the average spacing between layers. The XRD pattern for the GO synthesised through the Modified Hummers method is illustrated in Fig. (2.3a) [75]. The diffraction peak of pure graphite is observed at approximately 26° , indicative of its well organised layered structure with an interlayer spacing of 0.34 nm, as illustrated in the insert of Fig. (2.3a). The absence of the peak at 26° and the emergence of a peak at 10° signify complete oxidation of graphite into GO, resulting in an increased d-spacing from 0.34 nm to 0.82 nm [75].

Raman spectroscopy proves to be a non-destructive technique offering valuable structural insights into carbon-based materials. Key features observed in Raman spectra include the G and D peaks, occurring around 1580 cm^{-1} and 1350 cm^{-1} , respectively. The G peak corresponds to the stretching bond of sp^2 carbon pairs in chains, and rings. The D peak represents the breathing mode of aromatic rings, indicative of structural defects. The intensity of the D peak serves as an indicator of the degree of disorder, while the presence of the overtone 2D peak at 2680 cm^{-1} , correlates with the number of graphene layers (N) [76]. The Raman spectrum of GO, obtained under excitation at 532 nm, is illustrated in Fig. (2.3b). The pronounced D peak at 1348 cm^{-1} , exhibiting intensity comparable to that of the G peak at 1592 cm^{-1} , and a bandwidth indicate significant structural disorder of GO. Moreover, the presence of weak and broad 2D peaks further indicate disorder within the material. Additionally, a defect-activated peak labelled D+G is visibly present near 2950 cm^{-1} [76]. This Raman spectroscopy analysis contributes valuable insights into the structural characteristics and disorder level of synthesised GO.

The FT-IR spectrum of GO, depicted in Fig. (2.3c), exhibits distinctive features providing insights into its properties. In the high-frequency range of the FT-IR spectrum, a broad peak ranging from 3000 to 3700 cm^{-1} , accompanied by a sharp peak at 1635 cm^{-1} , signifies the stretching and bending vibrations of OH groups from H_2O molecules adsorbed on GO [75], indicating strong hydrophilicity. Further analysis reveals absorption peaks at 2930 cm^{-1} and 2850 cm^{-1} , corresponding to symmetric and anti-symmetric stretching vibrations of CH_2 . Within the medium frequency range, peaks observed at 1630 cm^{-1} and 740 cm^{-1} are attributed to the stretching vibrations of C=O and C=C , originating from carbonyl and carboxylic acid groups present at the edges of GO. The absorption peaks at 1110 cm^{-1} and 1385 cm^{-1} are correspond to the stretching

vibration of C-OH (alcohol), and C=O (carboxylic acid), respectively [76]. These peaks indicate the presence of oxygen-containing group, revealing the oxidation of graphite.

SEM images offer valuable insights into the structure and morphology of nanomaterials. In Fig. (2.3d)-(i), the SEM image of typical graphite illustrates how sheets are stacked together. The SEM image of Fig (2.3d)-(ii) displays exfoliated GO, clearly showcasing the process of graphene sheets exfoliation. Observing the SEM images of GO reveals 2D nanosheet morphologies characterised by folded and wrinkled textures, occasional rough surfaces, irregular edges, and crumpling due to scrolling. Further analysis of grain size and surface morphology was conducted using Field Emission Scanning Electron Microscopy (FESEM). The obtained FESEM images reveal distinct and interconnected three-dimensional graphene sheets, creating a porous network that resembles a loosely woven sponge-like structure, as illustrated in Fig. 2.3d-(iii,iv) [75]. Notably, SEM has provided insights into the size range of GO sheets, revealing lateral dimensions ranging from as large as 200 μm to as small as a few microns within the sample [77]. This comprehensive morphological examination contributes to a deeper understanding of the structural characteristics of GO.

TEM stands as a valuable instrument for the identification of single layer and few layer GO sheets in research studies. The technique utilises electron passing through the sample, revealing contrast based on variations in electron density. Consequently, single sheets appear brighter compared to multiple sheets due to their reduced thickness. TEM images (Fig. (2.3e)) of ultrasonically exfoliated GO showcase a unique wrinkled morphology, indicating the successful exfoliation of GO into single or very few layers. These distinctive wrinkles and folds within the exfoliated GO sheets serve as prominent indicators characteristic features of single-layer structures. The GO nanosheets, whether single- or few-layered, displayed a flat morphology with a width exceeding 1.5 μm . The selected area electron diffraction (SAED) pattern of GO represents a polycrystalline nature [77-79].

XPS involves directing X-rays onto the surface of a sample to measure the number and kinetic energy of emitted electrons. This process widely used for analysing the elemental composition of the surface. In XPS analysis of GO in Fig. (2.3f), the C1s peak undergoes deconvolution into five distinct components: sp^2 carbons from graphite (284.6 eV), carboxylic acid (289.1 eV), carbonyls (288.0 eV), C atoms attached to hydroxyl groups (285.7 eV), and epoxy/ether groups (286.7 eV), [77]. Within the O1s spectra of GO, two main components are observed: C-O (hydroxyl and epoxy, 532.5 eV) and C=O (531.6 eV), accompanied by two minor components attributed to O-H (533.5 eV) and quinones (530.5 eV) [77]. XPS analysis is utilised to ascertain both the atomic composition and the C/O ratio of GO. The obtained C/O atomic ratio

of 3.0 indicates a substantial introduction of oxygen-containing groups during the oxidation of graphite [80].

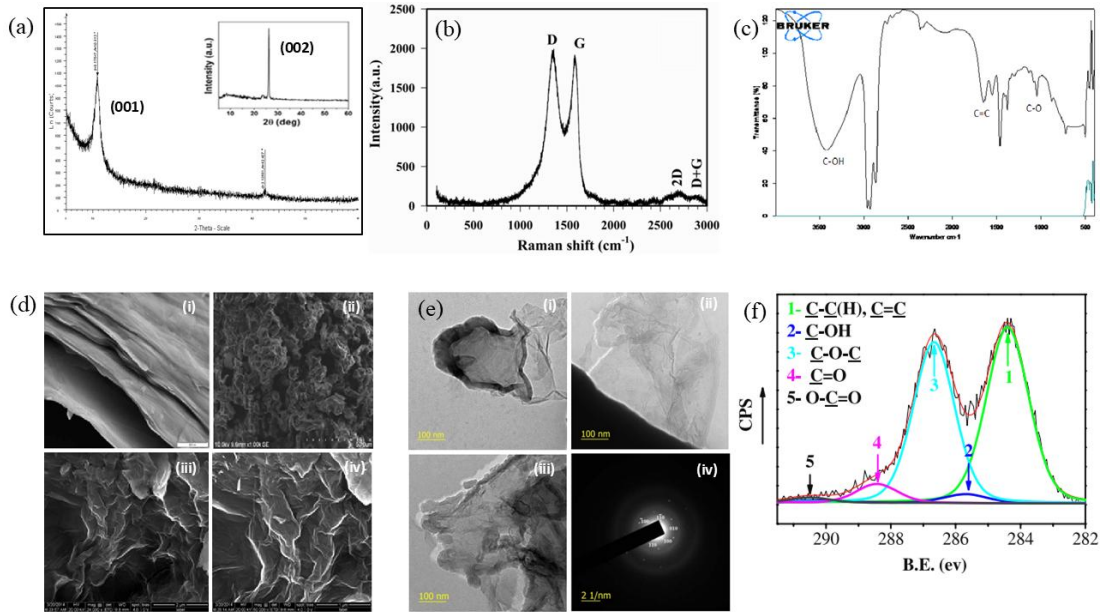


Figure 2.3 a) XRD pattern of GO (insert shows XRD of graphite) [75], b) Raman spectrum of GO [76], c) FT-IR of GO, d) SEM images of Graphite (i), GO (ii), FESEM images of GO (iii,iv) [75], e) HRTEM of GO (i)-(iii), SAED pattern of GO (iv) [78], f) XPS spectra in the C1s region [80].

2.5 Synthesis of GO from waste materials and its characterisations

Managing and utilising waste pose substantial global challenges. Researchers worldwide are currently focusing on converting waste into value-added products, with a particular focus on carbon-based nanomaterials [81]. The synthesis of GO from waste has gained significant recognition and value owing to its exceptional properties. The use of natural graphite and synthetic graphite as precursors for GO synthesis is hindered by various limitations. Natural graphite availability is restricted in certain countries, while the production of synthetic graphite demands exceedingly high temperatures (≥ 2500 °C) and incurs significant costs [82]. Conversely, carbon residues and biomass are increasingly proposed as promising precursors for graphene material synthesis. This is attributed to their high carbon content, environmental-friendly nature, lower processing temperatures, widespread availability and cost-effectiveness [83]. Numerous studies have explored the utilisation of different carbon precursors and biomass sources, including coconut shells [32], sugarcane bagasse [84], tea [31], oil palm leaves [85], pine leaves [86], rice straw [64] and industrial scraps such as tyres [66], bio-soot [87], Zn-C batteries [88] for synthesising GO (Fig. 2.4).

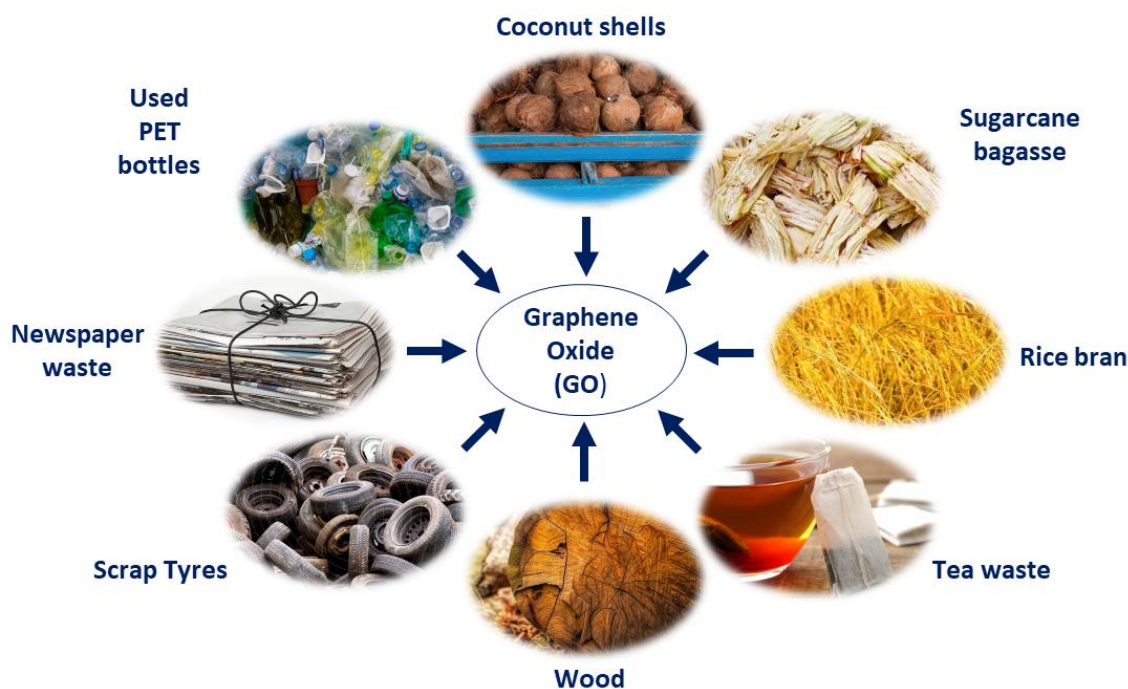


Figure 2.4 Various waste precursors for the synthesis of GO.

Agricultural wastes, comprising residues from the initial processing of crops, fruits, and vegetables, pose significant environmental challenges globally. Recycling these wastes into valuable products offers a bio-based approach to addressing both local and global environmental challenges. However, high-temperature methods are typically required due to the abundance of cellulose, hemicellulose, and lignin in the presence of agricultural waste [89]. The production of carbon-based materials presents an alternative approach to reduce and elucidate issues associated with waste-related biomass.

In recent decades, synthetic polymers such as polyethylene terephthalate (PET) and electronic products such as batteries and electronic devices have become integral to our community. The exponential growth in industrial waste production has resulted in significant environmental issues. However, industrial waste is rarely repurposed for useful applications due to its unfavourable mechanical characteristics, thermal stability, and low electrical conductivity [90]. Consequently, the appropriate management of this waste presents a considerable global issue. One common method utilised for the disposal of industrial scraps is through their incineration within designated landfill areas. It has long been a standard procedure for managing industrial waste. However, this method can have adverse environmental impacts, such as soil and groundwater contamination, release heat and volatile compounds, and cause climate change [91]. The next approach to eliminate industrial waste is incineration with energy recovery, feedstock or chemical recycling to generate liquid products and gaseous along with carbon-enriched materials [92]. Carbon waste is a promising precursor for synthesising carbon-based materials,

including microspheres, nanotubes, and graphene derivatives [93]. Most industrial scraps are rich in carbon and contain minimal mineral impurities in their chemical composition, making them suitable for synthesising carbon materials [94]. Therefore, a current issue is finding efficient waste utilisation techniques that can convert waste into value-added materials like GO while eliminating impurities. However, there are still limitations with the existing methods for synthesising GO using carbon and biomass sources.

The advancement of carbon-based materials derived from renewable resources such as agricultural, industrial, and plastic is paramount. However, several challenges are linked to the process of producing graphite from carbonous and biomass wastes, such as processing conditions, impurities, and production costs. The primary motivation behind utilising these sources is to offer “green and sustainable” alternatives, utilising cost-effective raw materials for the mass production of carbon-based materials. Recycling carbon precursors and biomass to produce GO offers substantial economic and environmental advantages, unlocking a broad range of applications. Table 2 illustrates the summary of the synthesis of GO from different carbon precursors and biomasses and their possible applications.

2.5.1 GO from Agricultural residues

Agricultural residues and raw biomass offer an abundant, carbon-neutral, cost-effective source for bulk scale production of valuable carbonaceous materials [103, 104]. Various types of agricultural waste, including coconut shells, sugarcane bagasse, tea and rice husk, have been investigated for their potential in graphite production [31]. The main precursor for synthesising GO is graphite powder. Given the escalating demand for commercial graphite, there is an exploration of alternative raw materials that are cost-effective and environmentally friendly. Graphite occurs naturally in three forms: crystalline flakes (90–98%), crystalline lumps (90–99%) and amorphous (70–80%), [105]. It can be further categorised as natural or synthetic graphite, depending on the process of graphitisation utilising heat-induced hydrocarbon precursors. There were reported different methods for the graphitisation of carbon precursors and biomass, including pyrolysis, the template method, foaming technique, and catalytic graphitisation [106]. Agricultural bio-waste generally contains many volatile compounds and impurities, posing a potential disruption to the production method and compromising the quality of the resultant graphitic carbon. Additionally, achieving optimal conditions for converting agricultural biomass into graphitic carbon presents considerable challenges. Precise control of pressure, temperature, catalyst, and other parameters is essential to achieve the intended product. Utilising agricultural biomass as raw materials for graphitic carbon synthesis holds the potential for cost reduction. However, optimising the cost-effectiveness of this method involves considering factors such as feedstock availability, processing expenses, and the market demand for the end product.

Table 2.2 The summary of the synthesis of GO from different carbon precursors and biomasses with their possible applications.

Type	Source	Methods and conditions	Characterisation techniques and Remarks	Potential applications	Ref.
Agricultural	Coconut shell	Carbonised at 600 °C for 3h, followed by Modified Hummers method	XRD, Raman, SEM-EDX, FTIR GO samples tended to form a rGO presence of granular particles	Semiconductor properties	[32]
		Carbonised at 1000, 800 and 400 °C with maintaining 3 and 5 hours	XRD, SEM, TEM, TGA Form turbostratic structure	Electronic industry	[34]
	Sugarcane bagasse	Oxidation with ferrocene under muffled furnace at 300 °C for 10 min under atmosphere (SOMA-GO)	XRD, Raman, FESEM, HRTEM well graphitized structure, more environmentally friendly method	Energy and environmental applications (gas sensors, energy storage, functional devices)	[84]
		Two-step pyrolysis utilising ferric citrate, followed by conc. H ₂ SO ₄	XRD, Raman, SEM, UV-Vis, FTIR Simple, efficient, cost-effective, eco-friendly method		[95]
	Sugarcane bagasse, rice straw, pinewood sawdust, lignocellulosic material	SOMA-GO method	XRD, SEM, TEM, FTIR more environmentally friendly	Water treatments (adsorbent for Ni (II))	[33, 96, 97]
	Sugarcane bagasse, orange peel, rice bran	Like SOMA-GO method	XRD, SEM, HRTEM, TGA/DTA, FTIR Used tri-composite waste to prepare GO successfully.	Energy devices, degradation of dye, wastewater treatment, biomedical applications	[89]
	Sugar beet bagasse	Carbonisation at 400-600	XRD, SEM, UV-Vis, TEM, FTIR	For colorimetric and visual	[98]

		°C, catalysed with FeCl ₃ , followed by Modified Hummers method		detection of trace Hg ²⁺ in the water samples	
	Rice straw	Carbonisation at 450 °C for 45 min and followed by Hummers method	XRD, SEM, TEM, ATM, FTIR	For treatment of dye rich wastewater	[64]
	Tea	Carbonisation at high temperature, followed by a Modified Hummers method	XRD, Raman, FESEM, FTIR,	Degradation of various water pollutions (using as low-cost photocatalytic nanocomposite)	[31]
	Coffee	Carbonisation at 700 °C for 4 hours, followed by a Modified Hummers method	Raman, SEM, FTIR	For tissue engineering applications	[99]
	Oil palm waste: leaves, empty fruit bunches, kernel shells	Carbonised and followed by Improved Hummers method	XRD, Raman, SEM, FTIR, TGA, BET surface area analysis	Preparation of reduced GO	[67]
	Oil palm leaves	Catalytic acid spray technique facilitated by Co silicate as catalyst	XRD, Raman, FTIR, TEM, TGA	Innovative adsorbent for Cu (II) ion removal from synthetic wastewater	[85]
	Pine leaves	Pyrolysis and Modified Hummers method	XRD, Raman, FTIR, SEM	Energy storage and corrosion protection	[86]
	Bagasse, fruits, wood, leaves and	Carbonised and followed by Modified Hummers method	Raman, XPS, current-voltage characteristics	Economical mass production of high-grade graphene	[55]

	animal waste				
	Tasar silk cocoons (Biological source)	Carbonised and oxidised with nitric acid	Raman, FTIR, SEM, TEM	For fluorescent and magnetic properties	[100]
Industrial	Soot powder, newspapers	Carbonised and followed by Modified Hummers method	Raman, XPS, current-voltage characteristics	Cost-effective, mass scale synthesis of high-quality graphene	[55]
	Bio-soot	Modified Hummers method	XRD, Raman spectroscopy, FESEM, HRTEM, FTIR,	Highly effective adsorbent for hazardous Congo red dye	[87]
	Scrap Tyres	Regeneration of carbon black from tyres and followed by a Modified Hummers method	XRD, Raman spectroscopy, FESEM, FTIR		[66, 101]
	Electronic scraps, metal finishing waste, spent petroleum catalysts, batteries	Combination of leaching and Modified Hummers method	XRD, TEM, FTIR		[65]
	Used Zn-C batteries	Modified Hummers method	XRD, SEM, EDX and FTIR, BET	For Removal of U(VI) Ions from aqueous sources	[88]
		Sonication-assisted oxidation and exfoliation process	XRD, SEM, FTIR, UV-Vis	For electrochemical applications	[102]

2.5.1.1 Coconut Shell and Husk

Hydrocarbon compounds are naturally found in various materials, and one such material is coconut shell charcoal [32], stands out with its substantial carbon content, recorded at 74.3% [107]. In a study conducted in 2020, Sujiono and colleagues employed a modified Hummers method to synthesise GO from coconut shell. Simultaneously, graphite powder was derived from the coconut shell through the process of pyrolysis for graphitisation. The thermally dried coconut shell sample was carbonised at 600 °C for 3h to synthesis charcoal with a significant carbon content. In a previous research endeavour, Wachid and his research group (2014) experimented with different heating temperatures (400, 800 and 1000 °C) to generate nanocrystalline graphite from coconut shells. Their findings indicated that the sample heated at 1000 °C with a holding time of 3 hours exhibited the highest crystalline percentage. Compared with the Sujiono and Wachid works, nanocrystalline graphite was obtained when the sample was heated at the most elevated temperatures (1000 °C).

Apart from coconut shell, coconut husk, which contains a significant amount of silica and carbon, was used by Grace and Colleagues [30] to synthesise graphite. The carbonised sample underwent grinding and sieving to obtain a powdered form, followed by treatment with hydrofluoric acid (HF) to eliminate silica impurities. The resulting solution underwent further washing with deionised H₂O and NaOH until it reached a pH level between 6–7. Finally, the sample was subjected to oven dry at 110 °C for a duration of 12 h. The resulting graphite powder was characterised by XRD, Raman, FTIR, SEM.

Sujiono and the research team [32] obtained in two distinct forms of GO samples: as a colloid solution and as powder. In XRD analysis (Fig. 5a) revealed that the GO sample exhibited a significant presence of graphite 2H phase, accounting for 71.53% of the observed structure. This observation indicated the tendency of the GO sample to undergo a transformation into a reduced graphene oxide (rGO) phase [108]. This occurs due to the utilisation of an amorphous material as the precursor in the synthesis process and the alternations in the oxidation degree throughout this procedure. While graphite possesses a high oxidation rate, it was noted that certain samples experienced reduction when subjected to oven dry. This case to the separation of oxygen compound groups from the GO bonding layer [109]. The D and G bands in Raman spectrum (Fig. 2.5b) correspond to the stretching vibrations of sp² and sp³ carbon, respectively, with the D band originating from carbon defect sites and the G band representing sp² carbon. The I_D/I_G intensity ratio in high-quality samples is typically below 2. The I_D/I_G intensity ratio of GO derived from coconut shell waste was found to be 0.89, indicating good quality. FTIR spectroscopy analysis (Fig. 2.5c) indicated the presence of different oxygen-containing functional groups, such as carboxyl, hydroxyl, epoxy, and alcohol, thereby confirming its hydrophilic nature. Furthermore, the SEM image (Fig. 2.5d) revealed a surface morphology abundant with granular particles,

exhibiting varied size distributions ranging from 4.26 μm to 47 μm , alongside pores measuring 2.71 μm in size.

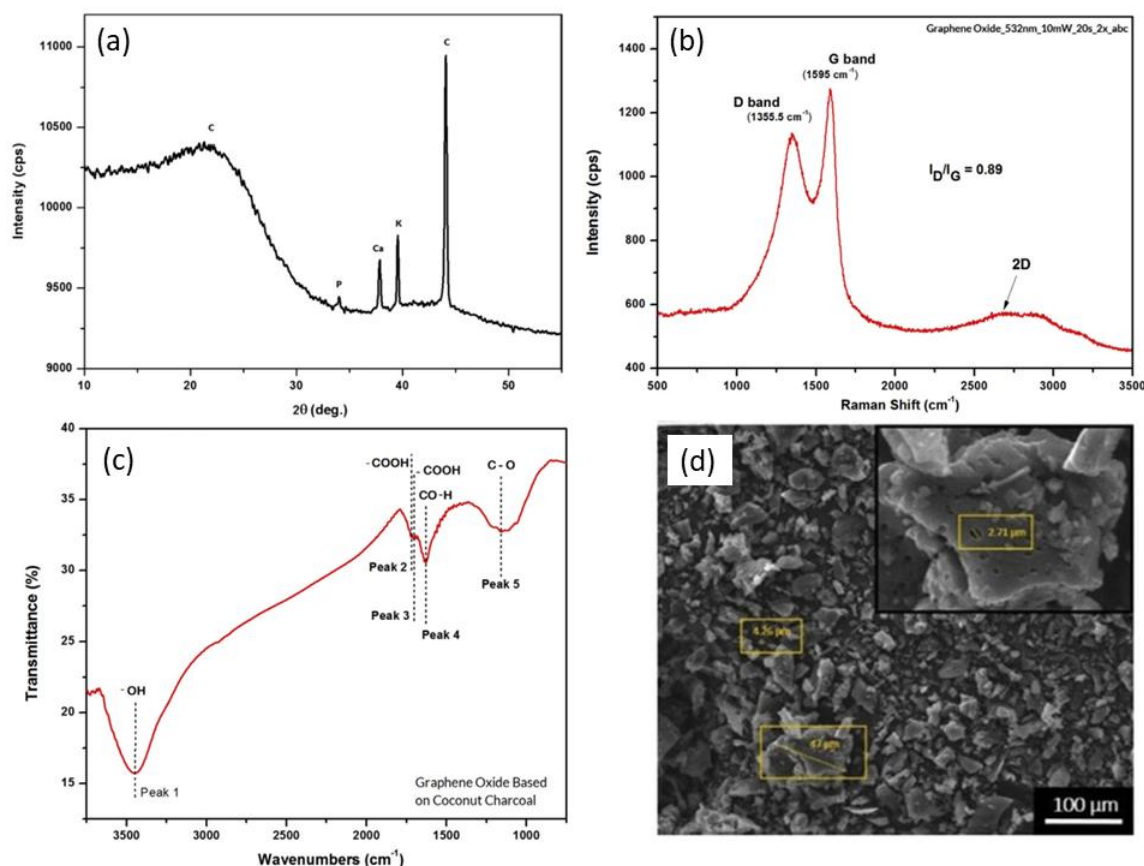


Figure 2.5 The characterisation of GO samples derived from coconut shell a) XRD pattern, b) Raman spectrum, c) FTIR spectrum, d) SEM image with scale 100 μm [32] .

Similarly, Wachid's research [34] showed that the development of graphite in their study had an intermediate structure between crystalline and amorphous, referred to as turbostratic. The existence of the non-crystalline phase in the sample was attributed to the utilisation of raw materials sourced from natural resources. Moreover, Tamilselvi et al. (2020) conducted the direct production of rGO from coconut coir and shells through carbonisation in a muffled furnace with ferrocene as an oxidising catalyst. This approach utilised oxidising agents instead of wet chemical methods such as thermal decomposition and microwave-assisted synthesis to prevent contamination and by-product formation in the rGO production process [110].

2.5.1.2 Sugarcane bagasse and Lignocellulosic materials

In 2014, Akhavan and colleagues [55] conducted a study on the synthesis of GO and graphene derived from natural and industrial wastes, followed by the modified Hummers method. This research used vegetations such as bagasse, fruit, wood, leaves, and animal bones, cow dung for the carbonisation process. Based on Raman, XPS, atomic force microscopy (AFM), and

current-voltage characteristics, the properties of the synthesised graphene sheets, including single-layer and multi-layer structures, composition, carbonaceous structure, and electrical properties were investigated. The results indicated that these properties were largely independent of the starting materials, demonstrating comparable characteristics to high-quality graphene sheets that were achieved using highly pure graphite.

In 2015, Somanathan et al. conducted a study focusing on GO synthesis from sugarcane bagasse via the direct oxidation within a muffled atmosphere that was called “SOMA-GO” method. The method involved crushing the bagasse fibre into a fine powder after juice extraction. This powdered sugarcane bagasse was then combined with ferrocene and introduced directly into a muffle furnace at 300 °C for 10 minutes under atmospheric conditions. The XRD pattern (Fig. 2.6a) obtained in this study exhibited well-graphitised two-dimensional structures composed of GO sheets. The presence of a peak at $2\theta = 11.6^\circ$ indicated the complete oxidation of agricultural sugarcane bagasse into GO with an interlayer distance of 0.79 nm. The Raman spectrum (Fig. 2.6b) demonstrated an I_D/I_G intensity ratio of 0.76 for GO, aligning with findings from previous investigations. The FTIR spectroscopy (Fig. 2.6c) confirmed the introduction of oxygen-containing functional groups, including carboxylic, hydroxyl, and epoxy groups, resulting from the oxidation of sugarcane bagasse. The surface morphology analysis (Fig. 2.6d) of the sugarcane bagasse-derived GO revealed sheet-like (Fig. 2.6d-(i,iii)) and flake-like structures (Fig. 6d-(ii,iv)), consistent with observations reported by previous researchers. High-resolution Transmission electron microscopy (HRTEM) analysis (Fig. 2.6e) exhibited wrinkles, bends, and edges on GO nanosheets in multiple locations. The selected area (Fig. 2.6e-(iv)) of the electron diffraction pattern confirmed the existence of a polycrystalline structure indicative of GO. Compared with other methods, the SOMA-GO method employed in this study offers environmental advantages as it eliminates the emission of toxic gases such as NO_2 , N_2O_4 , and ClO_2 during the synthesis. Additionally, this method effectively converted solid sugarcane bagasse into value-added GO simply and rapidly, yielding a well-graphitised GO structure.

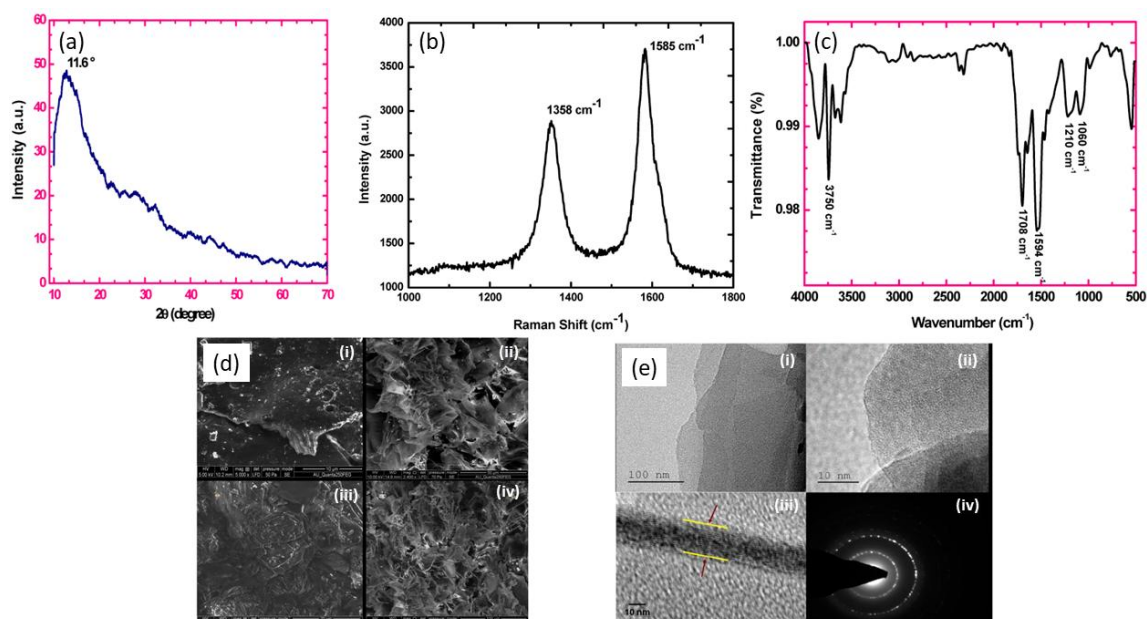


Figure 2.6 The characterisation of GO samples based on sugarcane bagasse a) XRD pattern, b) Raman spectrum, c) FTIR spectrum, d) FESEM images, e) HRTEM images [84].

Thangaraj et al. (2023) employed a two-step pyrolysis process with utilising ferric citrate as a catalyst and subsequent treatment with conc. H_2SO_4 to synthesise GO from sugarcane dry leaves (Fig. 2.7). The synthesised GO was confirmed by a dominant peak at 12.47° in XRD (Fig. 2.8a) with an interlayer distance of 0.71 nm. The Raman spectrum (Fig. 2.8b) exhibited distinct D and G bands, signifying the presence of both sp^2 and sp^3 hybridised carbon atoms in the synthesised sample. Furthermore, the FTIR spectrum (Fig. 2.8c) identified various oxygen-containing functional groups in the GO structure. Morphology analysis (Fig. 2.8d) revealed sheet-like structures of prepared GO. TEM images (Fig. 2.8e) are shown few wrinkled textures throughout the GO sheets. The SADE pattern (Fig. 2.8e) analysis of GO sheets revealed diffused concentric diffraction rings, indicating the semi amorphous nature of the material, and confirming its poor crystallinity. The prepared GO exhibited numerous oxygenated functional groups covalently attached to a graphene basal plane, resulting in C/O atomic ratio of 4.46. Notably, the pyrolysis approach employed in this study stands out for its simplicity, reliability, efficiency, and cost-effectiveness compared to other methods. However, no applications were explored in this study.

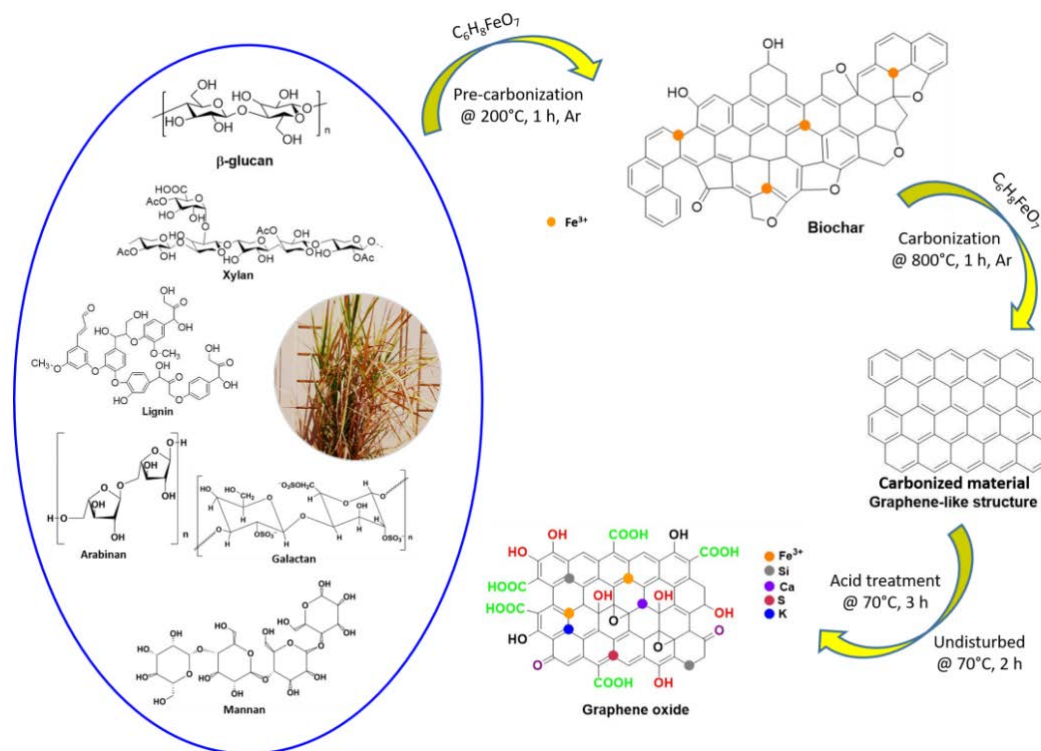


Figure 2.7 The schematic representation of the two step pyrolysis utilised for producing GO from dried sugarcane leaves [95].

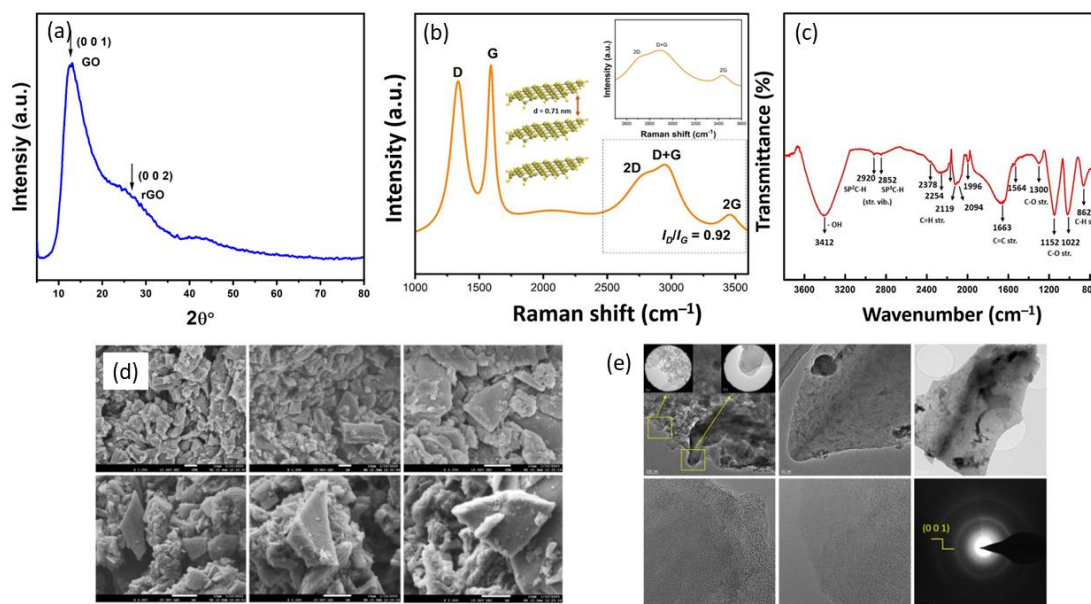


Figure 2.8 The characterisation of GO samples based on sugarcane dry leaves a) XRD pattern, b) Raman spectrum, c) FTIR spectrum, d) SEM images, e) TEM images [95].

In 2020, Tohamy and his research group [96] conducted a study in which GO was synthesised from four different agricultural residues: sugarcane bagasse, pinewood sawdust, rice straw, and lignocellulosic materials using the SOMA-GO method. Their findings revealed that

GO derived from sugarcane bagasse exhibited higher hydrophilicity and better water dispersibility, attributed to the presence of numerous hydrophilic functional groups, as confirmed by FTIR analysis [96]. Furthermore, in the same year, the research group [97] examined the thermal properties of GO synthesised from these various agricultural waste sources. The thermal decomposition process of these four various agricultural residues with the presence of ferrocene exhibited the three main reaction steps, consistent with GO synthesised from pure graphite. In 2022, the same research group [33] introduced a novel magnetic hydrogel loaded with a nanocomposite of GO for Ni(II) removal from wastewater. The GO nanocomposite was prepared using a single-step method, involving the oxidation of sugarcane bagasse using ferrocene, following the same procedure as SOMA-GO synthesis. The characteristics of the nanocomposite were comparable to those of the SOMA-GO product, with one exception: the XRD pattern analysis. The Raman spectra exhibited a smaller I_D/I_G peak intensity ratio (0.59), indicating reduced defects and disorders within the material. However, the XRD analysis of GO exhibited signals at $2\theta = 9.3$ and 21.8° , corresponding to the (001) and (002) plans, suggesting incomplete oxidation of sugarcane bagasse. It is worth noting that GO is a non-stoichiometric compound, and the ratio of carbon to oxygen is influenced by both the preparation technique and the extent of material oxidation.

In 2020, Hashmi and colleagues [89] conducted a research focusing on the fabrication of GO using various agricultural wastes including sugarcane bagasse, orange peel, rice bran and a combination of these wastes referred to as the tri-composite. The method employed for GO synthesis was like the SOMA-GO approach and used individual agricultural wastes and the tri-composite forms. Comparative analysis revealed that successful synthesis of GO was achieved only when using the tri-composite agricultural waste. The presented results highlight a distinct diffraction peak in the XRD pattern at $2\theta = 12.70^\circ$, indicating a corresponding d-spacing of 0.70 nm. Additionally, the average particle size, as determined through SEM analysis, is reported as 2.04 nm. The intense and sharp peak observed in the GO sample indicated good crystallinity, confirming the successful synthesis of GO from the tri-composite agricultural waste. This sustainable, time-efficient, cost-effective method holds significant potential for industrial-scale GO fabrication. Moreover, this approach is environmental friendliness and biocompatible. It enables the utilisation of various types of solid agriculture waste containing carbon, eliminating the need for sanitation as feedstock. Consequently, this method allows to produce high-quality and value-added GO.

Faghiri et al. (2020) produced GO using sugar beet bagasse through a modified Hummers method, which was further employed for the stabilising silver nanoparticles (AgNPs). The process of converting carbonaceous waste into graphite powder involved a two-stage approach. The initial step encompassed carbonisation, followed by utilising FeCl_3 as a catalyst in the second stage.

Subsequently, the Hummers method was adapted to attain a high-quality GO product. The synthesised GO was characterised through XRD, FTIR, SEM, TEM, and UV-vis spectroscopy. The UV-vis spectrum of GO showed that carbon-based materials display distinctive features with a peak in the range of 200–300 nm, which is related to sp^2 hybridisation [111]. The spectrum of the synthesised GO exhibited an absorbance peak at approximately 230 nm, representing the $\pi \rightarrow \pi^*$ transition and a weaker shoulder peak at 300 nm, indicating the $n \rightarrow \pi^*$ transition. All the analyses were confirmed the successful synthesis of GO.

In 2017, Goswami and associates [64] introduced the pioneering use of rice straw biomass as a sustainable precursor for the cost-effective and scalable GO production via the Hummers method. This method initially subjected the oven-dried straw to carbonisation in a muffle furnace under a nitrogen atmosphere at 450 °C for 45 minutes, forming biochar. Afterwards, the biochar underwent a series of steps, including crushing and sieving, resulting in a homogeneous powder. This powder was then utilised as a replacement for graphite in the synthesis of GO via the Hummers method. The resulting GO nanoplatelets were characterised using XRD, FTIR, AFM, SEM and TEM. The comprehensive analysis conclusively established structural and functional equivalence to those traditionally prepared from graphite.

2.5.1.3 Tea and Coffee

Azurahanim and colleagues [31] studied converting tea waste into GO by carbonisation at high temperatures, followed by the modified Hummers method. This research highlights the potential of tea as a low-cost and temperature-effective starting material for GO synthesis. The process of preparing chemically modified graphitised biomass followed a standard route of modified Hummers method. The tea residues revealed its potential in producing GO at a low cost and temperature. Increasing the oxidation time, a similar GO structure derived from tea was achieved, comparable to that prepared from commercial graphite. The tea waste samples were carbonised at three specific temperatures: 650 °C (S1), 750 °C (S2) and 850 °C (S3). However, the carbonisation yield remained consistent across all the samples. The XRD studies indicated that the prominent peak ($2\theta = 26^\circ$) width narrowed as the carbonisation temperature increased, indicating increased structural ordering and graphitisation of the carbonised tea residues. Raman analysis demonstrated I_D/I_G ratio for S1= 0.84, S2= 0.92, S3= 0.96, signifying increased defects in the carbon structure and greater disorder in sp^2 carbon formation with rising carbonation temperature. The connection between the I_D/I_G ratio and heating temperature indicates that elevated temperatures affect the defects in the sp^2 carbon structure. Subsequently, GO was produced through the modified Hummers method, with the S1 carbonised sample as the precursor. The synthesised GO was confirmed through FTIR and SEM analysis. Furthermore, the

synthesised GO underwent loading with titanium dioxide (TiO_2) through the hydrothermal method, forming a nanocomposite of rGO/ TiO_2 .

Challa et al. (2023) investigated the synthesis of GO nanoparticles using spent coffee grounds, an abundantly discarded carbonaceous source. The oven-dried ground coffee waste was carbonised in a tube furnace at 700°C for 4 hours under argon gas flow. The resultant black char served as a precursor for GO production employing the Modified Hummers method. The synthesised GO was confirmed through the Raman spectroscopy, FTIR, and SEM analysis. In the Raman spectra (Fig. 2.9a), the D and G bands appeared at 1339 cm^{-1} and 1598 cm^{-1} respectively, characteristic of GO, while the presence of the 2D band at 2770 cm^{-1} indicated the multi-layer stacking of graphene sheets. FTIR (Fig. 2.9b) confirmed the formation of GO, while SEM (Fig. 2.9c) revealed a reduction in particle sizes to the nanoscale following increased ultrasonication. The produced GO was then used in electrospun cellulose acetate scaffolds, indicating potential applications in tissue engineering.

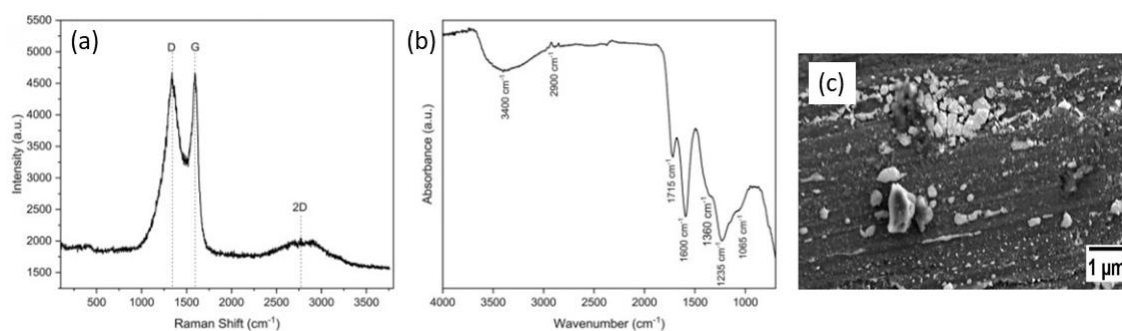


Figure 2.9 The characterisation of GO samples synthesised from ground coffee a) Raman spectrum, b) FTIR spectrum, c) SEM images [99].

2.5.1.4 Oil palm Waste and Pine Leaves

Nasir et al. (2017) introduced a novel approach for producing rGO from GO utilising oil palm waste, including leaves, empty fruit bunches, and kernel shells. Before synthesis GO and rGO, they investigated the impact of heating temperature on the production yield. The waste materials were carbonised in a furnace under N_2 gas for 3 hours at 400°C to 900°C with a heating rate of $10^\circ\text{C}/\text{min}$. Following carbonisation, the GO was synthesised using an improved Hummers method. Raman, XRD, FTIR, SEM, TGA and BET analysis were used to analyse the products. Subsequently, the GO underwent reduction through low temperature annealing at 300°C in a furnace under N_2 gas for 1 hour. The Raman analysis revealed an increase in the I_G/I_D ratio, indicating enhanced graphitisation in the rGO samples derived from different oil palm waste components. This method offers scalability and cost-efficiency in producing carbon nanostructured materials and needs to further investigate into potential applications.

Moubark et al. (2019) produced GO from oil palm leaves via the catalytic acid spray (CAS) process, employing Co silicate as a catalyst for Cu (II) ion removal from wastewater. In this method, pre-treated microcrystalline cellulose fraction from oil palm leaves were subjected to mixing with conc. H_2SO_4 for 10 min, followed by thorough washing and drying at 40 °C for 6 hours. Subsequently, the material underwent decantation, cobalt silicate addition, and heating at 40 °C for 30 min. Finally, the resulting GO was then cooled and dehydrated. The synthesised GO was characterised using Raman, XRD, and FTIR. According to the Raman spectroscopy, GO has been synthesised as a single sheet with a broader 2D band, between 2650 cm^{-1} and 2700 cm^{-1} . However, the intensity ratio of I_G/I_D is 4, indicating low-quality GO. In XRD, the broadband was indicated of GO synthesis, possibly due to combining GO sheets with silicate content catalysts or cellulosic precursors. The FTIR showed that GO comprises carboxylic acids, carbonyl, and hydroxyl groups. This study pioneers the use of the CAS method for GO synthesis, which is a simple, low-cost, scalable method. However, compared with other methods, synthesised GO has low quality due to the catalyst effect.

In 2022, Singhal et al. investigated using pine leaves as a sustainable and environmentally friendly source for producing biochar, which was further transformed into GO (Fig. 2.10). The process commenced with the preparation of biochar, achieved through pyrolysis of pine leaves at 750 °C for 3 hours in an N_2 environment. The subsequent conversion of biochar to GO was facilitated using a modified Hummers method. Raman, XRD, FTIR, SEM and elemental analysis, confirmed the biochar and respective GO. The XRD analysis revealed a decrease in the crystallite size of biochar after its conversion into GO. The Raman spectra analysis of GO exhibited a notable blue shift in the G band at 1595 cm^{-1} , along with a clearly defined broad D band at 1380 cm^{-1} , indicative of the presence of epoxy and hydroxyl groups. Both biochar and the corresponding GO were examined for their potential in long-term electrochemical energy storage and resistance to corrosion in a potassium hydroxide solution (KOH). However, it is worth noting that a significant limitation of this synthesis pathway was the utilisation of the modified Hummers method.

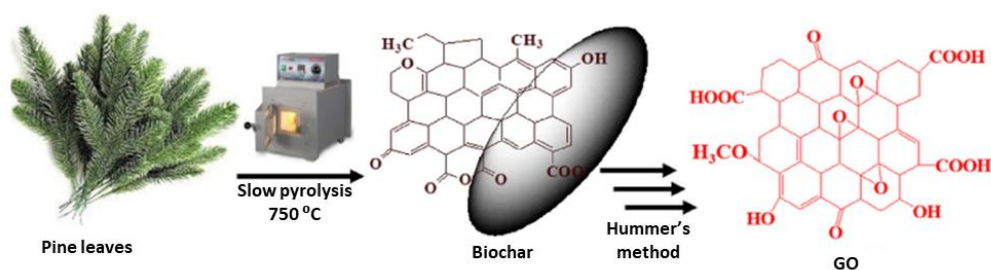


Figure 2.10 Schematic representation of Biochar and GO synthesis from Pine Leaves [86].

2.5.1.5 Biological Source

Manas et al. (2013) introduced an innovative and cost-effective method for synthesising GO by pyrolysing Tasar silk cocoons followed by oxidation using conc. HNO_3 (Fig. 2.11). This work opened new possibilities for utilising Tasar silk cocoon as a magnetic-fluorescent biomaterial. Initially, Tasar silk cocoons were ground and pyrolysed in a muffle furnace at 400 °C for 2 hours under an argon atmosphere. After purification, the carbonised cocoon underwent oxidation through treatment with conc. HNO_3 for 24 h. The final product was analysed using Raman, FTIR, SEM and TEM analysis. Raman analysis (Fig. 2.12a) compared the position and intensity of the D band and G band for both raw and synthesised GO samples. In the synthesised GO, two prominent bands appeared at 1592 cm^{-1} (G band) and 1359 cm^{-1} (D band), showcasing a blue shift compared to the raw carbon. This shift was attributed to the conversion of graphite crystals into graphene sheet and the presence of more defects. FTIR spectroscopy (Fig. 2.12b) revealed the various oxygen functionalities present in the synthesised GO. The SEM images provided insights into the surface morphology changes induced by oxidation, with the raw carbon (Fig. 2.12c-(i)) displaying layered sheets with carbon particulates with its amorphous nature, while the oxidised carbon exhibited multilayer GO sheets with a width of 2.6 nm (Fig. 2.12c-(ii-iv)). TEM images (Fig. 2.12d-(i-iii)) displayed oxidised carbon, indicating the presence of multilayered of GO. The SAED (Fig. 2.12d-(iv)) confirmed a hexagonal lattice with typical sixfold symmetry for GO. These characterisations demonstrated similarities with commercial GO. The synthesised water-soluble GO exhibited remarkable fluorescence properties, expanding its potential applications.

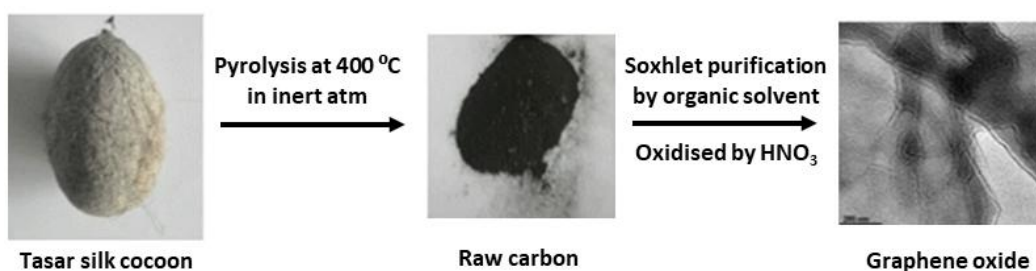


Figure 2.11 The schematic diagram of GO synthesis from Tasar silk cocoon [100].

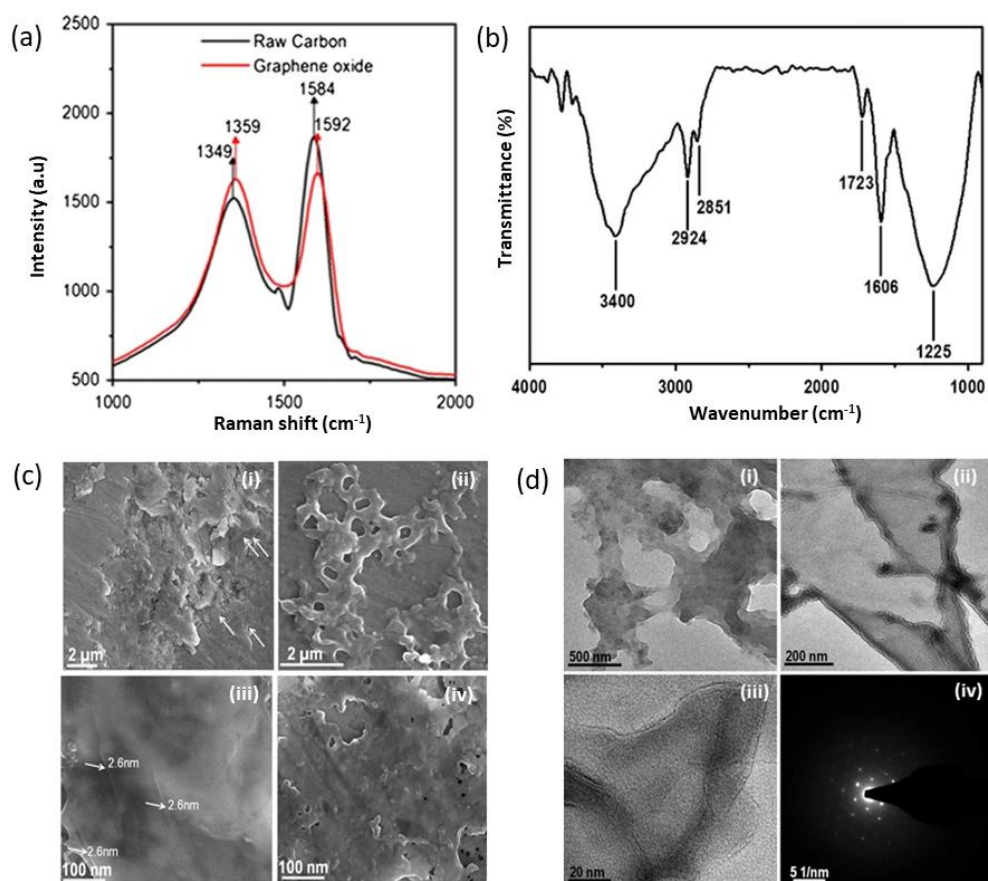


Figure 2.12 The characterisation of GO synthesised from Tasar silk cocoon and raw carbon a) Raman spectrum b) FTIR spectrum c) SEM images (i) raw carbon (ii-iv) GO sheets d) TEM images (i-iii) GO (iv) SAED pattern of GO [100].

2.5.2 GO from Industrial Scarps

Industries produce large quantities of scarps, promoting exploration into utilising these waste materials for the synthesis of GO – a concept offering both environmental and resource conservation advantages. Various waste sources such as soot [87], newspapers [55], scarp tyres [66], electronic components [65], and used batteries [65] have been explored for their viability in GO synthesis. Researchers are employing innovative methodologies to convert suitable constituents from industrial waste into GO. The resulting GO exhibits distinctive properties that render it suitable for diverse applications.

2.5.2.1 Soot Powder and Newspapers

In 2014, Akhavan [55], mentioned earlier in the context of GO synthesis from agricultural residues, explored the synthesis of GO using semi-industrial and industrial waste such as newspaper, soot powders (generated from diesel vehicle exhaust), respectively. The industrial waste was initially carbonised within the temperature range of 400–500 °C and used a Hummers method was employed for chemical exfoliation of the graphitised materials. The surface morphology, including chemical composition, sheet thickness, carbonaceous structure, and

electrical properties of the sheets synthesised from different sources were observed to be nearly identical and comparable to those of the graphene sheets derived from highly pure graphite.

In 2020, Kumar Sahoo et al. synthesised GO from bio-soot (diesel engines) to adsorb the highly noxious Congo red dye. The investigation of the morphological structure of the bio-soot revealed a higher degree of graphitisation compared to carbon black or activated charcoal. The process of preparing (Fig. 2.13) GO involved oxidising the bio-soot powder using the modified Hummers method. The resulting GO was characterised through Raman, XRD, FTIR, BET, FESEM and HRTEM. The XRD (Fig. 2.14a) study showed a strong peak at 10.8° (002) corresponding to an interlayer spacing of 0.86 nm. This observation suggests the existence of oxygen-containing groups within the graphitic layers.

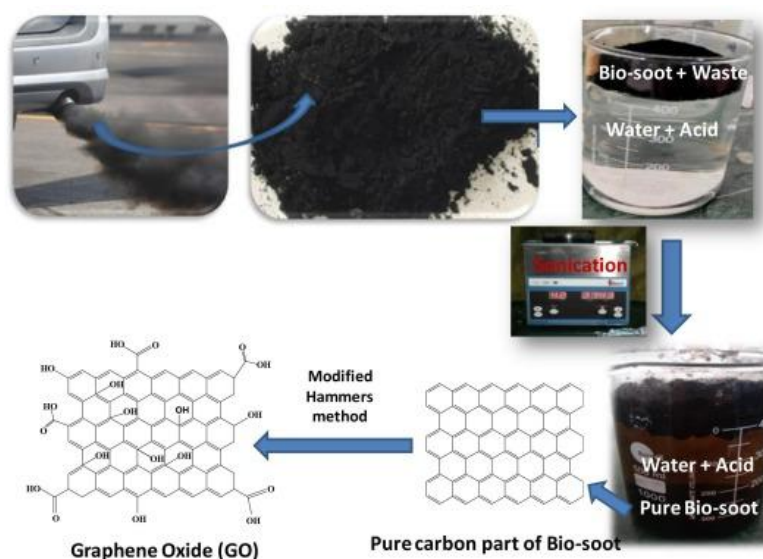


Figure 2.13 Synthetic procedure for GO from bio-soot [87].

In the Raman spectra of GO (Fig. 2.14b), the observation of the D band at 1360 cm^{-1} and the G band at 1610 cm^{-1} confirmed the successful production of GO from bio-soot. This formation was further validated by FTIR (Fig. 2.14c). The FESEM image of GO (Fig. 2.14d) showed a few flaky layered and wrinkled large sheet-like structures with smooth surface, and the TEM images of GO (Fig. 2.14e) represented a single sheet-like structures. The EDX spectra (Fig. 2.14f) of GO exhibited the presence of carbon and oxygen, with weight ratios of 94.34 and 5.66 respectively. The advantageous aspect of bio-soot lies in its readily available as a by-product of diesel engine exhaust, thus converting an environmental pollutant into a valuable product.

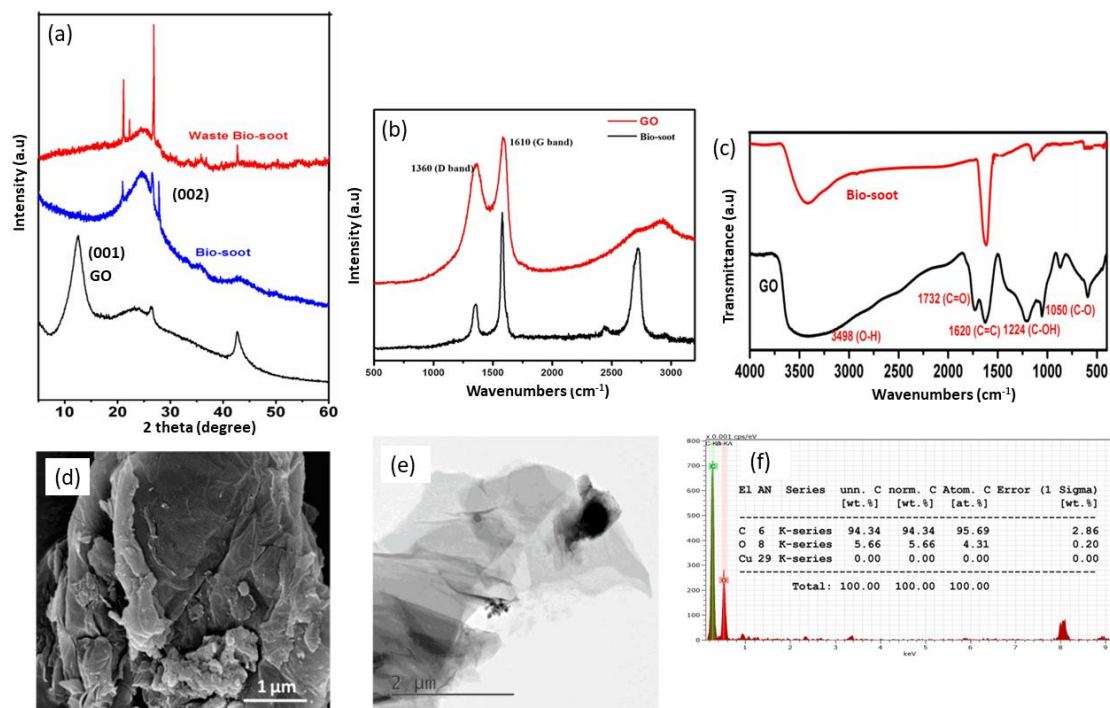


Figure 2.14 a) XRD pattern of GO, bio-soot and waste, b) Raman spectra of GO and bio-soot, c) FTIR spectra of GO and bio-soot, d) FESEM image, e) TEM image, and f) EDX Spectra of GO derived from bio-soot [87].

2.5.2.2 Scrap tyres

Bonnia et al. and Anuar et al. in their respective studies [66, 101] have been investigated the synthesis and characterisation of GO derived from discarded tyres using a modified Hummers method. The study aimed to convert regenerated carbon black from tyres into GO, turning waste into a valuable resource. The presence of GO was confirmed through analysis using Raman, XRD, FTIR, and FESEM. The study revealed an I_D/I_G ratio of 0.82 for GO-1% carbon waste tyres (CWT), indicating the successful production of high-quality GO. The presence of defects in the GO structure was significantly influenced by the acids employed as oxidation reagents during the synthesis, with the weight percent of the precursor playing a role. The XRD analysis exhibited a broad and wide peak, indicating that the synthesised GO was in the amorphous phase. Furthermore, the FTIR results further supported the presence of hydroxyl and epoxy groups within the GO structure, contributing to its hydrophilic properties.

Tatrari et al. (2022) introduced an innovative methodology for the mass-scale production of zinc doped rGO spheres (ZGS) from scrap tyres using an environmentally friendly double step pyrolysis technique. Comprehensive characterisation of the prepared samples was conducted using advanced spectroscopic techniques including XRD, Raman spectroscopy and FTIR. The XRD results exhibited two broad peaks at $2\theta = 25^\circ$ and $2\theta = 44^\circ$, indicating the graphitic nature of the sample and the transformation of amorphous structure into reduced carbonic moieties. The Raman analysis revealed well-defined D, G and 2D bands at 1366 cm^{-1} , 1560 cm^{-1} , and 2791 cm^{-1} .

¹, respectively, confirming the graphitic nature of the product. Furthermore, FT-IR data revealed evidence of partial oxidation at the ZGS, which could potentially be attributed to interactions with ZnO and acid treatment during the synthesis process. Finally, the synthesised ZGS demonstrated promising applications in supercapacitors.

2.5.2.3 Electronic scraps and Other Industrial waste

Siaw et al. 2020 investigated a synthesis of GO from various industrial waste, including electronic scraps, used batteries, metal finishing scraps, and spent petroleum catalysts. This was achieved through a combination of leaching and modified Hummers method. During the leaching step, impurities were efficiently eliminated by dissolution in 6 M HCl at 70 °C for 210 minutes, resulting in a graphite residue with a purity of 92.28 %. Following this, GO was synthesised via a modified Hummers method using conc. H₂SO₄ and KMnO₄. The KMnO₄ ratio was adjusted from 1:3 to 1:5 to enhance the oxidation process, eliminating the need for NaNO₃. Additionally, the production time for each GO synthesis step was reduced from 330 minutes (using the Hummers method) to 150 minutes. The elemental analysis revealed that heavy metals constituted the predominant impurities in industrial waste. The leaching process effectively removed most impurities, particularly when employing 6 M HCl at temperature 70 °C, a liquid-to-solid ratio of 1:10 and a leaching duration of 210 minutes. The XRD and FTIR analyses confirmed the synthesis of GO. Initially, the XRD analysis of the graphite present in the industrial scraps exhibited a diffraction peak at $2\theta = 26.6^\circ$, indicating an interlayer distance of 0.34 nm. The conversion of graphite into GO was evidenced by a shift in the XRD peak to $2\theta = 10.35^\circ$, indicating a d-spacing of 0.73 nm. Additionally, TEM observations revealed the presence of both monolayer and multilayer GO with wrinkles surface, indicating the characteristic morphology of GO.

Hassanin et al. (2022) synthesised GO through a modified Hummers method, using Zn-C batteries as precursors, which reacted with SiO₂ sourced from rice husk. The products were characterised using Raman, XRD, BET, SEM, EDX, and FTIR. The Raman spectrum exhibited distinctive peaks at 1585 cm⁻¹ for the G band and 1355 cm⁻¹ for the D band. The XRD analysis (Fig. 2.15a) revealed a broad peak at $2\theta = 14^\circ$, and the FTIR (Fig. 2.15b) was confirmed the oxygenated functional groups on its surface. The SEM image (Fig. 2.15c) demonstrated definite shapes and included distinct irregular composition. The C to O atomic ratio was shown in EDX spectrum (Fig. 2.15d) as 91.84 and 6.59 respectively. The BET analysis (Fig. 2.15e) highlighted its high surface area as 37.37 m²/g. All analytical results collectively confirmed the successful synthesis of GO, although the method relied on a modified Hummers approach. Moreover, the study showcased the utilisation of available carbon waste to produce a silica/GO composite as a sorbent material.

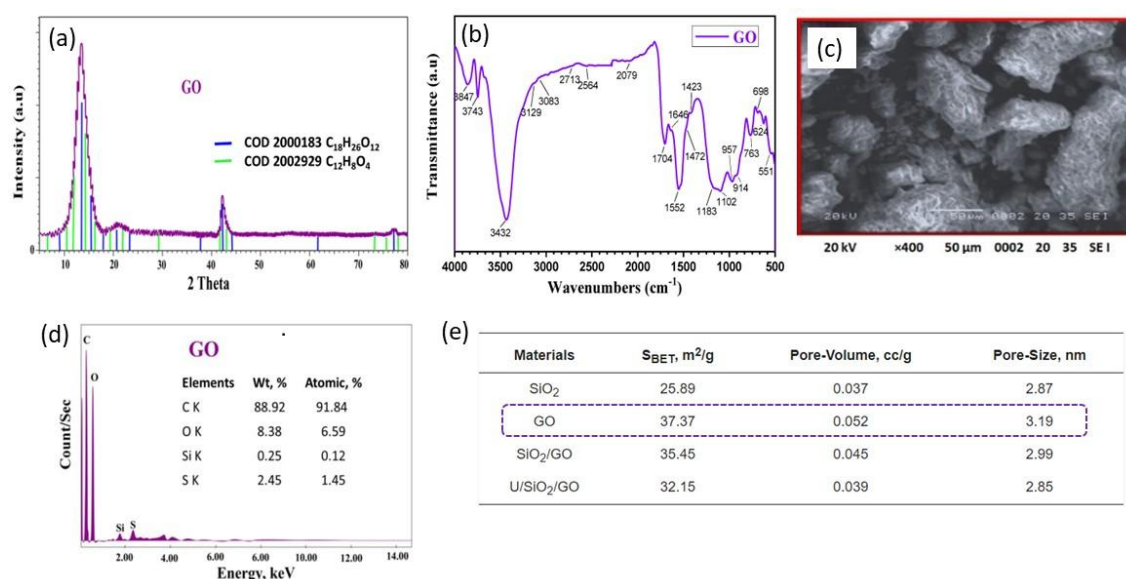


Figure 2.15 a) XRD pattern, b) FTIR spectrum, c) SEM image, d) EDX Spectra, e) BET Analysis of GO synthesised from Zn-C batteries [88].

Loudiki et al. (2022) developed a synthesis method for GO using carbon rods extracted from used ZnC batteries, employing a newly optimised electrochemical approach. The method incorporates sonication for the recycling of carbon rods, providing a rapid and cost-effective technique. The study aimed to establish a simple synthesis process incorporating ultrasonication with standard Hummer's reagents to produce GO, utilising carbon rods from ZnC batteries. The standard Hummers reagents were used for graphite oxidation and exfoliation while the sonication favoured the reaction. The proposed method prevented explosion problems and energy reaction time. The GO derived from carbon rods was characterised by XRD, FTIR, UV-Vis and SEM. The XRD analysis indicated a highly crystalline structure in the hexagonal carbon graphite powder from the battery rods, exhibiting a peak resembling that of graphite at 26.5°. However, the synthesised GO were exhibited a broad peak at 2θ extending from 10 to 45°, indicating an amorphous structure due to the presence of impurities in the carbon rods powder. FTIR was used to compare the different functional groups of the ZnC based graphite and synthesised GO. The SEM images showed that the two-dimensional flat morphology of the ZnC material, while the GO has randomly oriented sheets indicating the high degree of exfoliation. Then the electrochemical performances of GO were investigated and compared to the Hummers GO.

2.5.3 GO from Plastic Waste

Research on GO synthesis from plastic waste is limited; however, El Essawy et al. (2017) [112] reported on the sustainable synthesis approach for graphene production using recycled PET bottle for dye adsorption in aqueous solutions. The research focused on the production of graphene through the thermal dissociation of Poly-ethylene-terephthalate (PET). The crushed PET was inserted into a sealed stainless-steel reactor, heated to 800 °C with a rate of 8 °C min⁻¹, and maintained at this temperature for 1 h. The resulting dark products were then cooled and analysed. Characterisation techniques such as Raman, SEM, TEM, BET, TGA, and FTIR were used to analyse the synthesised graphene. The elemental analysis of PET indicated its potential as a precursor for graphene synthesis owing to its notable carbon amount and lack of inorganic constituents and impurities. SEM images showed a fibrous network morphology with void spaces, indicative of porosity, while TEM image displayed relatively transparent graphene layers entangled and rippled with observed graphite deposits. The XRD analysis revealed broad peaks corresponding to disordered graphite like carbons. The intensity ratio of Raman D and G bands indicated the degree of disorder in the prepared graphene. BET surface area measurements indicated significantly higher surface area and micropore volumes for the synthesised graphene compared to PET, suggesting its potential as an effective adsorbent for dye removal from aqueous solutions. Overall, the study demonstrated the feasibility of using graphene synthesised from PET waste as a low-cost and efficient adsorbent for removing methylene blue (MB) and acid blue (AB25) from aqueous solutions. However, further research is needed to explore the production of GO from plastic waste.

GO has emerged as a central focus of research due to its diverse applications across various fields. However, the reliance on conventional and limited graphite as a raw material may not be sustainable in the near future. GO synthesised from waste and other organic precursors displays properties akin to conventionally derived GO. Nonetheless, further studies are necessary to identify suitable waste precursors, considering factors such as availability, processing conditions, and product quality. The present study identifies Agro waste as a promising carbon-rich precursor, particularly sugarcane-derived GO, which stands out among agricultural wastes. The findings show that GO derived from sugarcane bagasse exhibits higher hydrophilicity and better water dispersibility, attributed to numerous hydrophilic functional groups. The SOMA-GO method and direct ferric citrate pyrolysis prove to be the best methods for synthesising GO from sugarcane bagasse, offering simplicity, reliability, efficiency, cost-effectiveness, and environmental friendliness compared to the Modified Hummers method. While waste-derived GO may contain impurities and dispensable elements, the necessity for additional purification processes raises economic challenges. For instance, tyre-derived char used for synthesising GO contains significant impurities such as Zn and S, highlighting purity issues that need resolution

before adapting tyre char as a raw material. On the other hand, bio soot emerges as a promising industrial precursor for GO synthesis compared to other industrial wastes.

To ensure a selective and sustainable approach for GO production, extensive research is required to identify the best methods for producing GO with desired characteristics. Typically, GO has a carbon-oxygen ratio of 1.5 to 2.5, and various chemical methods can produce it, with the Hummers method being the most common. However, none of the waste materials in this study fall within this range, except for sugarcane dry leaves derived GO from direct pyrolysis from ferric citrate, which exhibited a C/O atomic ratio of 4.46. Moreover, the average particle size of GO derived from these waste precursors ranged from 200 μm to nanometres. Despite addressing environmental concerns and offering a sustainable and cost-effective method for GO production, the unique properties of resulting GO from waste materials introduce in its applications.

2.6 Applications of GO from waste materials

The innovative application of GO derived from waste has garnered significant attention in recent years. GO, a remarkable two-dimensional carbon-based nanomaterial, exhibits a diverse range of exceptional properties that render it highly versatile for various applications. Numerous researchers have explored the applications of GO derived from waste material such as coconut shells [32], sugarcane bagasse [84], rice straw [64], tea [31], pine leaves [86] etc.

The synthesis of GO from coconut shells, as investigated by Sujiono et al. 2020, was analysed using the Tauc plot method, revealing a band gap energy value of 4.38 eV, indicative its semiconductor properties. Initially, coconut shell is an insulator material [113], characterised by a band gap energy ≥ 5 eV. However, after being synthesised into GO material, it transforms into a semiconductor with a bandgap energy of less than 5 eV [114]. This reduction in bandgap energy is attributed to the exfoliation of graphite powder and the sonication of the sample throughout the synthesis method [115]. In 2020, Tamilselvi and the research team [116] reported an effective method for rapidly synthesising high-quality rGO with properties well-suited for high-performance flexible supercapacitor devices. Additionally, Mohan, and his team [117] presented a scalable strategy for synthesising GO and graphene-tin oxide from coconut shells and wood. Their study highlighted the potential of the graphene-tin oxide nanocomposite derived from charcoal of coconut shell as an antimicrobial agent in various applications. Further investigations are required to explore its potential applications in sanitary agent manufacturing, sewage treatments, and food packaging.

In 2015, Somanathan and his team proposed a simple and cost-effective method called SOMA-GO for synthesising GO from sugarcane bagasse. This method presents promising opportunities for economical production of graphene-based materials used in energy storage, gas

sensors, and other functional devices [84]. Building upon the SOMA-GO approach, Kamel and his team (2022) [33] synthesised GO and developed magnetite GO hydrogels. These magnetite hydrogels exhibited remarkable enhancement in Ni (II) adsorption from wastewater, with a removal efficiency of 98.82% [33]. Despite various adsorbents being explored for Ni (II) removal, including green algae, aerobic activated sludge, fly ash, activated carbon, and crab shell, their limited adsorption efficiency hinders their widespread application [33]. Consequently, there is a growing demand for novel adsorbents with higher capacity. Carbon-based nano sorbents like graphene (G), graphene oxide (GO), and carbon nanotubes (CNTs) have emerged as effective usage for wastewater purification [118]. Additionally, using sustainable composites offers numerous advantages including affordability, biodegradability, low density, eco-friendliness, and reduced energy consumption, in contrast to synthetic materials. However, despite the potential of adsorbents derived from sugarcane bagasse, particularly in Ni (II) adsorption, further optimisation is required to enhance their effectiveness.

In 2020, Hashmi and colleagues introduced the synthesis of GO using a combination of agricultural waste, including sugarcane bagasse, orange peel and rice bran, under a muffled atmosphere. They suggested that this straightforward technique leads to new opportunities for various applications such as energy devices, dye degradation, wastewater treatment and biomedical purposes. In a parallel study, Faghiri et al. (2020) conducted the production of GO from sugar beet bagasse employing a modified Hummers method. Subsequently, they employed the stabilization of silver nanoparticles (AgNPs) for the colorimetric and visual detection of trace amounts of Hg^{2+} in environmental water samples. The optimisation results suggested that Ag-GO exhibited high selectivity for detecting Hg^{2+} at a pH of 5.0 and a response time of 2 minutes, with a detection limit of 0.64 nM. This approach proved effective in quantifying Hg^{2+} in environmental samples, highlighting the promising application potential and significant market value of Ag-GO in environmental studies.

In 2017, Goswami and associates introduced an innovative study where biochar derived from rice straw biomass served as a sustainable precursor for the cost-effective and large-scale production of GO. This novel GO synthesis method was applied for the crystal violet (CV) adsorption from an aqueous solution. The experimental findings demonstrated that the produced GO nanoplatelets achieved a remarkable 90–99.8% CV removal. The sustainable synthesis procedure, affordability, minimal energy consumption and high treatment efficiency marked this method as highly effective for removing dyes from solutions. Furthermore, the study has shown the possible use of these GO nanoplatelets in the real-time treatment of both industrial and domestic wastewater.

Amir Faiz et al. (2020) prepared graphitized tea waste and oxidized it through the modified Hummers method. The resulting GO was then combined with titanium dioxide (TiO_2) through hydrothermal processes, resulting in a nanocomposite of rGO/TiO_2 . The photocatalytic efficiency of the rGO/TiO_2 nanocomposite was assessed through the degradation of methyl orange (MO) under ultraviolet (UV) light exposure. Their findings indicated that incorporating GO at a concentration of 11.11% of the total weight of the rGO/TiO_2 nanocomposite significantly inhibited electron recombination, thereby enhancing its photocatalytic efficiency compared to using TiO_2 solely. This work contributes to preparing low-cost photocatalytic nanocomposite materials for the degradation of various water pollutants. Challa et al. (2023) synthesised GO from spent coffee grounds for tissue engineering applications (Fig. 2.16). The investigation demonstrated that incorporating GO as a matrix modifier is non-toxic and promotes cell growth. The biocompatibility of the resulting fibres is influenced by the oxygen-rich and hydrophilic properties of GO. Utilising Agro-residual biomass, such as spent coffee, for the production and modification of biomaterials is highlighted. These findings contribute to the exploration of sustainable bio-composites and align with efforts in environmental conservation.

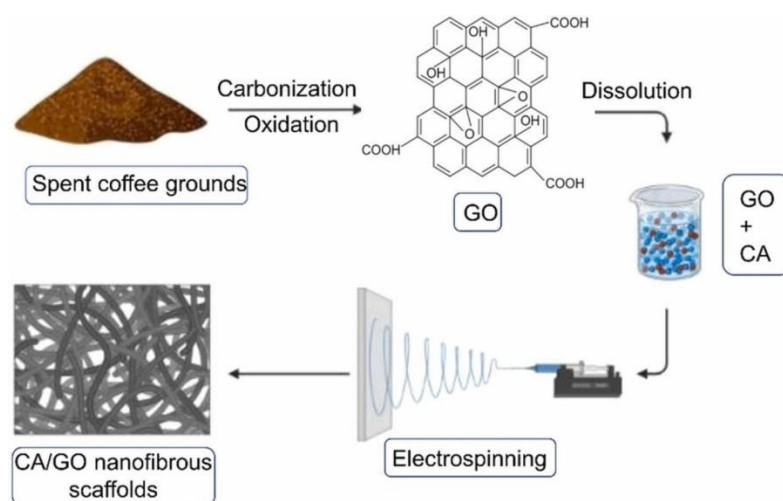


Figure 2.16 The schematic diagram of synthesised GO from spent coffee grounds for the application of tissue engineering [99].

Singhal et al. (2022) synthesised GO using biochar derived from pine leaves, following a subsequent modified Hummers method. The resulting pine biochar and corresponding GO were examined for their potential in long-term electrochemical energy storage and corrosion protection in a 2.0 M KOH solution (Fig. 2.17). The working electrodes (WE) were prepared using biochar (WE_{BC}) and GO (WE_{GO}) with hydroxy methyl propyl cellulose serving as a binder. WE_{GO} exhibited a 24.49% increase in supercapacitance compared to WE_{BC} under identical electrochemical conditions, showcasing the capacitive behaviour of GO. Electrochemical impedance spectra (EIS) revealed stability of WE over 24 h, exhibiting potentiodynamic

polarisation within the ranging -1.5 to 1.0 @ 0.005 V/s. This indicated a corrosion rate (mm/year) of WE_{GO} @ 4.69×10^{-4} , that was much reduced over WE_{BC} (2.27×10^{-3}) under equivalent conditions. Notably, GO displayed superior corrosion protection performance (4.69×10^{-4} mm/year) compared to bare electrodes during the potentiodynamic polarisation. This research introduces a sustainable approach to fabricating working electrodes using biochar-derived GO, resulting in enhanced electrochemical supercapacitance, stability, and corrosion resistance.

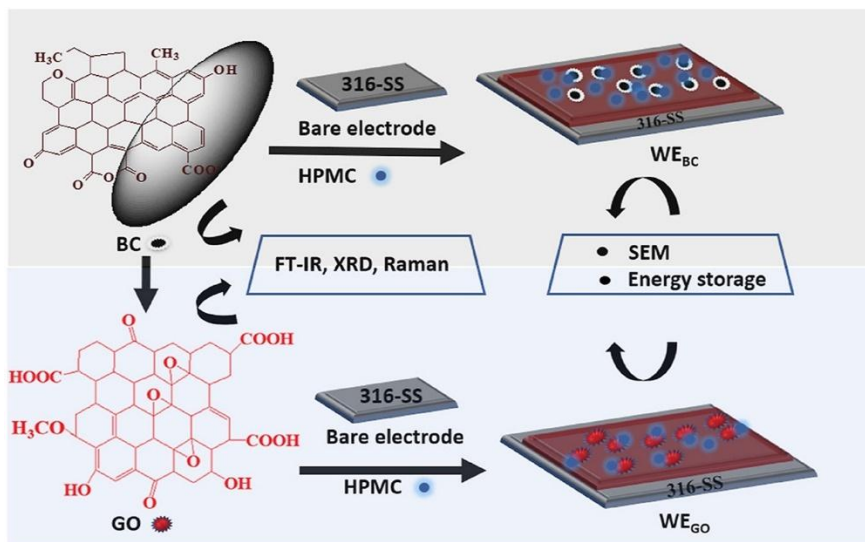


Figure 2.17 The schematic diagram of sustainable synthesis of GO from pine leaves for applications in energy storage and corrosion protection [86].

Research conducted by Manas et al (2013), GO was produced from Tasar silk cocoon through a process involving pyrolysis followed by treatment with conc. HNO₃. The oxidised sample showed remarkable fluorescence, magnetic properties, and multi-photon imaging. Notably, an increase in the excitation wavelength corresponded to a rise in the fluorescence emission intensity of the GO, peaking at a wavelength of 380 nm. These observed magnetic properties and fluorescence were attributed to defects induced within the GO structure during oxidation, resulting in the incorporation of oxygen containing hydrophilic groups. Moreover, the GO displayed soft ferromagnetic behaviour along with single and two-photon fluorescence features, suggesting its potential applications in spintronics, magneto-optics, carbon-based magneto resistance, and magnetic memory devices. This research not only presents a novel synthesis approach but also highlights the multifaceted properties for innovative applications.

The research by Kumar Sahoo et al. (2020) focused on synthesising GO from bio-shoot, specifically utilising biodiesel soot powder obtained from automobile. They utilised the Modified Hummers method to oxidise the extracted biodiesel soot and produce GO. The synthesised GO was then employed as an adsorbent for the effective removal of Congo red dye, a highly noxious substance, as illustrated in Fig. 2.18. Congo red (CR) dyes, known for their anionic properties,

served as model organic pollutants to evaluate the absorption capabilities of GO. Studies were conducted on varying parameters such as adsorbent dosages, pH levels of the solution, contact time and concentration. Additionally, isotherm studies and kinetic were investigated to gain insights into adsorption process of CR. The result indicated that the adsorption process adhered to both the Langmuir isotherm model and pseudo-second-order kinetic. The GO surface exhibited a maximum adsorption capacity of 120.20 mg/g, a significant improvement compared to bio-soot, which was 70.23 mg/g. This highlights the superior adsorption capabilities of GO due to its increased amount of adsorption sites. The adsorption process of CR onto GO was observed to occur spontaneously and endothermic.

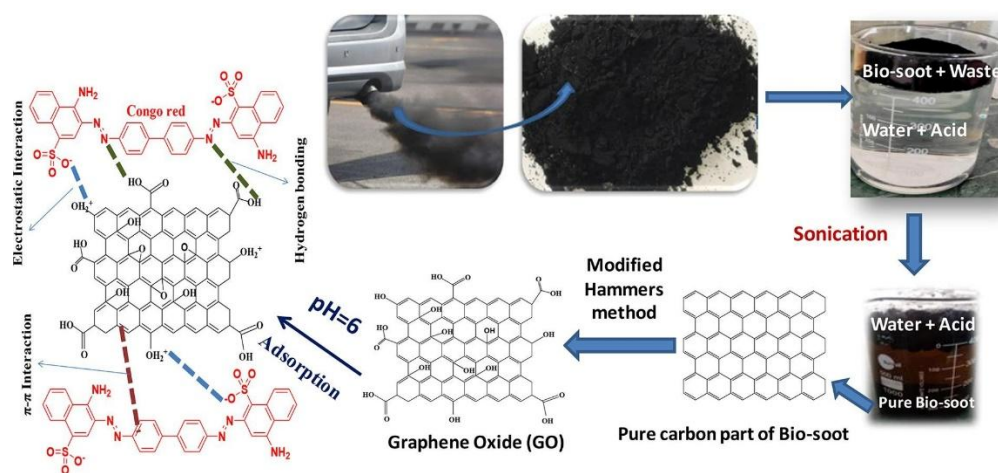


Figure 2.18 The schematic diagram of preparation of GO from bio-soot and its utilisation as an adsorbent [87].

In 2014, Akhavan and colleagues synthesised high-quality GO and rGO sheets using industrial carbonaceous and various natural residues as starting materials and investigated the electronic properties. Their findings revealed that the electrical resistance of both GO or rGO sheets remained consistent regardless of the starting materials utilised, with values of approximately $105 \text{ M}\Omega \text{ sq}^{-1}$ for GO and $1 \text{ M}\Omega \text{ sq}^{-1}$ for rGO sheets [55]. The most recent work by Bonnia et al. (2021) and Anuar et al. (2023) synthesised GO from scrap tyres. Despite this achievement, the practical applications of this synthesised GO have not been implemented yet. However, Tatrari and colleagues [119] used synthesised zinc-doped graphene spheres to supercapacitor application. These spheres were synthesised on a large scale using a cost-effective modified pyrolysis method. Density Functional Theory (DFT) analysis revealed a significant increase in the quantum capacitance of the graphene spheres, approximately 5.5 times higher than pristine graphene, upon zinc incorporation. The electrochemical performance of the supercapacitor device based on these zinc-doped spheres exhibited exceptional power density and energy density.

In 2022, Hassanin et al. prepared silica/GO composite from environmental solid waste and applied it for U(VI) sorption (Fig. 2.19). The SiO₂/GO adsorbent was derived from GO via the Hummers method using spent carbon rod batteries, while the silica component was sourced from rice husk. The study considered various factors influencing U(VI) sorption on SiO₂/GO, such as sorption time, pH, SiO₂/GO dosage, temperature, and concentration of U(VI) ions. The experimental data revealed that the U(VI) uptake capacity of SiO₂/GO is 145.0 mg/g at a pH of 4.0. Kinetic analysis aligned well with the pseudo second order model, and the sorption isotherm exhibited consistency with the Langmuir model. The sorption processes were found to be spontaneous, random, and exothermic in nature. Moreover, SiO₂/GO was effectively regenerated using 0.8 M H₂SO₄ and a 1:50 solid: liquid phase ratio after 60 min of agitation. Furthermore, seven cycles of sorption and elution confirmed the persistent effectiveness of SiO₂/GO in U(VI) adsorption from aqueous sources. In a separate study, Loudiki et al. (2022) employed a novel optimised approach to synthesise GO from carbon rods extracted from used (Zn/C) batteries for electrochemical applications. The electrochemical characteristics of the synthesised GO was assessed through cyclic voltammetry (CV) and current-voltage techniques. The findings indicate that sonication-based GO exhibits superior electrocatalytic properties compared to GO obtained through the standard Hummers method. Oxygen functionalities in GO allow for easy dispersal in organic solvents and water [48]. This unique property makes GO a valuable additive in ceramic and polymer manufacturing processes, enhancing their electrical and mechanical properties, including tensile strength, elasticity and conductivity [120, 121]. Furthermore, GO and its composites offer diverse applications in the fields of energy storage/conversion [5] and environmental protection [20]. These include applications in hydrogen storage materials [122], air pollutant removal [123], photocatalysis [124] for water splitting and purification, and electrode materials [125] for various supercapacitors and lithium batteries. Additionally, GO finds utility in the oil and gas industries as an additive for drilling fluid [126], cementing [127], enhanced oil recovery [128], desalination [18], oil spill clean-up [20], and emulsion stabilization [129]. It can also improve fluid loss control, lubrication, rheology, and shale stability [130]. The current body of literature on the applications of waste-derived GO is limited. Therefore, there are still many ways to use waste-based GO materials that have yet to be tried, offering exciting opportunities for the future.

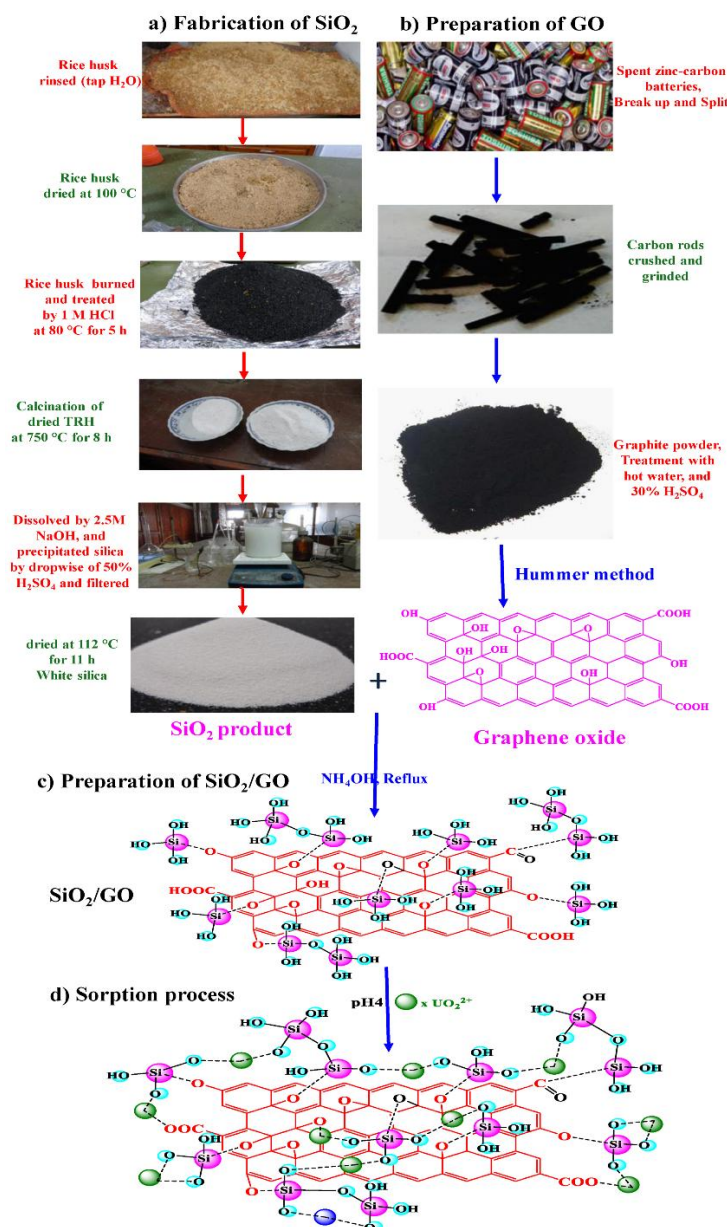


Figure 2.19 The schematic representation of a) silica synthesis from rice husk, b) GO synthesis from spent Zn-C batteries, c) SiO₂/GO synthesis, d) U(VI) sorption at SiO₂/GO [88].

2.7 Conclusions and Perspectives

This review has underscored the significance of innovative research in the synthesis of GO using diverse waste, including agricultural, industrial, and plastic, while also exploring their potential applications. An issue associated with graphite, especially highly pure graphite (HPG), as the main starting material of GO synthesis is its high cost. To overcome this challenge, it is worth considering the production of suitable and cost-effective graphitic materials derived from carbonaceous waste. Recent studies have proposed using agricultural residues such as coconut shells, sugarcane bagasse, orange peel, tea, oil palm and industrial wastes such as soot powders, scrap tyres and electronic scraps for GO synthesis. However, the choice of carbon precursor significantly influences key properties of the resulting GO. For instance, GO derived from

sugarcane bagasse exhibits enhanced hydrophilicity and superior water dispersibility due to the abundance of hydrophilic functional groups. Yet, challenges arise from unwanted elements, impurities, and contaminants in waste materials, necessitating pre-treatment processes for high-quality GO production. The utilisation of industrial residues for GO synthesis introduces notable impurities like Zn, and S that must be addressed before considering them as a viable raw material. Conversely, sugarcane bagasse and bio soot emerge as promising agricultural and industrial precursor for GO synthesis, displaying favourable characteristics compared to other alternatives.

While most efforts have revolved carbonising biomass or carbonaceous waste and utilising the Modified Hummers method for GO synthesis, only a few researchers have used the alternative routes. For instance, Optimal techniques, such as the SOMA-GO and direct ferric citrate pyrolysis have been used for synthesising GO from sugarcane bagasse. A comparative analysis has revealed that the Modified Hummers method exhibits significant limitations, including long synthesis time, complex separation and purification steps, high toxicity, limited environmental friendliness, excessive oxidant use, and scalability issues. In contrast, the pyrolysis and catalytic processes are straightforward, rapid, reliable, efficient, cost-effective, and eco-friendly alternatives. However, there needs to be more exploration of GO synthesis utilising exclusive pyrolysis techniques, especially microwave assisted. Microwave-assisted pyrolysis offers distinct advantages, including enhanced efficiency, rapidity, simplicity, and cost-effectiveness. This approach represents a promising avenue for advancing GO synthesis methods, emphasizing the need for further exploration.

The practical utility of these materials remains somewhat limited compared to conventional GO and are mainly focused on water purification and biomedical. However, the widespread application of GO derived from waste materials still needs to be improved, leaving opportunities for further exploration in areas such as composite material, solar cells, cementing and desalination. It is crucial to standardise the characteristics and sources of the carbon precursors, as well as the methods used, to produce GO with optimal properties while maintaining eco-friendliness. Reproducing waste materials into GO is a critical challenge, requiring a comprehensive optimisation of method variables and techniques to control the quality, size, and morphology of produced GO. Integrating improved morphological properties into scalable and affordable procedures is essential for advancing the field. While research has explored waste precursors, none have transitioned into commercially viable products. Future investigations are anticipated to focus on developing sustainable and scalable methods for the mass production of GO. To secure sustainable production, it is imperative to select starting materials and processes based on life cycle assessments and economic analyses. This might produce more waste-based GO and uncover novel applications in emerging technologies.

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Chapter 3

Synthesis and Characterisation of Tyre Char-based Graphene Oxide

Chapter 3 explores the synthesis and characterisation of GO derived from tyre char (TC), demonstrating the feasibility of producing GO from waste tyres as a sustainable approach. It details a two-step microwave-assisted pyrolysis process, followed by chemical treatments that enhance efficiency and minimise environmental impact. Advanced analytical techniques are used to characterise the synthesised GO, highlighting its structural and chemical properties. Overall, this chapter introduces novel, sustainable methods for converting tyre waste into valuable GO.

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Abstract

Every year, approximately one billion used tyres accumulate globally, posing significant environmental and economic challenges. Managing this waste sustainably has proven difficult, while traditional methods for producing graphene oxide (GO) from natural or synthetic graphite face limitations such as high costs, scarcity, and environmental impact. To address these issues, this study investigates the conversion of scrap tyres into GO using a two-step microwave pyrolysis process, offering a sustainable alternative for GO production. The process involves microwave pyrolysis of waste tyres with ferric chloride (FeCl_3) as a catalyst, followed by concentrated sulfuric acid (H_2SO_4) treatment. Microwave irradiation is highlighted for its rapid, energy-efficient heating of microwave-absorbing materials. The resulting tyre char-based GO (TC-GO) was characterised using X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). TC-GO exhibited a sheet-like morphology, with a crystalline size of 26.09 nm. Raman analysis showed distinct D (1344 cm^{-1}) and G (1590 cm^{-1}) bands with an I_D/I_G ratio of 0.99, indicating a graphitic structure. XPS confirmed a carbon content of 54.81% and oxygen at 28.52%, while SEM and TEM revealed disordered, overlapping sheets with wrinkled edges, consistent with poor crystallinity from SAED patterns. All these results were compared with the tyre char (TC). This study demonstrates the feasibility of producing GO from tyre char, offering significant potential for cost reduction in GO production. The use of microwave irradiation underscores the environmental and operational advantages of the method. The TC-GO produced is promising for diverse applications, including composite materials and as an additive in the cement industry, providing a practical solution for waste tyre management and advancing GO-based technologies.

Keywords

Microwave-assisted Pyrolysis; Scrap tyres; Tyre-char; Graphene Oxide

3.1 Introduction

The quantity of scrap tyres generated globally continues to grow every year. In 2020, around 20 million tons of waste tyres were produced, and it is estimated that this amount could rise to 1.2 billion tons by the late 2030 [1]. The most common waste tyres disposal methods, including landfilling and open burning, pose significant environmental and waste management challenges. Tyres are bulky, non-biodegradable, and highly flammable, and they can endure various environmental and mechanical stresses, making their disposal difficult. To address these challenges, researchers have been investigating effective and economical methods for recycling waste tyres and reusing them. Among these methods, pyrolysis technology has emerged as one of the most promising approaches for recycling waste tyres [2, 3].

Pyrolysis is a thermal method that decomposes organic compounds and volatile plasticisers at specific temperatures, depending on the feedstock, in the absence of oxygen. During pyrolysis, waste tyre rubber can produce pyrolytic oil, gas, and tyre char [4]. Pyrolytic oil can be utilised as a direct fuel source or be blended with petroleum refinery feedstock. The non-condensable gas, which has a heating value comparable to natural gas, is also suitable as a fuel. Additionally, tyre char can be used as a smokeless fuel or as a precursor for carbon-based materials [5]. Various heating technologies can be used for pyrolysis, and among them, microwave (MW) technology stands out for its capacity to rapidly and directly heat materials that absorb microwaves. Tyres, which contain up to 30 wt.% carbon black, are excellent MW absorbers, enhancing the pyrolysis process and increasing char yield [6]. This makes MW pyrolysis a particularly efficient and promising method for recycling waste tyre rubber.

Graphene oxide (GO) exhibits exceptional chemical and physical properties, making it highly applicable in diverse technological fields, including electronics [7], biomedicine [8], energy [9], construction [10] and environmental applications [11]. Graphene oxide (GO) is a two-dimensional carbon material derived from a single layer of graphite oxide. It features a polyaromatic structure and is characterised by oxygenated functional groups like hydroxyl (-OH), carbonyl (C=O), and epoxy (C-O) groups located on its basal planes and edges. This configuration creates a hybrid structure that incorporates both sp^3 and sp^2 hybridised carbon atoms [12]. During GO synthesis, the oxidation process introduces structural defects, giving GO distinct physical properties compared to pure graphene. Additionally, the surface of GO has exhibited a significant hydrophilic nature. The key benefits of GO are its single-layer thickness, low toxicity, flexibility, high mechanical strength, and the potential for chemical functionalisation [12].

Over time, oxidative-exfoliation chemical methods have been established for synthesising GO. These comprise the methods of Brodie (1859) [13], Staudenmaier (1898) [14], Hofmann (1937) [15], Hummers (1958) [16], Tours method (2010) [17], and Modified and

Improved Hummers method (2013) [17]. Some limitations of these methods include the use of oxidising agents, lengthy reaction times, the production of harmful gases and inorganic salt residues, high levels of hazard, and low overall yield. Recently, numerous studies have focused on modifying these methods, particularly the Hummers method, to synthesise graphene oxide (GO) from graphite. However, both natural and synthetic sources of graphite present various challenges.

Natural graphite is costly, and processing of synthetic graphite requires extremely high temperatures. Considering these limitations, biomass and carbon-rich waste materials present viable alternatives for producing nanostructured carbon materials [18]. Studies have shown that Agro- waste resources such as coconut shells power [19], sugarcane bagasse [20, 21], tea leaves [22], coffee [23], and industrial bio-shoot [24] can be converted into GO.

Anuar [25] and Bonnia [26] have conducted GO synthesis from carbon scrap tyres using the Modified Hummers method. In contrast, this study focuses on using scrap tyre rubber as a precursor for Go preparation via the microwave pyrolysis technique. Compared to the Hummers method, microwave-assisted synthesis offers advantages such as higher efficiency, cost-effectiveness and environmental benefits. Scrap tyres are converted into GO through a two-step microwave pyrolysis process, using Ferric chloride, followed by treatment with concentrated H_2SO_4 . The precursor (tyre rubber) and synthesised TC-GO are analysed and compared using different characterisation techniques, including X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM).

3.2 Experimental

3.2.1 Materials and Reagents

For the production of TC-GO, scrap tyres were collected from Mycar Tyre & Auto, Townsville. Ferric Chloride ($FeCl_3$), Conc. Sulfuric acid (H_2SO_4 , 95%), Hydrochloric acid (HCl, 95%) and ethanol (C_2H_5OH , 95 %) were purchased from Sigma-Aldrich, Australia. All the chemicals were used as received.

3.2.2 Tyre Char Production

The microwave-assisted pyrolysis process involves converting scrap tyres into three by-products: tyre char, tyre oil and gas, through volumetric heating. Fig. 3.1 shows the custom-designed microwave-assisted pyrolysis system used in this study. The system includes a nitrogen gas (N_2) flow controller ($4L\ min^{-1}$) (a) that ensures an inert atmosphere throughout the experiments, and a custom-designed chamber (b) for placing the feedstocks (tyre pieces) are placed. The system includes a 3-kW microwave producer (d), linked to both a manual tuner (c) and a control unit (e). Cooling is managed by a recirculating water chiller (f), while a series of

condensers (h) collect the liquid (g) and gaseous by-products. At the end of the flask connection, a vacuum pump (i) maintains a negative pressure range of 50 to 80 kPa throughout the experiments.

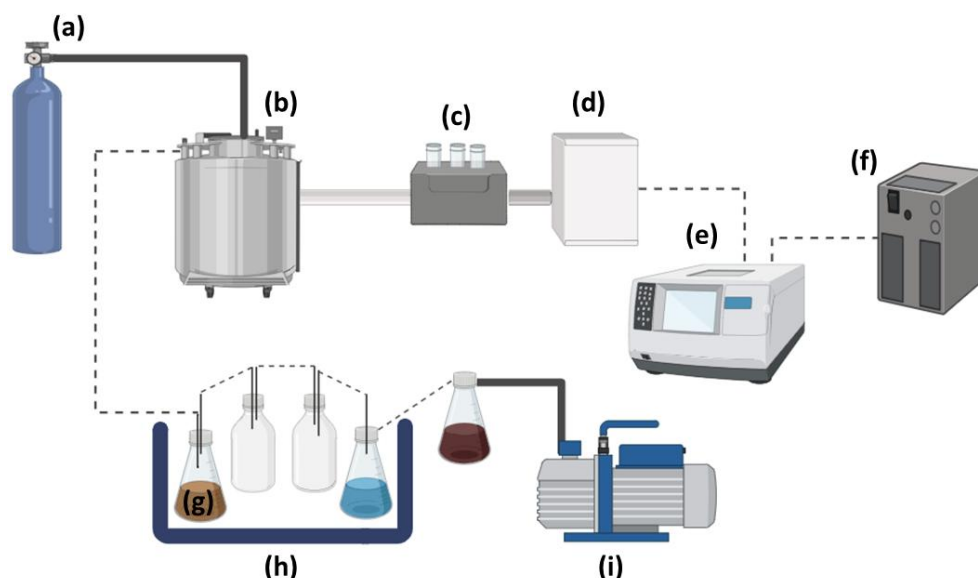


Figure 3.1 Microwave-assisted pyrolysis setup used for the tyre char production (a) N₂ cylinder (b) Custom-made chamber (c) Manual tuner (d) Microwave generator (e) Microwave controller (f) Recirculation water chillier (h) Condensers (g) Oil collector (i) Vacuum pump.

The collected scrap tyres were initially washed with an ordinary detergent solution, followed by rinsing with tap water. The tyre rubber was then chopped into small square fragments measuring approximately 1 cm × 1 cm. Around 100 g of these fragments were placed into a microwave camber. The tyre fragments were subjected to two phases of microwave power: first 0.8 Kw for 15 minutes, followed by 1.0 Kw for 45 minutes, completing a total of 1 h of the pyrolysis process. To enhance the heating efficiency, activated carbon was used as a microwave susceptor and was added at a 10% of feedstock weight.

Within the chamber, higher aliphatic hydrocarbons are released as fuels, while lower hydrocarbons are emitted as biogas. The remaining material inside the chamber is collected as char. The TC was treated with diluted HCl acid to eliminate contaminants and impurities. Subsequently, the char underwent a several-step washing process using distilled H₂O until the pH reached 7. Finally, the sample was dried in an oven at 105 °C to obtain the tyre char.

3.2.3 Synthesis of Tyre Char Derived GO

The previously obtained tyre char and the desired amount of FeCl_3 (1:1 ratio of tyre char: FeCl_3) were combined in distilled H_2O to make a suspension. This suspension was then sonicated for approximately 10 minutes using an ultrasonic sonicator. The yellow-coloured solution was subsequently evaporated in an oven at 80°C for 24 hours, resulting in a black solid. The black solid was subjected to a second microwave pyrolysis process: 0.8 Kw for 15 minutes, followed by 1.0 kW for 30 minutes, completing a total 45 minutes of pyrolysis. After cooling the chamber, the FeCl_3 -treated sample was collected and rinsed with diluted HCl and distilled H_2O . The oven-dried sample was then treated with conc. H_2SO_4 at 70°C while stirring at 250 rpm for an hour. Following this, the mixture was left undisturbed at the same temperature for an additional 1 h. Once the reaction was completed, the mixture was diluted with distilled H_2O to decrease the H_2SO_4 concentration. The solution was decanted, and the resulting product was thoroughly washed with ethanol and distilled H_2O . Finally, the material was dried in an oven at 105°C to remove any remaining moisture. The obtained final product was then subjected to various characterisation techniques.

3.2.4 Characterisation

X-ray diffraction (XRD) patterns were obtained with a Bruker D2 Phaser X-ray diffractometer with Cu-K α radiation ($\lambda = 0.15406\text{ nm}$) at a scanning rate of 8° per minute. Scanning was performed over a 2θ range from 5° to 80° . Raman spectrum was recorded with WITec Raman spectrometer using a 532 nm laser at room temperature. The scans were conducted across a broad range of 100 to 4000 cm^{-1} . The material was sonicated in ethanol and then deposited onto a silicon wafer prior to analysis.

X-ray photoelectron spectroscopy (XPS) data were obtained using a Kratos Axis Ultra XPS with an Al K α X-ray source. Binding energies were calibrated to the C1s peak at 284.8 eV from incidental carbon. Scanning electron microscopy (SEM) examinations were performed with a Hitachi SU 5000 scanning electron microscope operating at 15 kV. Before observation, the samples were coated with a thin layer of platinum through a spray-coating process. The EDS analysis was conducted using the Oxford Instruments X-MaxN detector.

Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were received using a JEOL 2100F microscope operating at an accelerating voltage of 200 kV. For TEM analysis, the sample was dispersed in ethanol through sonication and deposited onto an amorphous carbon film on a copper grid.

3.3 Results and Discussion

Scrap tyres mainly consist of rubber, carbon black, textiles, metals, and additives such as silica, and vulcanisation agents. The composition of the rubber in tyres can vary. For this study, medium vehicle tyres (MVT), which contain a high proportion of styrene-butadiene rubber (SBR) [27], were used. These tyre rubbers were converted to tyre char, oil and gas through pyrolysis [28]. Microwave pyrolysis method does not need any pretreatment process of the tyres, even grinding and crushing; the tyres were simply washed and cut into pieces for this experiment. The tyre pieces were converted into tyre char in the first MW pyrolysis phase at 0.8 Kw for 15 minutes, followed by 1.0 kW for 45 min, completing 1 h of the pyrolysis process. To enhance the heating process, activated carbon was used as a microwave susceptor, and was added at 10% of feedstock weight. The resulting solid product was an odorless black powder, indicating that the material had been fully pyrolysed. At 1.0 kW of MW power, the product yield was 37.88 wt. % tyre char, 10.58 wt. % oil, and 51.54 wt. % gas. The TC was then washed with diluted HCl to remove contaminants and impurities. Subsequently, a several washing process with distilled water was used until the pH of the wash water reached 7. Finally, the sample was oven-dried at 105 °C to obtain the tyre char. The tyre char and the FeCl₃ (1:1 ratio) were combined in distilled H₂O to make a suspension. To better disperse char into the FeCl₃ solution, ultrasonication was used. Then the solvent was evaporated at 105 °C in air and form the layered crystal structure during the recrystallisation process.

The two-step microwave pyrolysis process, while involving sequential heating, cooling, and chemical treatment, was selected for its unique advantages in efficiency, sustainability, and material performance. Unlike conventional methods such as the Hummers process, which relies on natural graphite and produces large volumes of chemical waste, this approach utilizes waste tyres as a carbon source, promoting a circular economy and reducing environmental impact. Additionally, microwave-assisted pyrolysis significantly enhances energy efficiency by enabling rapid heating, reducing processing time, and minimizing energy consumption compared to traditional thermal methods. Although the process has multiple steps, it allows better control over how tyre char transforms into GO, which can lead to improved material properties. Furthermore, ongoing optimisation efforts, such as refining reaction conditions and exploring scalable adaptations, can enhance the cost-effectiveness of this method.

3.3.1 Mechanism of Two-Stage Microwave Pyrolysis for Synthesising TC-GO

In this study, the iron precursor (Fe³⁺) infiltrated the pores of the carbon material. During the second pyrolysis stage (0.8 Kw for 15 minutes, followed by 1.0 Kw for 30 minutes), Ferric (III) chloride facilitated the formation of graphene-like materials through templating and carburisation [29]. The Fe³⁺ ions interact with the tyre char, and Fe³⁺ ions penetrate the carbon atoms of the precursor, creating a compact Fe₃C layer. Subsequently, carbon atoms in Fe₃C are

released, transforming the material into alpha-Fe. The out-diffused carbon atoms accumulate on the surface of the iron-based template, initiating the nucleation and expansion of a dense, graphene-like 2D carbon layer. Due to the significant Fe content from the catalyst, carbon growth is restricted within the 2D plane as a result of the template effect [21]. The quality of the graphene produced depends on factors such as the precursor type, type of catalyst, rate of the inert gas flow, duration of the reaction, and pressure in the microwave environment, as these conditions influence the activation energy for graphene nucleation on the catalyst surface. The carbonised graphene-like material is converted into GO by reacting with a strong oxidising agent such as conc. H_2SO_4 at 70 °C. The strong acid damages the graphitic structure of graphene, with sulfuric acid penetrating between the graphene layers and reacting rapidly with carbon atoms to form GO.

The synthesis mechanism of TC-GO from scrap tyres is illustrated in Fig. 3.2. Compared to the Modified Hummers method commonly used for GO synthesis from graphite, this method is more efficient, effective, cost-effective, and environmentally friendly.

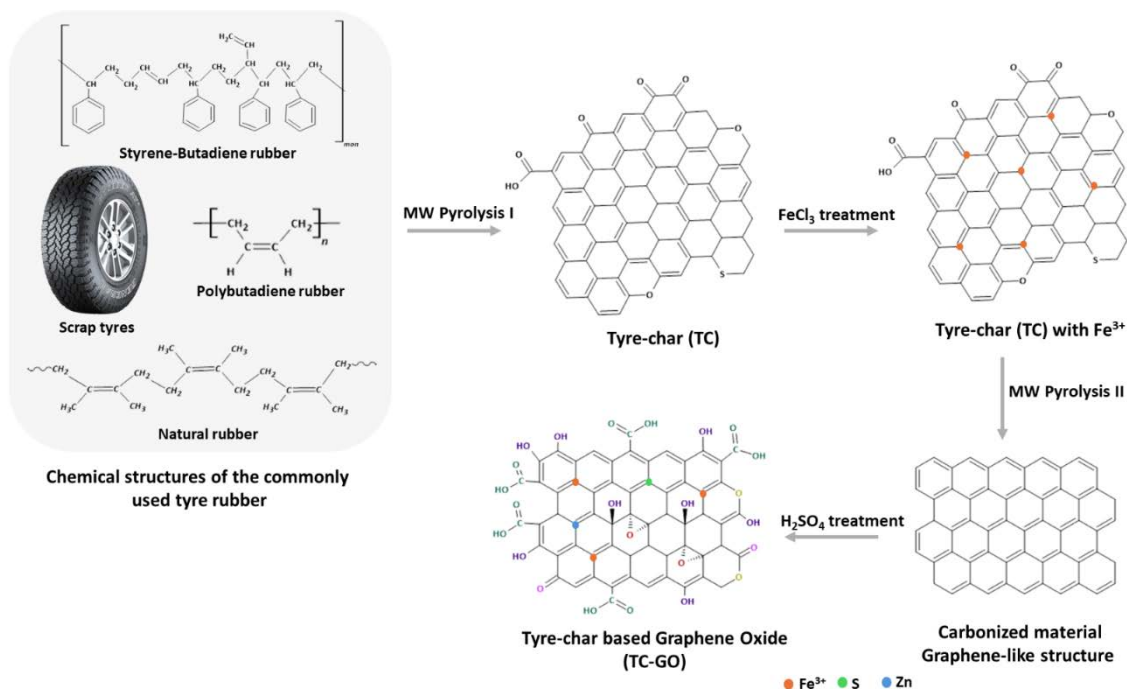


Figure 3.2 Mechanism of TC-GO synthesis from scrap-tyres using two stages of MW pyrolysis.

3.3.2 Characterization of Tyre Char and Tyre Char-Derived GO

3.3.2.1 X-ray Diffraction

X-ray diffraction (XRD) analysis is used to characterise the crystalline structure and interlayer spacing of the material. The interlayer spacing of TC and TC-GO was calculated based on the Bragg equation: $2d\sin\theta = n\lambda$, where d represents the interlayer spacing, θ refers the scattering angle, n denotes order of diffraction, and λ is the X-ray wavelength corresponding to Cu-K α radiation ($\lambda = 0.15406$ nm). Furthermore, the crystallite size ($\text{\AA}$) of tire char-derived GO

was calculated using the Debye-Scherrer equation: $n\lambda/\beta\cos\theta$. In this formula, n specifies the diffraction order, λ stands for the X-ray wavelength, β is the full width at half maximum (FWHM) of the XRD peak, and θ represents the scattering angle.

The XRD patterns of both TC and TC-GO are displayed in Fig. 3.3 that exhibits distinct peaks within the 2θ range of 5 to 80° . As shown in Fig. 3.3(a), the broad peak near $2\theta \sim 25.5^\circ$ indicates a lack of significant order in the bulk of the carbon materials, particularly related to the (002) plane [30], confirming the poorly crystalline nature of TC. The crystalline phases identified in TC include zinc sulfides sphalerite (β -ZnS), and wurtzite (α -ZnS) forms, consistent with previous studies on chars derived from tyre pyrolysis [31]. The generation of ZnS results from the reaction between H_2S and ZnO. H_2S is formed during thermolysis as a byproduct of the decomposition of sulfur compounds utilized in tire manufacturing, whereas ZnO serves as a raw material in tyre production [31].

In contrast, the XRD pattern of GO synthesised from TC, shown in Fig. 3.3(b), exhibits a strong peak at 9.8° (001), a broad peak at 25° (002) and a weak peak at 43° (100) [24, 32]. The intense peak at 9.8° is associated with an interlayer spacing of 0.90 nm, suggesting the presence of oxygen-containing intercalation groups within the graphitic layers [24]. Previous studies on GO synthesis have reported a diffraction peak shift from 26° to 11° , with an interlayer spacing change from 0.334 nm to 1.09 nm, due to the complete oxidation of graphite [33, 34]. The broader peak at 25° suggests a persistent poorly crystalline nature of the precursor used for synthesis [19]. The crystallite size of the peak at 9.8° of TC-GO (001) was determined to be 26.09 nm using Scherrer's equation. This XRD analysis confirms that TC contains bulk material as graphite carbon, while the XRD pattern of TC-GO shows GO formation with the presence of its amorphous precursor material and a reduced GO phase. The formation of rGO may result from the use of amorphous material and variations in oxidation levels throughout the synthesis process.

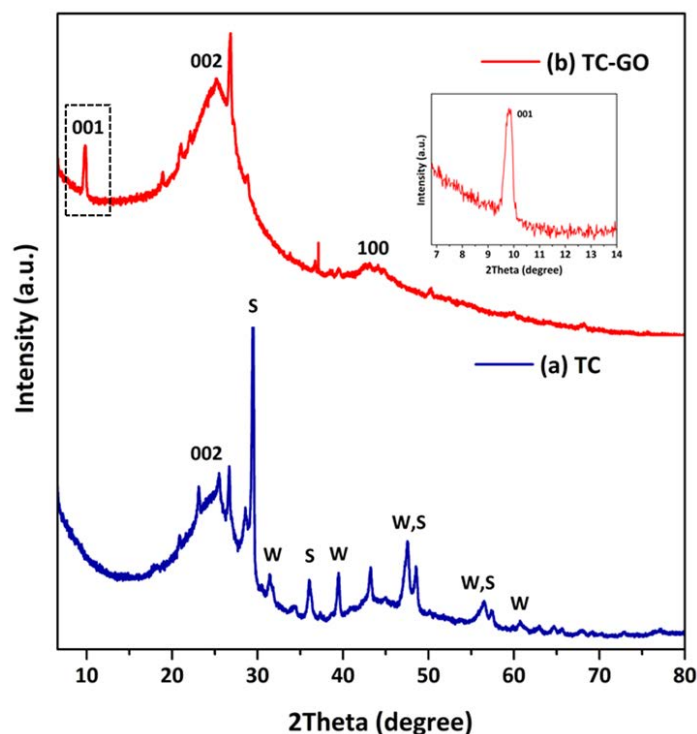


Figure 3.3 X-ray diffraction (XRD) patterns of (a) TC and (b) TC-GO (S = sphalerite (β -ZnS); W = wurtzite (α -ZnS)).

3.3.2.2 Raman spectroscopy

Raman spectroscopy is a prominent non-destructive technique for characterising graphene-based materials, providing valuable insights into their structures, as well as their ordered and disordered configurations. The detection of the D, G, and 2D bands, associated with in-plane and out-of-plane vibrations, validates the presence of the graphitic structure within the carbon framework [35]. Raman spectra of TC and TC-GO, shown in Fig. 3.4, reveal two prominent bands associated with defects (D-band) and graphitic (G-band) carbon. Both spectra exhibit a significant G-band, indicating the presence of graphite layers, appearing at 1586 cm^{-1} for TC and 1590 cm^{-1} for TC-GO. This G band reflects the in-plane vibrations of sp^2 orbitals [36]. Additionally, a distinct defect band (D-band) is observed around 1342 cm^{-1} for TC and 1344 cm^{-1} for TC-GO, signifying inherent disorders within the graphitic structure [37]. It is observed that both the shape and position of the D peak shift as the thickness of GO varies [38]. Specifically, a blue shift is noted with a reduction in the thickness of TC-GO. The intense D band in TC-GO results from structural irregularities introduced by oxygenated groups bonding to the six-membered carbon basal planes [39].

The intensity ratio of the defect band to the graphitic band (I_D/I_G) serves as an indicator of structural disorder, with a higher ratio indicating a greater number of defects [36]. For TC, the calculated (I_D/I_G) ratio is 0.88, suggesting relatively fewer disorders and a more ordered graphitic structure [36]. In contrast, TC-GO exhibits an I_D/I_G ratio of 0.99, indicating a higher number of

defects due to the attachment of functional groups such as hydroxyl and epoxy on the C skeleton [39].

Furthermore, the Raman spectrum of TC reveals a broad 2D band (G'), which is characteristic of a graphene-like structure in the tyre carbon. The shape and intensity of the 2D band are indicative of the number of graphene layers [40]. In the TC-GO spectrum, the presence of a 2D band and a D+D' band at 2700 cm^{-1} and 2930 cm^{-1} , respectively, indicates defect-activated combination of phonons [41]. The broadening of the 2D band in both spectra is attributed to the presence of few layers with some defects in TC and TC-GO. The intensity ratio of the 2D band to the G band (I_{2D}/I_G) is used to characterise the number of graphene layers [37]. The calculated I_{2D}/I_G values are 0.67 for TC and 0.80 for TC-GO, indicating the presence of a few layers in both samples. This comprehensive Raman spectra analysis confirms the graphitic nature of the tyre char and validates the preparation of GO from tyre char.

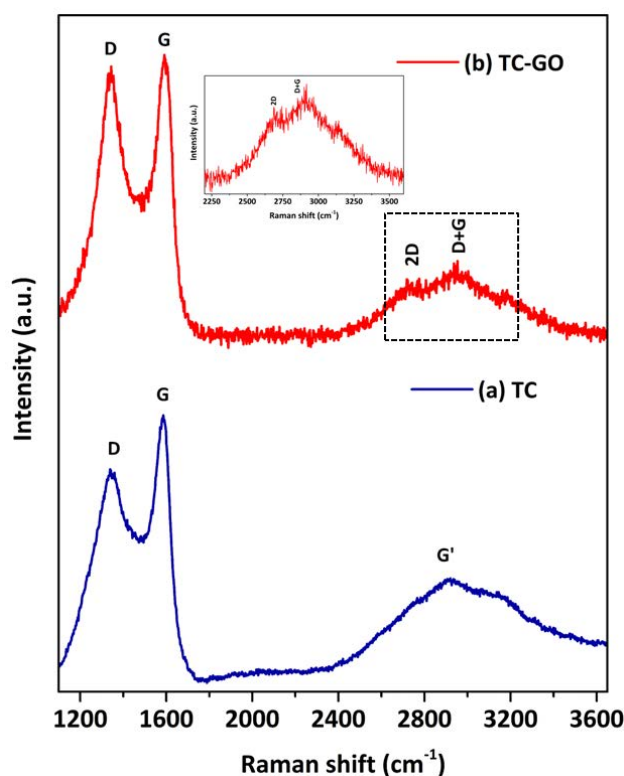


Figure 3.4 Raman spectra of (a) TC and (b) TC-GO.

3.3.2.3 XPS Analysis

Further, the TC and TC-GO samples were analysed using X-ray photoelectron spectroscopy (XPS) to assess the chemical states of different surface elements and identify functional groups. The survey scan spectra indicated that carbon and oxygen were the predominant elements on the surfaces of both samples, along with small quantities of sulfur and zinc, which were likely introduced during the processing [42].

The XPS spectra for TC and TC-GO are shown in Fig. 3.5(I). For TC, the surface composition was primarily carbon (76.84%), followed by oxygen (16.56%). In contrast, TC-GO had a surface composition of carbon (54.81 %) and oxygen (28.52%). The deconvoluted high resolution XPS C 1s spectra of TC and TC-GO are displayed in Fig. 3.5(II). The deconvoluted C 1s peaks for TC, shown in Fig. 3.5(II)-a, shows peak binding energies of 284.5, 285.2, 286.9 and 291.1 eV which correspond to Sp^2 C (41.85 at. %), Sp^3 C (40.44 at. %), C-O (5.36 at. %), and $\pi-\pi^*$ satellite bonds, respectively. For TC-GO, the deconvoluted C 1s peaks, shown in Fig. 3.5(II)-B, have binding energies of 284.4, 285.4, 286.8, 289.1 and 291.1 eV, assigned to Sp^2 C (34.06 at. %), Sp^3 C (38.92 at. %), C-O (16.60 at. %), O-C=O (10.43 at. %), and $\pi-\pi^*$ satellite groups, respectively.

Fig. 3.5(I) also shows high-resolution XPS spectra of O 1s region for both TC and TC-GO. The deconvoluted O 1s peaks for TC, shown in Fig. 3.5(III)-a, have binding energies of 532.5, and 533.9 eV, representing C-OH (37.84 at. %), and C-O-C (62.16 at. %), respectively. For TC-GO, the deconvoluted O 1s peaks in Fig. 3.5(III)-b have binding energies of 531.5, 532.6, and 533.9 eV represent the O-C=O (24.92 at. %), C-OH (30.90 at. %) and C-O-C (44.18 at. %), groups, respectively,

The carbon-to-oxygen atomic ratio (C/O) measured by XPS was determined to be 4.64 for TC and 1.92 for TC-GO. This analysis indicates a significant increase in the atomic concentration of oxygen-containing groups, such as carboxyl and carbonyl groups, in TC-GO compared to TC, suggesting that the surface of TC-GO is more hydrophilic.

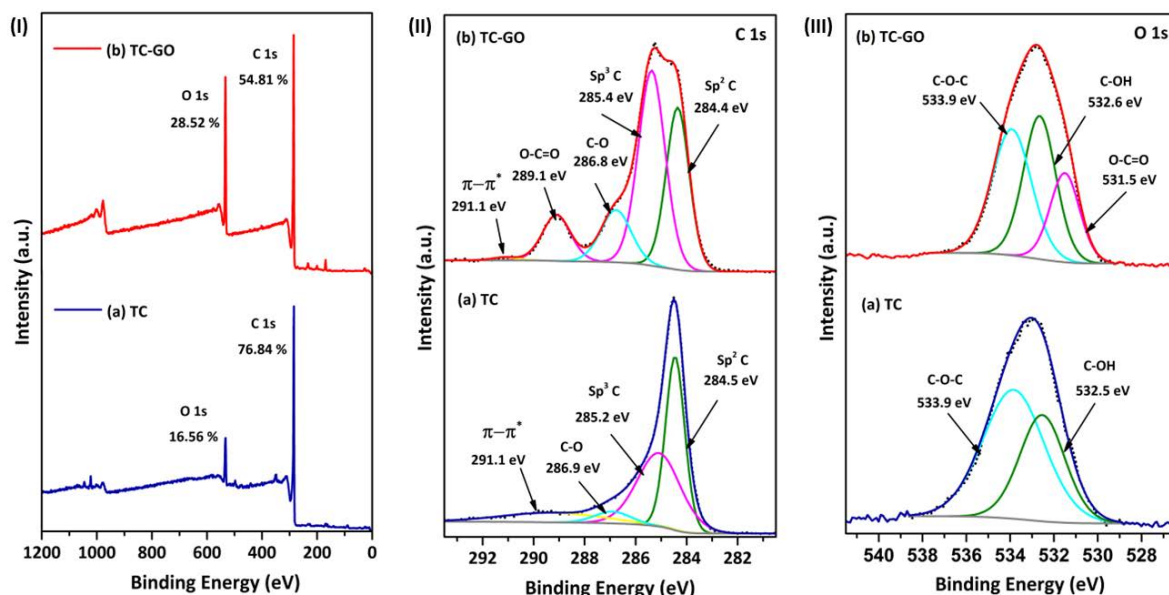


Figure 3.5 (I) The wide scan XPS spectrum of (a) TC and (b) TC-GO, (II) core level high resolution C1s spectra of (a) TC and (b) TC-GO, (III) core level high resolution O1s spectra of (a) TC and (b) TC-GO.

3.3.2.4 SEM and EDX Analysis

The surface properties of TC and TC-GO were examined using SEM. As illustrated in Fig. 3.6(a), the TC exhibits an aggregation of smaller particles to form a bigger particle. The surface is characterised by a granular texture with an irregular size distribution, roughness, irregular shape, and smaller pore sizes. Bright spots and large dark areas are visible in the backscattered electron image of the char, as depicted in Fig. 3.6(b). These varying brightness levels correlate with different metal distributions within the sample, as brighter areas indicate the presence of heavier elements [43].

The EDX revealed in Fig. 3.6(c) the presence of various metal particles, including zinc, calcium, sulfur and silicon on the surface. This is confirmed for bright spot in backscattered electron image showed higher amounts of metals than dark spots. These metals may also contribute to the binding of smaller char particles. Additionally, sulfur appears to promote agglomeration and can cause pore blockage [36]. The observed oxygen is likely attributed to inorganic compounds like ZnO or silicates.

The average particle size is approximately 275 μm , consisting of a significant number of larger diameter particles, with some exceeding 500 μm in size. This size distribution suggests that nano-sized particles in the tyre char aggregate to form larger micro-sized particles [4].

Compared to the morphology of TC, the SEM images of TC-GO in Fig. 3.6(d-e) revealed that it has a disordered solid of in-distinctly aggregated, thin, closely associated, and highly overlapping sheet structures. The wrinkling observed in TC-GO is attributed to interactions between oxygen-containing functional groups [44]. The EDX results obtained for the TC- GO sample are presented in Fig. 3.6(f), where the atomic percentage of C and O were 79.69 and 15.89%. These values are lower for carbon and higher for oxygen compared to TC, where the carbon content is greater, and the oxygen content is lower. The impurities identified in the EDX results are not apparent in the XRD analysis of TC-GO, as XRD primarily concentrates on examining the crystal structure and matching it with known structural databases [19].

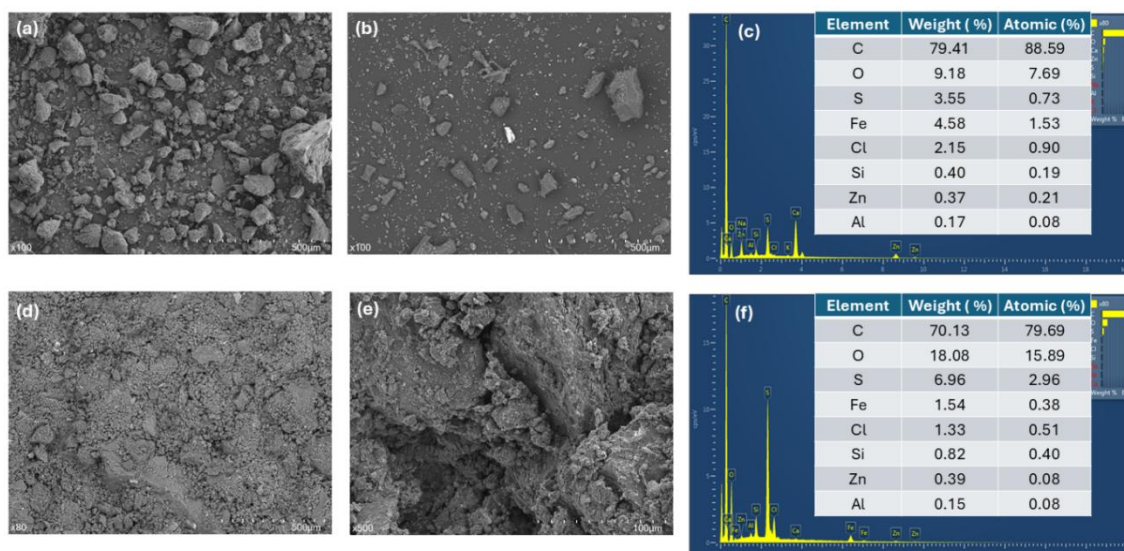


Figure 3.6 SEM images of TC (a-b) and TC-GO (d-e), the EDX analysis of TC (c) and TC-GO (f).

3.3.2.5 TEM Analysis

TEM micrographs in Fig. 3.7 (a) showed the TC primarily consists of nearly nanosized spherical particles measuring less than 100 nm, though there is a broad distribution of particle sizes. TEM images of TC-GO are shown in Fig. 3.7. It naturally exhibits sheet-like structures with wrinkled, transparent edges typical of carbon layers [21].

GO sheets appear to be agglomerated, because of the presence of strong π - π interactions [45]. It also contains various chemically reactive functional groups, including carboxyl, epoxy and hydroxyl groups, located on its basal planes. The TC-GO sample shows reduced transparency due to its multiple layers. However, as the oxidation level increases, the sample becomes significantly more transparent. This increased transparency results from a higher concentration of oxygen-containing functional groups, making it well-suited for exfoliation into monolayers or only a few layers of GO. The selected area electron diffraction (SAED) pattern of the TC-GO sample exhibits a characteristic ring pattern, reflecting its polycrystalline nature. These ring formations result from the overlapping of diffraction spots, which is attributed to the increased number of layers in the samples. The crystallinity of graphene oxide (GO) sheets, assessed using the SAED technique, showed diffused concentric diffraction rings, indicating that the material has low crystallinity, which aligns with the XRD findings. This analysis confirms that the synthesised GO exhibits a semi-amorphous structure, consistent with previous research. [21]. The amorphous region in GO arose from the formation of multiple sp^3 carbon atoms during the oxidation process [46].

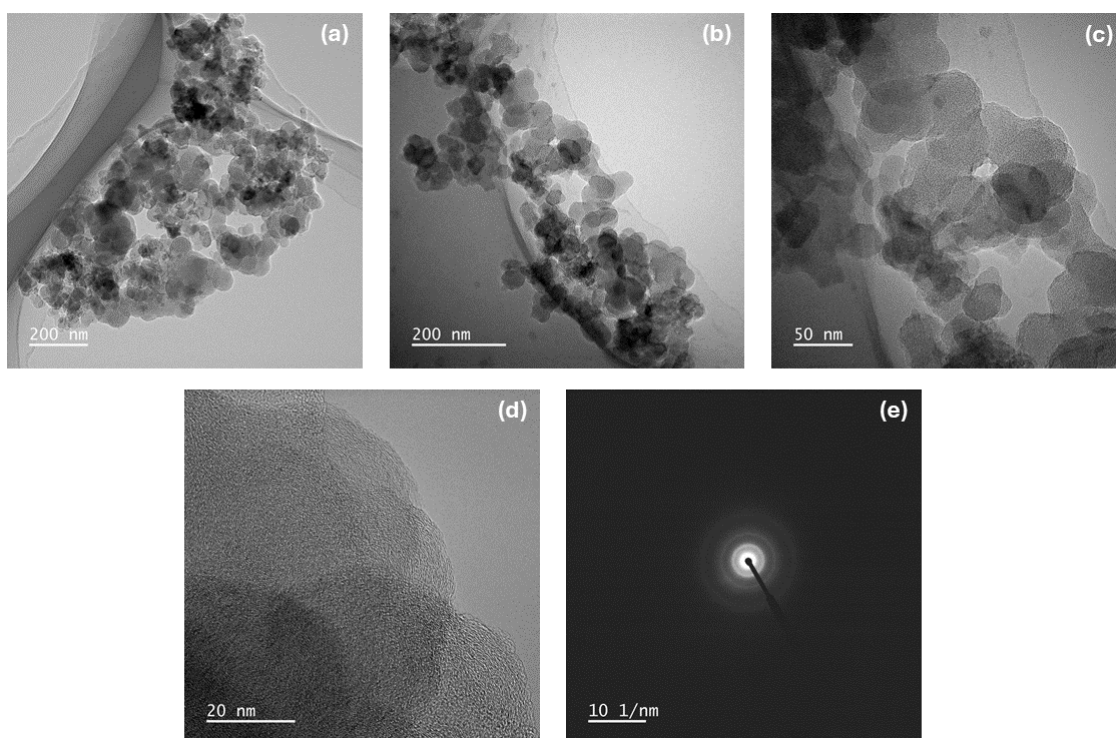


Figure 3.7 TEM images of (a) TC (b-c) TC-GO, (d) HRTEM image of TC-GO, (e) SAED pattern of TC-GO.

3.4 Conclusions

In summary, TC was converted into TC-GO using a two-step pyrolysis process with ferric chloride as a catalyst, followed by H_2SO_4 acid treatment. This method, compared to traditional approaches such as the Hummers method, proved to be simpler, faster, cost-effective, and environmentally friendly. The XRD analysis confirmed the successful formation of GO from TC, revealing the presence of both amorphous precursor material and a reduced GO phase. Raman spectroscopy further validated the graphitic nature of the tyre char and the conversion process to GO. The atomic ratio of carbon to oxygen (C/O), determined by XPS, decreased from 4.64 for TC to 1.92 for TC-GO. This significant reduction in the C/O ratio indicates a substantial increase in the concentration of oxygen-containing functional groups, such as carbonyl and carboxyl groups, making the surface of TC-GO more hydrophilic. The SEM and EDX revealed that TC-GO consists of disordered, thin, closely associated, and highly overlapping sheet structures. The atomic percentages of carbon and oxygen in TC-GO were 79.69% and 15.89%, respectively. The SAED patterns showed a polycrystalline nature. The study highlights the critical role of FeCl_3 as both a catalyst and template in producing high-quality graphene. The use of ultrasonication was necessary to overcome the challenge of poor compatibility between TC and aqueous iron salt solutions. Future research should explore the synthesis of GO from various biomass waste materials using different conditions and catalysts to further enhance understanding and optimise the process.

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Chapter 4

Tyre Char Derived Graphene Oxide Impact on Cement Mortar

This chapter examines the application of synthesised tyre char-based graphene oxide (GO) in cement mortar to assess its mechanical properties and microstructural characteristics. It includes tests for compressive and flexural strength, comparing the results with both tyre char-based and control cement mortars. The findings underscore the potential of tyre char-based GO to enhance the properties of cement.

This chapter is currently under review in the journal as Silva WCH, Jacob MV, Tuladhar R. *Tyre-Char Derived Graphene Oxide Impact on Cement Mortar: A Study of Mechanical and Microstructural Characteristics*.

Abstract

The incorporation of Graphene Oxide (GO) nanomaterial into cement has gained significant attention due to its potential to enhance mechanical and microstructural properties. However, due to the high cost of commercial GO, attention has shifted towards producing GO from waste materials. Therefore, this study investigates the synthesis of GO from tyre char (TC) and its application in improving the mechanical and microstructural properties of cement mortar. Discarded tyres present significant environmental challenges, highlighting the necessity for efficient recycling. Tyre char, a byproduct of tyre pyrolysis, contains carbonaceous components suitable for conversion into GO. Microwave-assisted pyrolysis (MAP) is used as the preferred method, offering efficiency, effectiveness, and minimal environmental impact. The MAP process converts the tyre rubber into char, which is further treated to develop GO and is analysed using various techniques including XRD, Raman spectroscopy, XPS and SEM. The synthesised tyre char-based GO (TC-GO) is then incorporated into cement mortar at 0.01%, 0.03% and 0.05% by weight. TC and control mortars are also prepared for comparison. Results show that workability decreases in both TC and TC-GO in cement. Mechanical properties, including compressive and flexural strength, are examined at 7 and 28 days. At 28 days, the highest compressive strength is achieved for TC and TC-GO at 0.01% and 0.03% respectively. The highest flexural strength is achieved for TC and TC-GO at 0.03%. Among all, the 0.03% TC-GO mortar exhibits the best overall mechanical performance compared to the control and TC mortars. Microstructural analysis of the 0.03% TC-GO sample reveals a densified surface. This research highlights the potential of tyre char-derived GO as a viable solution for enhancing cement mortar properties, contributing to sustainable practices in the construction industry.

Keywords

Tyre-char; Graphene Oxide; Cement mortar; Strength; Microstructure

4.1 Introduction

Graphene oxide (GO) is a graphene derivative, consisting of a layer of graphene with grafted oxygen functional groups. A common approach for synthesising GO involves the oxidation of natural or synthetic graphite using strong oxidising agents, followed by exfoliation through ultrasonication [1]. However, using both natural and synthetic graphite as precursors for GO synthesis presents several challenges. Natural graphite availability is geographically limited, and the production of synthetic graphite requires extremely high temperatures ($\geq 2500\text{ }^{\circ}\text{C}$), resulting in significant production costs [2]. In contrast, carbon-rich residues and biomass waste have emerged as attractive alternatives for synthesising graphene-based materials, including GO. These sources offer several advantages, including high carbon content, environment-friendliness, lower processing temperature, abundant availability, and cost-effectiveness [3]. Numerous studies have investigated the utilisation of different carbon precursors and biomass, such as coconut shells [4], sugarcane bagasse [5], tea [6], pine leaves [7], oil palm leaves [8], and industrial wastes like scrap tyres [9], bio-soot [10], and Zn-C batteries [11], in the synthesis of GO.

Among industrial wastes, scrap tyres have become a significant global environmental concern. It was estimated that 1.0 billion tyres are produced worldwide annually [12]. Every year, millions of discarded tyres are either thrown away or buried, posing severe risks to the environment, the economy, and public health. By 2030, there would be 1200 million tyres to be discarded yearly [13]. Recent research has focused on developing recycling methods for waste tyres. One promising approach is the pyrolysis of waste tyres, which allows for energy recovery and the production of reusable materials. There are different pyrolysis processes for treatment of the waste tyres including vacuum, microwave, catalytic and co-pyrolysis [14]. Among these, microwave pyrolysis is particularly effective for processing waste tyres. This is because, the reinforcing carbon black in the tire rubber, a material with low thermal conductivity, can improve the absorption of microwave energy within the rubber. This, in turn, promotes the pyrolysis of the rubber and leads to increased tire char production. [14]. Compared to the traditional pyrolysis methods, microwave pyrolysis not only reduces processing time and energy consumption but is also more environmentally friendly and cost-effective for tyre waste treatment [14].

GO demonstrates exceptional performance in cement applications by enhancing the mechanical and microstructural properties. The oxygen functional groups attached to GO decrease van der Waals forces and enhance electrostatic repulsion among GO sheets, which promotes its dispersion in water. As a result, GO can easily form stable dispersions in water, primarily comprising 1-nm-thick sheets, making it more compatible for integration into cement mixtures [15]. Additionally, these functional groups play a key role in physical or chemical interactions, enhancing the bonding at the interface with the host materials. GO introduces an extra dimension of interaction with the cement matrix, further strengthening the composite [16].

GO-enhanced cement is suitable for different environments, particularly those requiring improved mechanical properties, sustainability, and durability. Its superior properties, such as increased compressive strength, flexural strength, and abrasion resistance, make it especially suitable for high-traffic areas like roads, pavements, and bridges [17].

However, the high cost of commercial GO poses challenges for its widespread application. Most existing studies focus primarily on GO synthesis from graphite and its effects on cement paste and mortar. In contrast, this study investigates the synthesis of GO from tyre char and its impact on cement performance. To our knowledge, this is the first study to report the synthesis of GO from tyre char and its application in cement. GO was synthesised from tyre char using the microwave-assisted pyrolysis (MAP) method, followed by further chemical treatments. The synthesised tyre char-derived GO (TC-GO) was incorporated into cement at concentrations of 0.01%, 0.03%, and 0.05% to assess its effects on workability, compressive strength, and flexural strength. For comparison, control samples and those containing only tyre char (TC) were also prepared. Additionally, a microstructural analysis was conducted to evaluate the impact of TC-GO on the cement matrix.

4.2 Experimental Investigation

The experimental work consists of two stages. The first stage involves synthesising and characterising TC-GO through a two-step microwave-assisted pyrolysis process. The second stage focuses on the design and testing of cement mortar, evaluating flowability, the curing process, compressive and flexural strength, as well as microstructure.

4.2.1 Synthesis of Graphene Oxide from Tyre char

The synthesis of TC-GO was performed in two steps using a microwave-assisted pyrolysis technique. In this process, materials absorb microwave radiation and convert it into heat energy. The thermochemical reaction occurs in the absence of oxygen. A microwave susceptor absorbs the electromagnetic energy and transfers it to the biomass, initiating the heating process.

4.2.1.2 Chemicals and Materials

The materials used in this research included scrap tyres provided by Mycar Tyre & Auto, Townsville. Ferric Chloride (FeCl_3), Conc. Sulfuric acid (H_2SO_4 , 95%), Hydrochloric acid (HCl, 95%) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 95 %) were purchased from Sigma-Aldrich, Australia. All the chemicals were used as received.

4.2.1.3 Preparation and Characterisation of TC-GO

The scrap tyres were cleaned and cut into small square pieces ($1\text{cm} \times 1\text{cm}$). Approximately 100 g of these fragments were processed in a microwave pyrolysis process. The tyre pieces were exposed to two microwave power phases: first 0.8 kW for 15 minutes, followed by 1.0 kW for 45 minutes, for a total of one hour of pyrolysis. The resulting tyre char was washed

with distilled water and dried at 105 °C. To prepare a suspension, the dried tyre char was mixed with FeCl₃ in distilled water at a 1:1 ratio. After 10 minutes of sonication, the solution was evaporated at 80 °C in an oven for 24 hours. The produced black solid was then subjected to a second microwave pyrolysis procedure at 0.8 Kw for 15 minutes, followed by 1.0 kW for 30 minutes, for a total of 45 minutes of pyrolysis. The obtained sample was then rinsed with diluted HCl and distilled water before being treated with H₂SO₄. Following completion, the mixture was diluted and washed with ethanol. The resulting product was oven-dried and further analysed.

The crystal structure and interplanar spacing of the synthesised TC-GO were analysed using a Bruker D2 Phaser X-ray diffractometer. Raman spectra were recorded at room temperature with a WITec Raman spectrometer, using a 532 nm laser, to obtain information on the chemical structure and phase. X-ray photoelectron spectroscopy (XPS) data were collected with a Kratos Axis Ultra XPS to evaluate the quantitative atomic composition of the synthesised material. Surface microstructure analysis was conducted using a Hitachi SU 5000 scanning electron microscope (SEM), and energy-dispersive X-ray spectroscopy (EDS) was performed with an Oxford Instruments X-MaxN detector.

4.2.2 Preparation of Cement Mortar

In this section, the prepared TC-GO was incorporated into the cement to investigate its effects on strength and microstructural properties. For comparison, both control and TC cement mortars were also prepared.

4.2.2.1 Chemicals and Materials

General-purpose (GP) cement was used in this investigation to adhere to the specifications outlined in AS 3972-2010. The chemical composition of the GP cement is presented in Table 1. River sand was used as a fine aggregate. The previously described TC and TC-GO were used in this study. A polycarboxylic ether-based MasterGlenium SKY 8100 superplasticiser (PS) produced by Master Builders Solutions Co., Ltd was used for workability purposes.

Table 4.1 Chemical composition of GP cement.

Material	Chemical Composition (wt.%)									
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	K ₂ O	TiO ₂	Na ₂ O	LOI
%	64.8	20.7	6.0	3.3	2.8	1.4	0.5	0.3	0.2	2.7

4.2.2.2 Preparation of TC & TC-GO water suspension

TC and TC-GO were thoroughly combined with water and PS before being added to the dry cement materials to improve their dispersion inside the cement matrix. In this study, ultrasonic mixing was used to make an aqueous solution. The necessary quantities of TC powder, water, and PS were carefully measured. Water was gradually added until the specified water-to-cement (W/C) ratio was obtained. These components were then mixed to create an aqueous solution, which was subsequently dispersed to ensure a uniform distribution. The dispersion technique was conducted 30 min with a frequency of 40 kHz and a power of 100 W. This procedure was also repeated to prepare TC-GO water suspensions and control samples.

4.2.2.3 Preparation of TC & TC-GO incorporated cement paste

Cement mixing was conducted after preparing the TC-GO and TC suspensions. A high-speed ultrasonicator (Model FXP10DH) was used to prepare the cement mixture. The mixing procedures similar to AS 2350.12-2006 were followed. According to the cement mix design, the calculated amount of cement was combined with the prepared TC suspension in the mixing bowl. Immediately after adding the cement and suspensions, the mixer was started at a low speed for 30 seconds. The sand was then gradually added over the next 30 seconds. The mixer was set to high speed and allowed to run for an extra 30 seconds.. Afterwards, the mixer was stopped for 90 seconds. Using a scraper, all mortar adhering to the wall and bottom of the bowl was collected in the centre within the first 15 seconds. The mixing was completed at high speed for 60 seconds. After mixing, the cement paste mixture was promptly poured into molds and compacted on a vibrating table.

The molds were then covered with polyethylene sheets to prevent the mixture from escaping. The cement specimens were demolded after 24 hours and stored in a humidity cabinet at 23 °C and 50% humidity. The samples were then cured in a saturated lime water bath at 20 °C for 7 days and 28 days of testing. This procedure was repeated for preparing TC-GO as well as control samples. Table 2 lists the mixed proportions of the prepared TC-GO and TC cement mortar and paste.

Table 4.2 Mix proportions of cement mortar.

Sample	TC % (bwoc)	TC-GO % (bwoc)	W/C ratio	Cement (g)	TC (g)	TC- GO (g)	Sand (g)	Water (g)	PC (ml)
Control	0.00	0.00	0.73	450	0.000	0.000	1350	329	4.5
TC1	0.01		0.73	450	0.045		1350	329	4.5
TC3	0.03		0.73	450	0.135		1350	329	4.5
TC5	0.05		0.73	450	0.225		1350	329	4.5
TC-GO1		0.01	0.73	450		0.045	1350	329	4.5
TC-GO3		0.03	0.73	450		0.135	1350	329	4.5
TC-GO5		0.05	0.73	450		0.225	1350	329	4.5

4.2.2.4 Flow Table Test

Immediately after mixing, the fresh mixture was tested using a flow table to determine the workability of the cement paste. The flow table was used to determine a flow according to AS 2701.2001. This test method determines the relative water requirement by assessing the amount of water needed for a specified flow. Fig. 4.1 shows the setup for the flow table test.

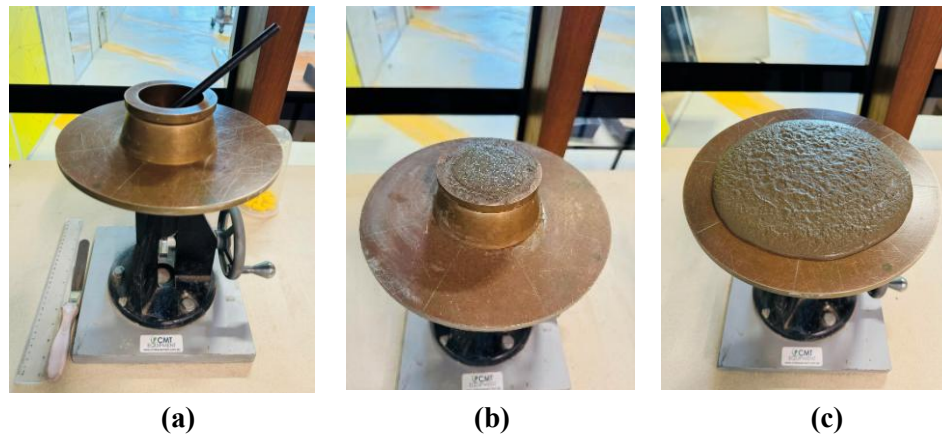


Figure 4.1 Flow table test setup.

4.2.2.5 Mechanical Properties

Table 3 presents a comprehensive summary of the testing methods employed in this research to assess the mechanical properties of control, TC, and TC-GO cement mortars. The test results reflect average values calculated from at least three samples, with an allowable deviation of 1%. Any values exceeding this range were considered outliers. Figure 4.2 illustrates the setup for each testing method. The Shimadzu Universal Testing Machine (Model AGS-50kNX) was used for both compressive and flexural tests. The flexural test was executed using a three-point bonding. All tests were conducted after curing periods of 7 and 28 days.

Table 4.3 Test Methods.

Test parameter	Test standard	Sample type	Sample dimensions	Loading rate (kN/s)
Compressive strength	AS/NZS 2350.11:2006	Prisms	40×40×160 mm	2.4 ±0.2
Flexural strength	ASTM C 348-08	Prisms	40×40×160 mm	2.6 ± 0.1

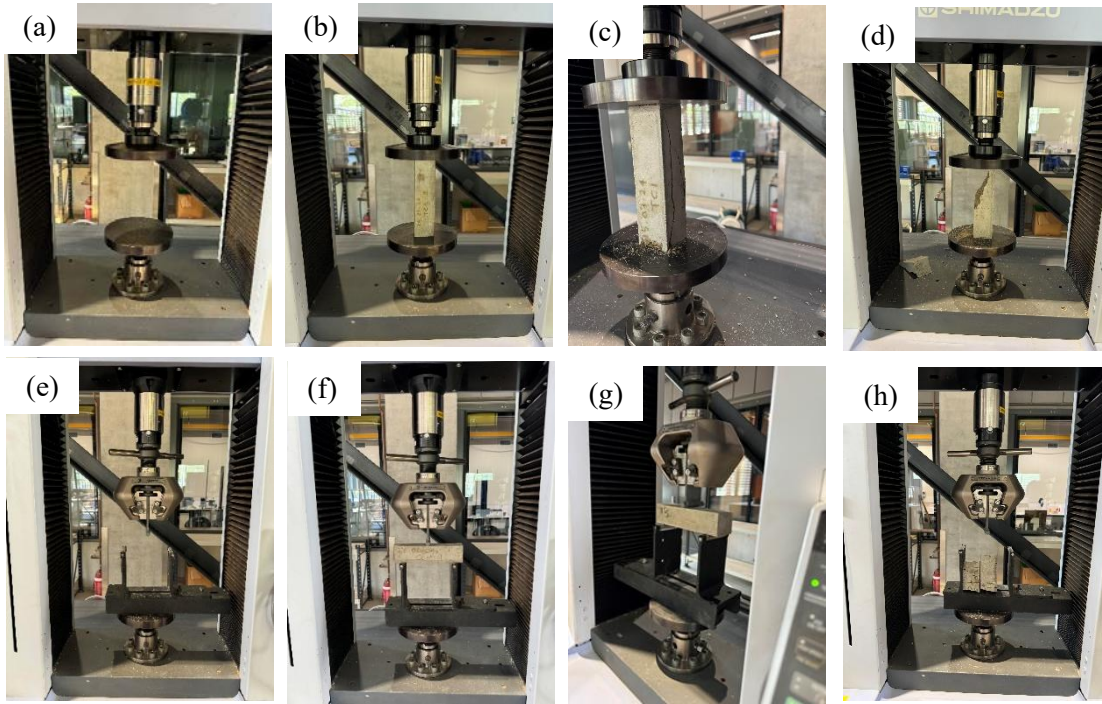


Figure 4.2 (a-b) Compressive strength test set up, (c-d) Compressive strength sample test, (e-f) Flexural strength test set up, (g-h) Flexural strength sample test.

4.2.2.6 Microstructure characterisation

Cement paste samples were prepared for microstructural analysis. Following 28-day compression testing, the central portions of the fractured samples were collected and immersed in acetone to halt hydration. Before SEM analysis, these samples were vacuum-dried in an oven at 105 °C for 3 hours and stored in a vacuum chamber until examination.

4.3 Results and Discussion

4.3.1 Characterisation of the prepared TC-GO

The XRD pattern of the synthesised TC-GO, shown in Fig. 4.3 exhibits a strong peak at 9.8° (001), a broad peak at 25° (002), and a weak peak at 43° (100) [10, 18]. The prominent peak at 9.8° corresponds to an interlayer spacing of 0.90 nm, indicating the presence of oxygen-containing intercalation groups with the graphitic layers [10]. The broader peak at 25° suggests a persistent poorly crystalline nature of the precursor used for synthesis [4]. The crystallite size of

the peak at 9.8° of TC-GO (001) was calculated using Scherrer's equation as 26.09 nm. The XRD pattern of TC-GO shows GO formation with the presence of its amorphous precursor material and a reduced GO phase. The formation of rGO may result from the use of amorphous material and changes in the oxidation degree during the synthesis process. The Raman spectrum of TC-GO, shown in Fig. 4.4 exhibits three different bands. Two of them are located at 1344 and 1590 cm^{-1} , corresponding to the D and G, respectively, while three smaller bands, at 2500–3250 cm^{-1} are designated as 2D peaks. The I_D/I_G ratio of 0.99 for TC-GO indicates a higher number of defects, which can be attributed to the attachment of functional groups, such as hydroxyl and epoxy groups, to the carbon skeleton [7].

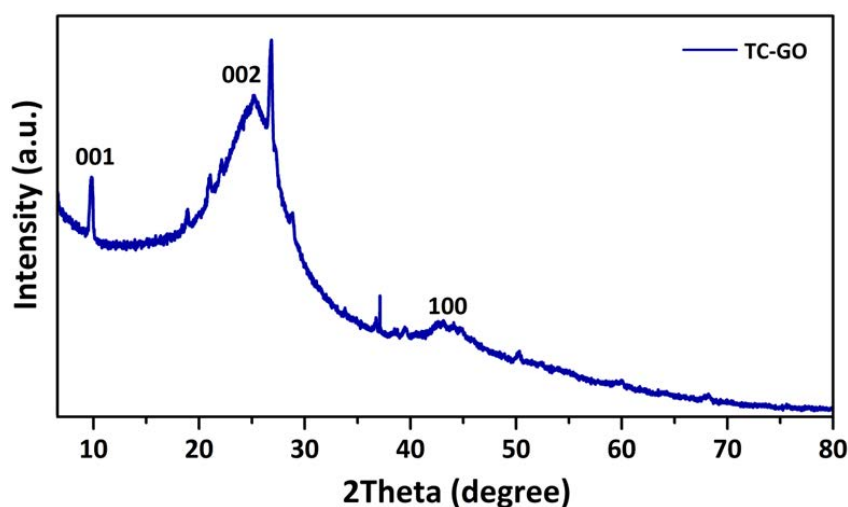


Figure 4.3 The XRD pattern of TC-GO.

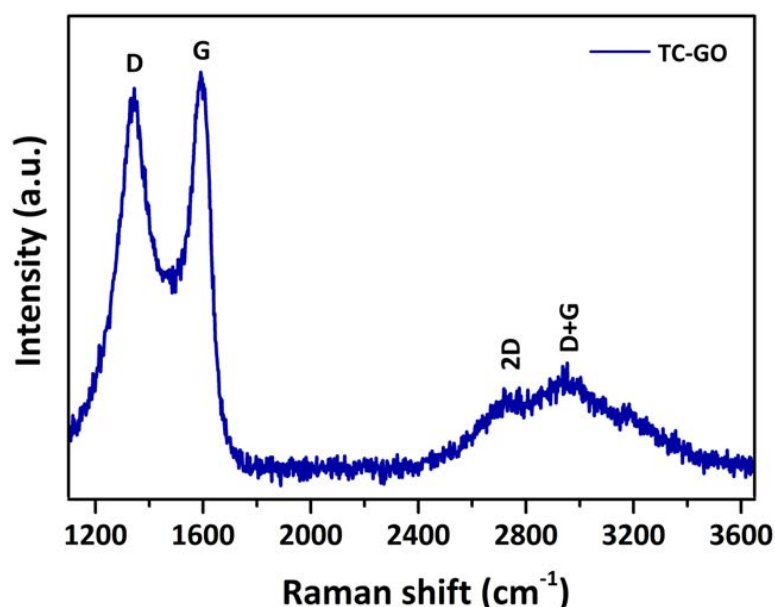


Figure 4.4 The Raman spectrum of TC-GO.

Fig. 4.5(a) shows the XPS data, which reveals that TC-GO primarily consists of C and O, with trace amounts of S and Zn detected as impurities originating from the precursor. The C1s spectrum in Figure 4.5(b) indicates four carbon states: sp^2 and sp^3 hybridised carbon, as well as C–O and O–C=O structures [19]. The atomic carbon-to-oxygen (C/O) ratio of TC-GO, as quantified by XPS, is 1.92. This analysis demonstrates a significant increase in the atomic concentration of oxygen-containing groups, such as carbonyl and carboxyl groups, in the TC-GO sample. SEM images of TC-GO reveal a disordered solid, comprising indistinctly aggregated, thin, closely associated, and highly overlapping sheet structures. The observed wrinkling is attributed to interactions between oxygen-containing functional groups [20]. The EDX analysis of the TC-GO sample, as shown in Figure 4.6(b), indicates atomic percentages of 79.69% for C and 15.89% for O, with impurities such as S, Fe, and Zn present. The characterisation of GO synthesised from tyre char confirms a defined interlayer distance, verifying the structure and highlighting some impurities from the original precursors.

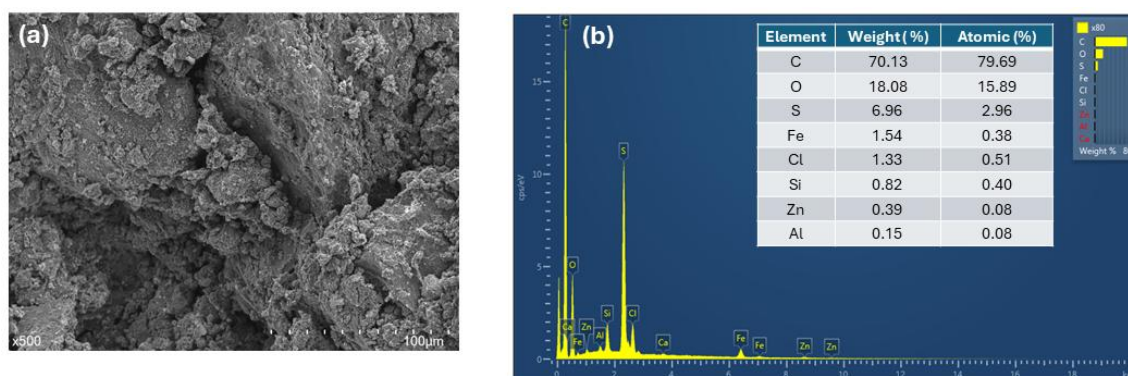


Figure 4.5 (a) SEM images, (b) EDX analysis of TC-GO.

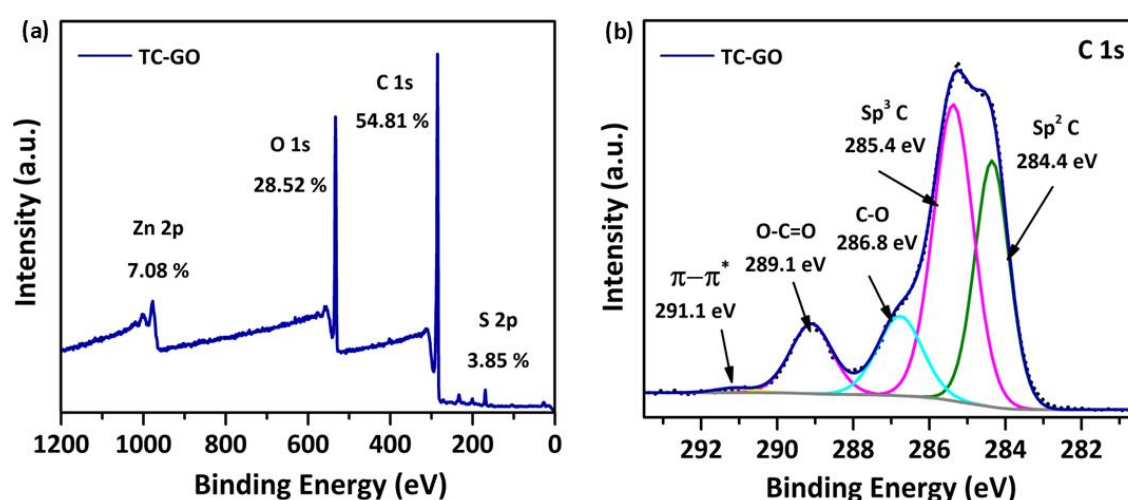


Figure 4.6 XPS characterisation of TC-GO (a) XPS survey spectrum (b) C1s spectrum.

4.3.2 Influence of TC & TC-GO incorporation on the workability of cement paste

A flow table test is used to determine the workability of TC and TC-GO of cement paste by measuring its flow. The data for the flow table test are tabulated in Table 4, which indicated flow data for TC and TC-GO of 0.01%, 0.03%, and 0.05% by weight of the cement added into the cement mixture. Fig 4.7. shows the graph of the flow table test with dosage and the flow in percentage. The flow table results show that the flow percentage reduced with the increase of TC and TC-GO content, compared to the plain cement paste. The incorporation of 0.01% by weight of TC slightly reduced the flow percentage. However, the incorporation of 0.01% TC-GO showed a sudden decrease. With the further increase of TC and TC-GO content to 0.03%, TC did not reduce flow diameter significantly, however, TC-GO reduced it slightly. The addition of 0.05 % of TC and TC-GO showed 9% and 20% reduction respectively, than that of the plain cement paste. The flow table test results indicated that the incorporation of TC and TC-GO reduced the workability of the cement paste. Moreover, the addition of TC-GO had more impact on the cement paste compared to the TC.

The results show that 0.03% is the threshold for maintaining workability in GO-incorporated cement paste. Below this threshold, GO addition significantly reduced workability, while above it, the impact was minimal. Li et al. [15] also found that GO nanosheets lowered the mini-slump values of cement paste. Similarly, Shang et al. and Gong et al. observed a marked decrease in fluidity and an increase in viscosity with GO addition. This effect is primarily due to the formation of GO agglomerates via chemical cross-linking with calcium cations, abundant in the pore solution of cement paste.

Table 4.4 Flow Table Test Results of TC and TC-GO Cement Paste.

Sample	TC % (bwoc)	TC-GO% (bwoc)	Flow %
Control	0.00	0.00	106.25
TC1	0.01		101.25
TC3	0.03		100.00
TC5	0.05		96.25
TC-GO1		0.01	95.00
TC-GO3		0.03	88.75
TC-GO5		0.05	85.00

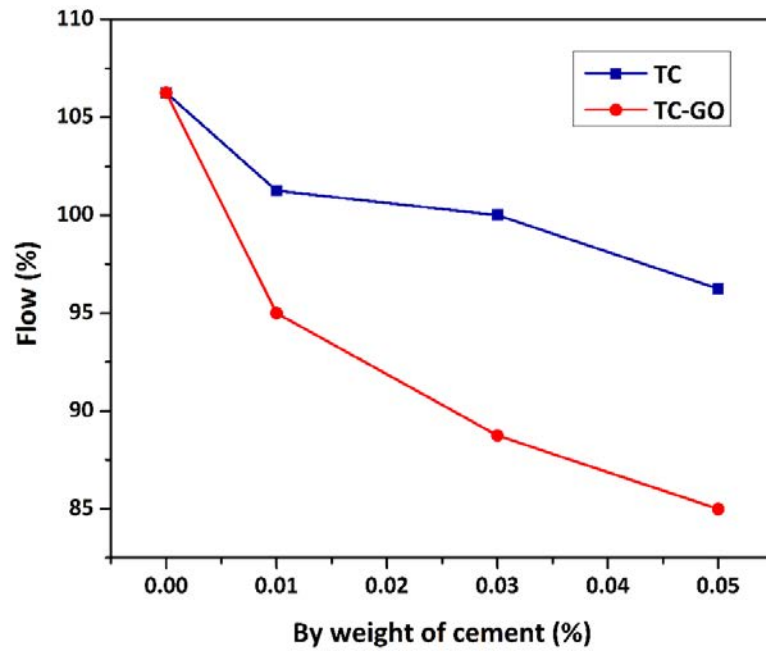


Figure 4.7 Flow Table Test Results of TC and TC-GO Cement Paste.

4.3.3 Mechanical Properties of TC and TC-GO cement mortar

Fig. 4.8 and 4.9 present the compressive strength results at 7 and 28 days for TC and TC-GO, respectively, using bar charts with error bars for each result. In Fig. 4.8, the compressive strength of the control mix at 7 days is 21.02 MPa, which increases to 26.06 MPa by 28 days. In the 0.01% TC sample, there is a slight improvement in compressive strength, with the 7-day strength increasing to approximately 22 MPa, and the 28-day strength reaching around 29 MPa. The 0.03% TC sample shows a 7-day strength of around 24 MPa, while the 28-day strength is slightly higher at 27 MPa. A slight decrease in strength is observed in the 0.05% TC sample, with values just below 24 MPa at 7 days and slightly above 27 MPa at 28 days.

In Fig. 4.9, the 7-day compressive strength for the 0.01% TC-GO sample is similar to the corresponding TC sample at 21.89 MPa, with the 28-day strength reaching above 27 MPa. The 0.03% TC-GO sample exhibits a 7-day compressive strength of 23.87 MPa, which exceeds 30 MPa at 28 days. The 0.05% TC-GO sample shows a slight decrease in strength compared to the 0.03% incorporation, with values around 25 MPa at 7 days and approximately 26 MPa at 28 days. Both TC and TC-GO improve the compressive strength of cement, with 0.03% TC-GO exhibiting the best overall performance. However, both graphs indicate a slight reduction in compressive strength at the 0.05% dosage for both 7-day and 28-day curing periods, suggesting that excessive addition of either material may hinder cement performance.

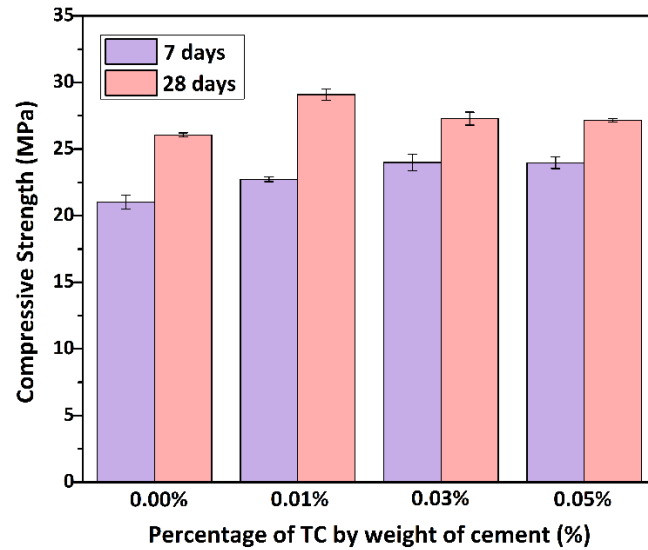


Figure 4.8 Compressive strength of TC incorporated cement mortar in 7 and 28 days.

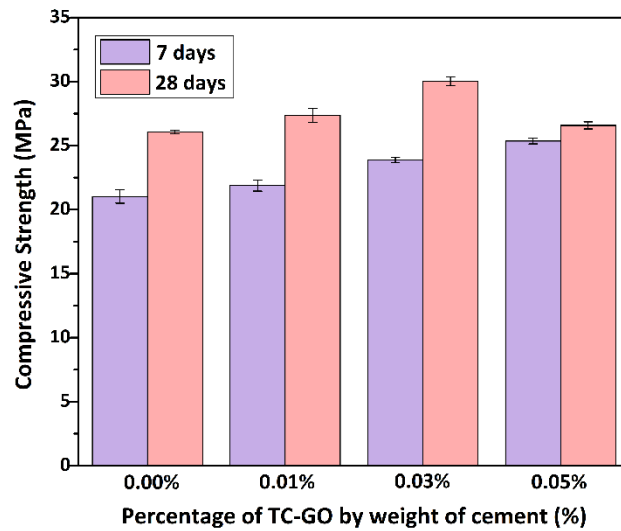


Figure 4.9 Compressive strength of TC-GO incorporated cement mortar in 7 and 28 days.

The increment in compressive strength of TC and TC-GO added cement mortar, compared to the control mix is illustrated in Fig. 4.10. At 7 days, the compressive strength increment of TC increases and remains relatively stable across the cement weight percentages from 0.01% to 0.05%. The value starts at around 8%, slightly increases near 0.03%, and stays almost constant at around 14% from 0.03% onward. In contrast, the opposite pattern is observed at 28 days. TC at 28 days shows a decreasing trend as the weight of cement increases. It starts at about 11% for 0.01%, then drops to just over 5% at 0.05%, suggesting a reduction in compressive strength increment over time at higher cement weights.

For TC-GO cement mortar at 7 days, the strength exhibits a steadily increasing trend, starting at 4% for 0.01%, and reaching almost 20% by 0.05%. However, in TC-GO at 28 days, the strength initially increases sharply to about 15% at 0.03%, before dropping dramatically to around 2% at 0.05%. This suggests that, at 7 days, the incorporation of TC-GO enhances compressive strength over time. However, at 28 days, the strength enhancement diminishes significantly beyond a certain cement weight percentage.

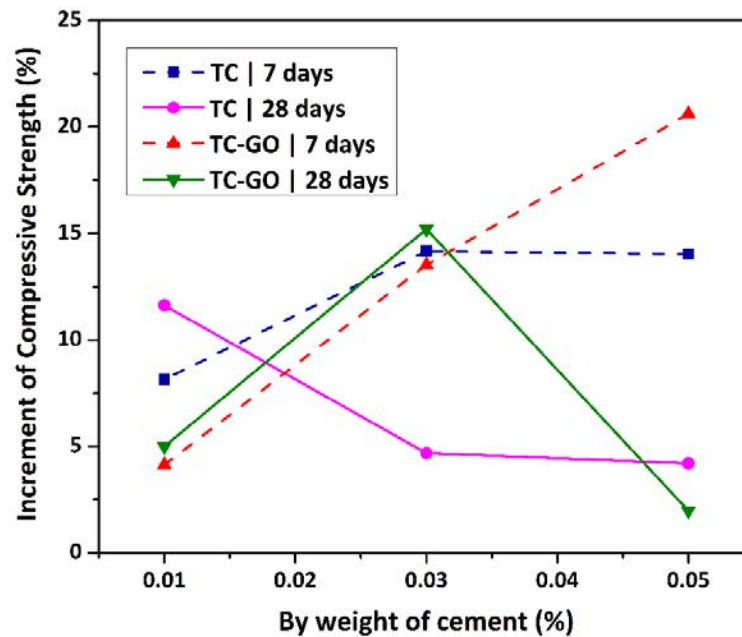


Figure 4.10 Compressive strength increment of TC & TC-GO added cement mortar in 7, 28 days.

Fig. 4.11 and 4.12 present the test results for flexural strength at 28 days for TC and TC-GO respectively. At 28 days, the control mix exhibits a flexural strength of approximately 6.60 MPa. The mixtures with 0.01% and 0.05% TC show slightly lower flexural strength values compared to the control, while the mixture with 0.03% TC achieves a higher flexural strength, reaching around 6.91 MPa, surpassing the control sample. In contrast, the TC-GO incorporated cement mortar displays an increasing trend, with a flexural strength of 7.62 MPa at 0.03% dosage, surpassing both the control and TC-only mixtures. However, at 0.05% TC-GO, the flexural strength decreases again, indicating that the optimal dosage lies around 0.03%.

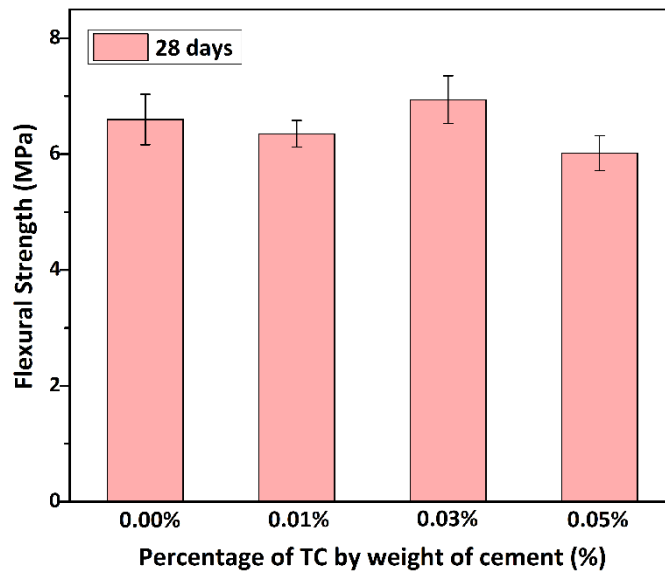


Figure 4.11 Flexural strength of TC incorporated cement mortar in 28 days.

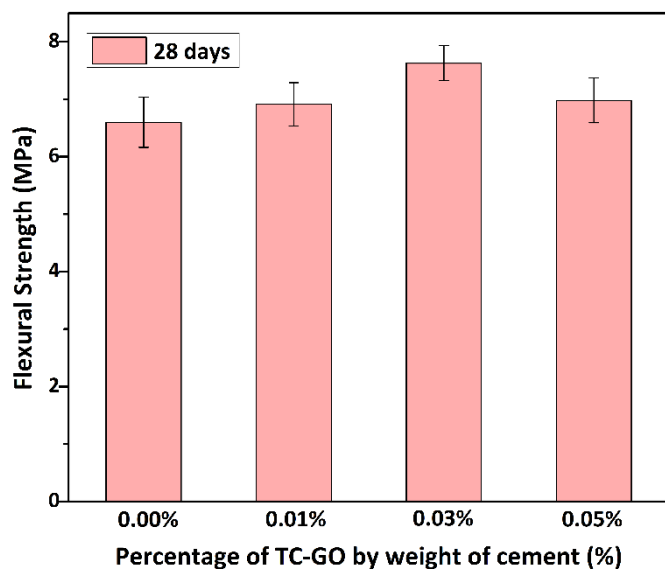


Figure 4.12 Flexural strength of TC-GO incorporated cement mortar in 28 days.

The increment in flexural strength of TC and TC-GO added cement mortar, compared to the control mix is illustrated in Fig. 4.13. The 0.01% dosage of TC experiences around a 4% decrease in flexural strength while 0.03% TC shows a 5% increase in flexural strength compared to the control. A significant 9% decrease is recorded for the 0.05% TC sample, which that shows higher percentages of TC lead to a decline in flexural strength. The 0.01% TC-GO results in a 5% increase in flexural strength, which is an improvement over the control and TC 0.01%. The largest increment is exhibited in 0.03% TC-GO, with a 16% increase. This indicates that 0.03% TC-GO is the most effective dosage for enhancing flexural strength. A 0.05% TC-GO still shows an improvement, with a 6% increase, though not as significant as at 0.03%. The optimal dosage for

improving flexural strength is 0.03% for both TC and TC-GO, with TC-GO providing the highest overall improvement. However, at higher percentages (0.05%), both TC and TC-GO mixtures tend to show a reduction in performance compared to the 0.03% dosage.

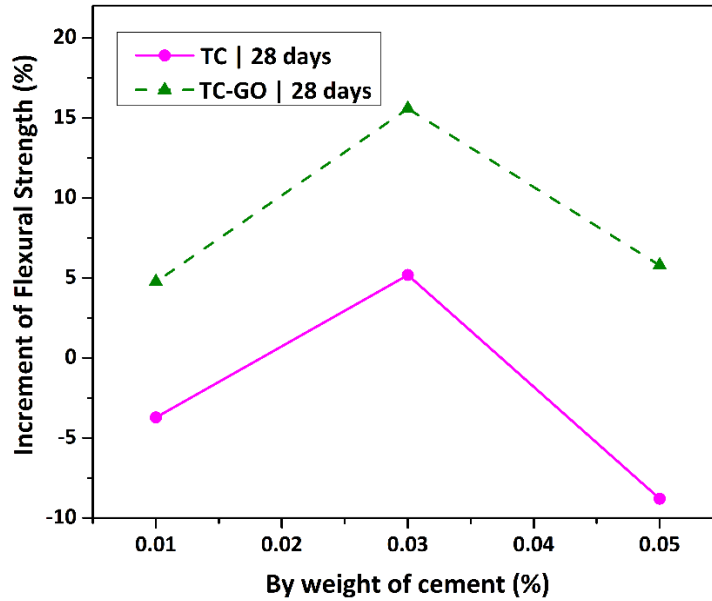


Figure 4.13 Flexural strength increment of TC and TC-GO added cement mortar in 28 days.

Incorporating TC-GO into cement mortar significantly improves compressive and flexural strengths by influencing the cement hydration process. During the induction phase of hydration, tricalcium silicate (C_3S), the primary component of cement, reacts with water to release calcium ions (Ca^{2+}), essential for forming hydration products. TC-GO absorbs these Ca^{2+} ions, reducing their concentration in the cement matrix and accelerating the hydration rate. This absorption leads to an accelerated hydration rate during the induction period compared to the control sample, as evidenced by the enhanced mechanical performance.

The large surface area of TC-GO offers additional nucleation sites for hydration products like calcium silicate hydrate (C-S-H) and calcium hydroxide [$Ca(OH)_2$], accelerating hydration and resulting in a denser microstructure compared to TC mortars. Ca^{2+} ions from the C-S-H structure bond with oxygen functional groups on TC-GO sheets, forming a more interconnected network. This intercalation effect densifies the C-S-H gel, enhancing both compressive and flexural strengths in TC-GO cement mortars.

According to Scrivener's hydration theory, C-S-H gel forms in two phases: the outer product (OP) and the inner product (IP). The OP forms around unhydrated cement particles (C), as shown in Fig. 4.14, and typically has a higher Ca/Si ratio, making it more porous and less mechanically robust. In contrast, the IP, with a lower Ca/Si ratio, is denser and stronger. Under compressive loads, cracks propagate through both IP and OP, contributing to compressive

strength. However, flexural cracks mainly propagate through the OP, making it a key factor in determining flexural strength.

The role of TC-GO in improving the mechanical properties can be attributed to its ability to increase the thickness and density of both the IP and OP. As observed, the optimal TC-GO dosage of 0.03% results in the greatest enhancement in both compressive and flexural strength. At this dosage, the increased thickness of the IP, combined with the improved pore-filling effect of the OP, contributes to the overall densification of the microstructure, as depicted in Fig. 4.14 (b). This balance between IP and OP leads to superior strength performance at 28 days.

On the other hand, TC samples exhibit a different hydration behavior. While the increase in compressive strength in TC samples is largely due to the thickening of the IP, the lower OP thickness contributes to a reduction in flexural strength, particularly at 0.01% and 0.05% TC concentrations. The thinner OP layer in TC samples as shown in Fig. 4.14 (a) allows for easier crack propagation during flexural loading, which explains the lower flexural strength compared to control samples.

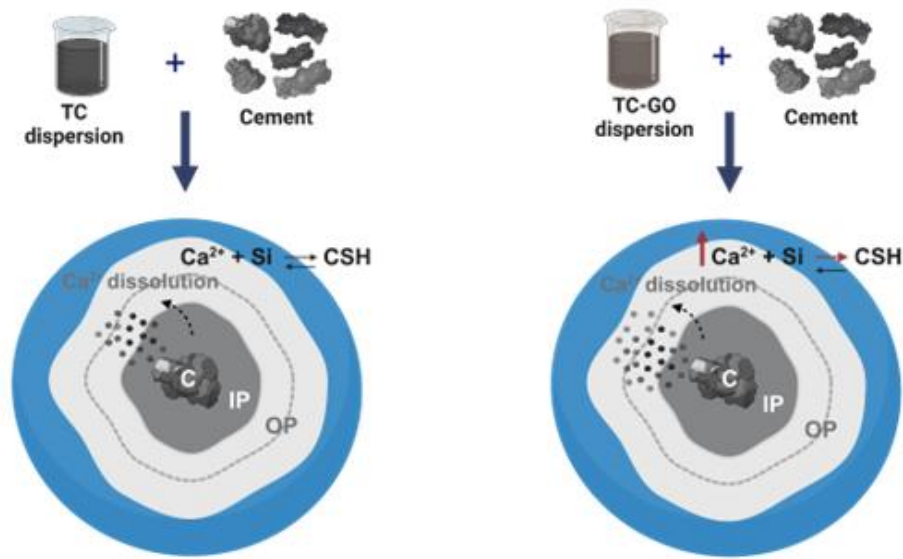


Figure 4.14 The control factors of mechanical properties of (a) TC (b) TC-GO cement mortar.

The compressive strength of TC-GO-added cement mortar gradually increases as the percentage of TC-GO rises, reaching a peak at the optimal dosage. This optimal TC-GO content promotes the formation of a densely packed microstructure. During the cement hydration process, all hydration crystals fully form and bond with the TC-GO sheets. At this point, the compressive strength of the TC-GO-added cement mortar reaches its maximum. However, beyond this optimal dosage, further additions do not enhance compressive strength. This is because all available hydration products have already been incorporated into the dense microstructure, and the additional TC-GO sheets cannot support the formation of fully developed hydration crystals.

Instead, partially formed crystal structures emerge. This mechanism explains the reduction in compressive strength when the TC-GO content exceeds the optimal dosage.

Incorporating TC and TC-GO into cement requires a specialised dispersion technique due to the challenges posed by their unique properties. Simply adding TC-GO directly does not yield optimal results, as the sheets tend to agglomerate because of strong Van der Waals forces. This leads to the formation of large clusters, which prevents uniform dispersion in the cement mixture [20]. Additionally, TC-GO particles are hydrophilic due to oxygen functional groups on their surface, they retain some hydrophobic characteristics from the graphene structure in TC, further complicating dispersion. Another issue is the high specific area of TC and TC-GO nanoparticles, which increases surface energy and promotes agglomeration. To address these challenges, an ultrasonic mixing technique was used. This method employs high-frequency sound waves to create and collapse microbubbles, generating shock waves and intense shear forces [21]. These forces are more effective than mechanical mixing, breaking down the surface energy between TC and TC-GO sheets at the nanoscale level. With better dispersion, the TC-GO nanoparticles provide more surface area for bonding with cement hydration products, creating numerous nucleation sites. This leads to a denser microstructure and improved strength in the cement.

The SEM images in Fig. 4.15 illustrate the microstructure differences between control cement mortar (0.00%) and TC-GO 0.03% cement mortar at 28 days. In images (a) and (b), representing the control sample, the microstructure reveals typical cement hydration products, including calcium silicate hydrate (C-S-H) gel and calcium hydroxide (CH) plates [22]. These images highlight a relatively loose and less dense arrangement of hydration products. In contrast, images (c) and (d) of the TC-GO 0.03% sample show a denser microstructure with more C-S-H and CH plates compared to the control. The presence of TC-GO clearly improves the arrangement of cement hydration products, contributing to a more compact and well-bonded structure. This increased density indicates that TC-GO not only facilitates the formation of more hydration products but also plays a key role in organising the microstructure, leading to better bonding between cement particles. The comparison of the SEM images shows that the TC-GO enhanced sample has fewer voids and a more integrated structure, which likely contributes to improved mechanical properties.

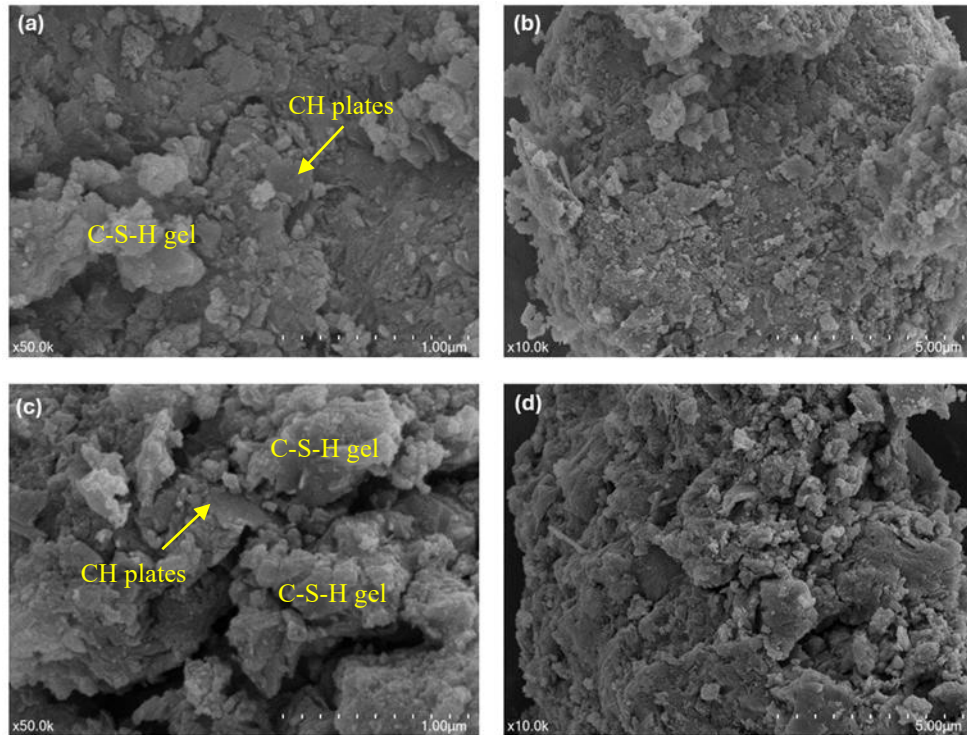


Figure 4.15 SEM images of Control (0.00%) cement mortar (a,b) and TC-GO 0.03% cement mortar at 28 days (c,d).

4.4 Conclusions

In conclusion, the incorporation of TC-GO into cement mortar significantly improves its mechanical properties by enhancing the microstructure. TC-GO was synthesised from tyre char using a two-step microwave pyrolysis process with ferric chloride, followed by treatment with sulfuric acid (H_2SO_4). The successful synthesis was confirmed through XRD, Raman, XPS, and SEM analyses. Mechanical strength testing revealed that a 0.03% dosage of TC-GO at 28 days was more effective than both 0.03% TC and the control sample. The addition of 0.03% TC-GO led to a 15% increase in both compressive and flexural strength compared to the control. The presence of polycarboxylate (PC) played a crucial role in achieving a uniform dispersion of GO. SEM analysis showed that the optimal dosage of 0.03% TC-GO resulted in a denser matrix with more calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) plates. These improvements in the microstructure contributed to the overall densification and enhanced strength of the 0.03% TC-GO cement mortar.

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Chapter 5

Conclusions and Recommendations

Graphene oxide (GO) is a highly promising material with unique optical, electronic, and chemical properties, making it useful for a range of applications. However, traditional GO synthesis methods face challenges, including the use of strong oxidising agents, lengthy reactions, toxic gas emissions, and hazardous byproducts, posing significant safety risks. Additionally, graphite, the common precursor for GO, is expensive and scarce, particularly in Australia where local production is minimal, further driving up costs. Given these limitations, biomass and carbon waste present viable alternatives for producing nanostructured carbon materials due to their high carbon content, lower processing temperatures, availability, and cost-effectiveness. This project focused on synthesising GO from waste tyres using microwave-assisted pyrolysis and applying tyre char-based GO (TC-GO) to cement to examine its strength and microstructural properties.

The following sections summarise the key conclusions of this project and discuss recommendations for future research and applications.

5.1 Synthesis and Characterisation of TC-GO

In Chapter III, tyre char (TC) was converted into tyre char-based graphene oxide (TC-GO) using a two-step pyrolysis process with ferric chloride (FeCl_3) as a catalyst, followed by treatment with sulfuric acid (H_2SO_4). Compared to traditional methods such as the Hummers method, this approach proved to be simpler, faster, more efficient, cost-effective, and environmentally friendly. XRD analysis confirmed the successful formation of GO from TC, indicating the presence of both amorphous precursor material and a reduced GO phase. Raman spectroscopy further validated the graphitic nature of the tyre char and its conversion into GO. The carbon-to-oxygen atomic ratio (C/O), determined by XPS, decreased from 4.64 in TC to 1.92 in TC-GO, reflecting a significant increase in oxygen-containing functional groups like carbonyl and carboxyl, which enhanced the hydrophilicity of TC-GO. SEM and EDX analyses revealed that TC-GO consists of disordered, thin, closely associated, and highly overlapping sheet structures. The atomic composition of TC-GO was 79.69% carbon and 15.89% oxygen. SAED patterns indicated its polycrystalline nature. The study emphasises the crucial role of FeCl_3 as both a catalyst and a template for producing high-quality graphene. Ultrasonication was employed to overcome the poor compatibility between TC and aqueous iron salt solutions, ensuring a successful conversion process. The successful synthesis of TC-GO from TC using the microwave pyrolysis process with chemical treatment underscores the potential of this method for sustainable material production.

5.2 Incorporation of TC and TC-GO in cement

In Chapter IV, the synthesised tyre char-based graphene oxide (TC-GO) was incorporated into cement mortar at concentrations of 0.01%, 0.03%, and 0.05% by weight. For comparison, TC and control mortars were also prepared. The results of the flow table test revealed a decrease in workability for both TC and TC-GO cement mortars. The reduction in workability was more pronounced with the addition of TC-GO, likely due to differences in surface properties between TC and TC-GO. Mechanical properties, including compressive and flexural strength, were evaluated at 7 and 28 days for both TC and TC-GO mortar samples. At 28 days, the highest compressive strength was observed in the 0.01% TC and 0.03% TC-GO samples. The 0.03% TC and 0.03% TC-GO samples also exhibited the highest flexural strength. Among all the samples, the 0.03% TC-GO mortar demonstrated the best overall mechanical performance compared to the control and TC mortars. Specifically, the addition of 0.03% TC-GO resulted in a 15% increase in both compressive and flexural strength compared to the control. Microstructural analysis of the 0.03% TC-GO sample showed a densified surface, with SEM analysis indicating a denser matrix containing more calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) plates. These microstructural improvements contributed to the overall densification and enhanced strength of the 0.03% TC-GO cement mortar.

5.3 Overall Conclusion

The research successfully demonstrated the sustainable synthesis of tyre char-based graphene oxide (TC-GO) using microwave-assisted pyrolysis, providing a cost-effective and environmentally friendly alternative to traditional GO production methods. Characterisation confirmed the conversion of tyre char into TC-GO, which was then incorporated into cement mortar. Mechanical testing showed that the optimal addition of 0.03% TC-GO significantly improved both compressive and flexural strength, with a 15% increase compared to control samples. Microstructural analysis revealed a denser matrix, highlighting the potential of TC-GO to enhance the performance of construction materials. Incorporating waste-derived GO, like synthesised TC-GO, into cement mortar provides a viable alternative to costly commercial GO, improving mechanical properties, preventing microcracks, and increasing the lifespan of cement-based structures. The key findings are summarised in Table 5.1, which outlines the overall conclusions regarding the synthesis, characterisation, mechanical performance, and implications for construction applications.

Table 5.1 Overall Conclusions

Aspect	Conclusion
Synthesis Method	The study successfully demonstrated the sustainable synthesis of tyre char-based GO (TC-GO) using microwave-assisted pyrolysis.
Cost-Effectiveness	TC-GO presents a cost-effective and environmentally friendly alternative to traditional methods of GO production.
Characterisation	Characterisation confirmed the successful conversion of tyre char into TC-GO, highlighting its structural integrity and functional properties.
Mechanical Performance	The incorporation of 0.03% TC-GO in cement mortar led to a significant improvement in both compressive and flexural strength, with a notable 15% increase compared to control samples.
Microstructural Analysis	Microstructural analysis indicated a denser matrix in the 0.03% TC-GO cement mortar, suggesting enhanced material performance and durability.
Implications for Construction	Incorporating waste-derived GO, such as TC-GO, into cement mortar provides a viable alternative to expensive commercial GO, improving mechanical properties

5.4 Recommendations for Future Research

For future research, several recommendations can be made based on the findings of this study:

Optimisation of TC-GO Synthesis: Further investigation into optimising the synthesis process of tyre char-based graphene oxide (TC-GO) is essential. Varying parameters such as microwave power, pyrolysis duration, and chemical treatment conditions could potentially yield even higher-quality GO with enhanced properties for broader applications.

Exploration of Other Carbon Wastes: While this study focused on waste tyres, other carbon-rich waste materials, such as agricultural residues or plastic waste, should be explored as potential sources for synthesising GO. Comparative studies could identify the most effective and sustainable feedstocks for large-scale GO production.

Long-Term Durability Studies: While improvements in mechanical properties were observed with TC-GO incorporation, long-term studies should be conducted to assess the

durability and performance of TC-GO cement mortar under various environmental conditions, such as exposure to moisture.

Development of Multi-Functional Materials: Given the promising results of TC-GO in cement, future research could explore the development of multi-functional cement composites by incorporating other nanomaterials alongside TC-GO. This could lead to cement mortars with enhanced properties such as self-sensing, electrical conductivity, or thermal stability.

Life Cycle Assessment and Cost Analysis: A comprehensive life cycle assessment (LCA) and cost-benefit analysis of using waste-derived TC-GO in cement should be undertaken to evaluate its economic and environmental feasibility for large-scale applications in the construction industry. Additionally, a detailed cost-effectiveness study of the two-step microwave pyrolysis process should be conducted to assess its scalability and commercial viability as a sustainable method of GO production.

Field Trials and Scalability: Pilot-scale or field trials should be conducted to assess the real-world applicability and scalability of using TC-GO in cement. This would provide valuable insights into the practical challenges and potential benefits of implementing this technology in construction projects.

By addressing these areas, future research can contribute to the continued development and optimisation of sustainable, high-performance materials using waste-derived graphene oxide. This waste-derived GO can then be applied not only to cement but also to concrete and other potential applications, such as coatings, composites, or environmental remediation. Expanding the use of waste-derived graphene oxide across various industries would highlight its versatility and value as a sustainable material. This approach could reduce dependence on traditional, costly raw materials while promoting a circular economy.

Appendix

The following picture illustrates a real-world microwave pyrolysis system that includes all the parts derived from Chapter 3, page 58.

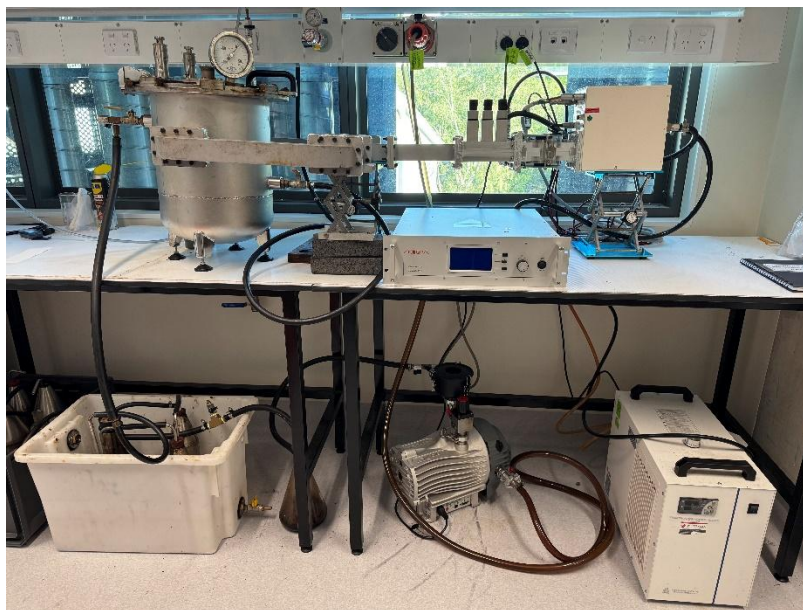


Figure 05. S1 Real-world microwave pyrolysis system.

To identify the difference between the physical properties of TC and TC-GO, images are included to support Chapter III, section 3.4.2 Characterization of Tyre Char and Tyre Char-Derived GO.

Colour:

- TC: Tyre char is usually black in colour due to its carbon content.
- TC-GO: TC-GO exhibits dark brown, because of the oxygen-containing functional group introduced during the oxidation process.

Particle Size and Morphology:

- TC: Tyre char tends to have irregular, larger particles with a relatively smooth surface compared to GO.
- TC-GO: The process of synthesising TC-GO often results in smaller, more uniform particles with a rough, sheet-like morphology, similar to other forms of GO.

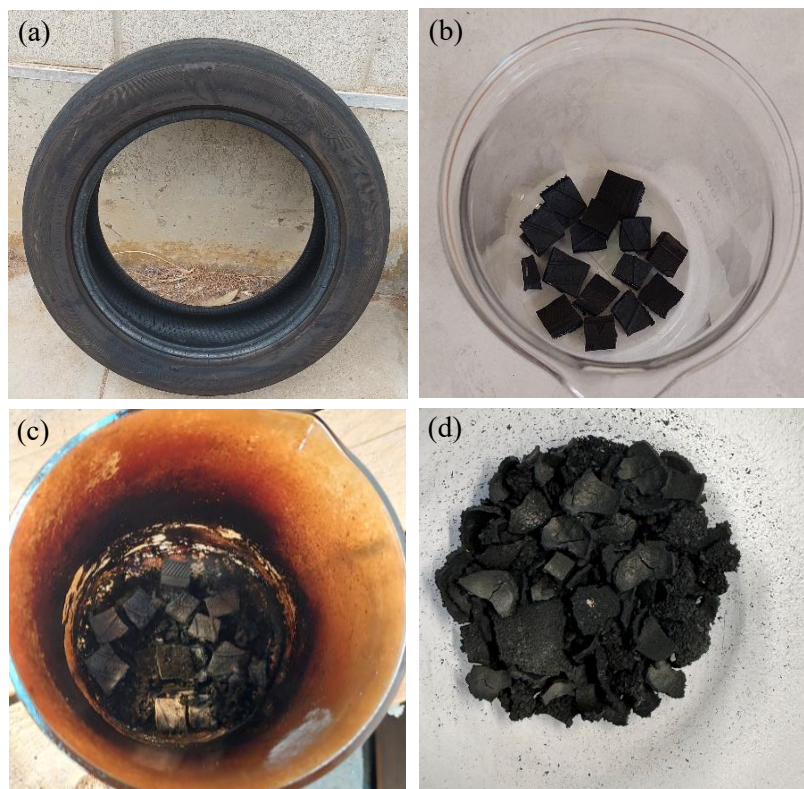


Figure 05. S2 (a) Tyre (b) Cut tyre pieces (c) TC (before grinding) (d) TC-GO (before grinding).

In Chapter III, commercial graphene has been characterised as obtained from First Graphene in addition to TC and TC-GO. The following diagrams show the XRD, Raman, XPS, SEM and TEM analysis.

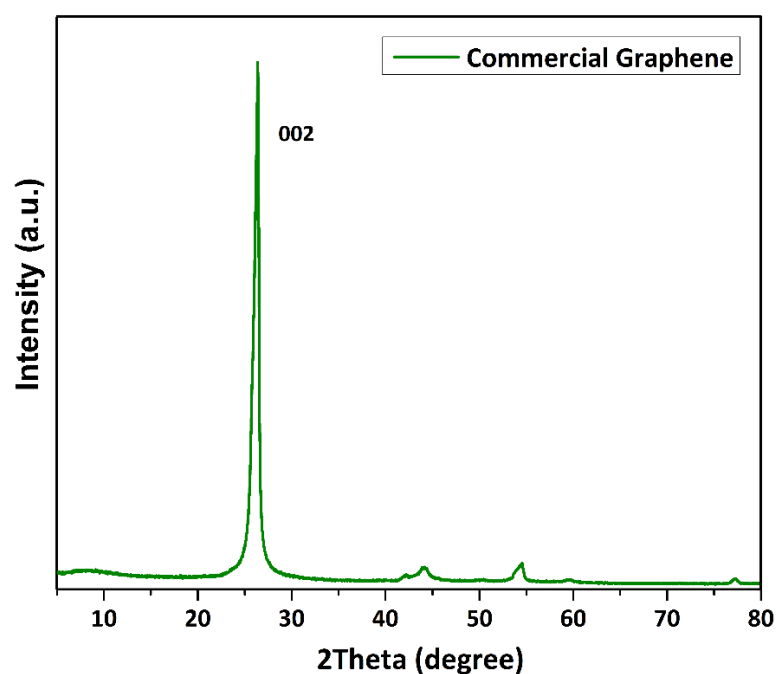


Figure 05. S3 The XRD pattern of commercial graphene.

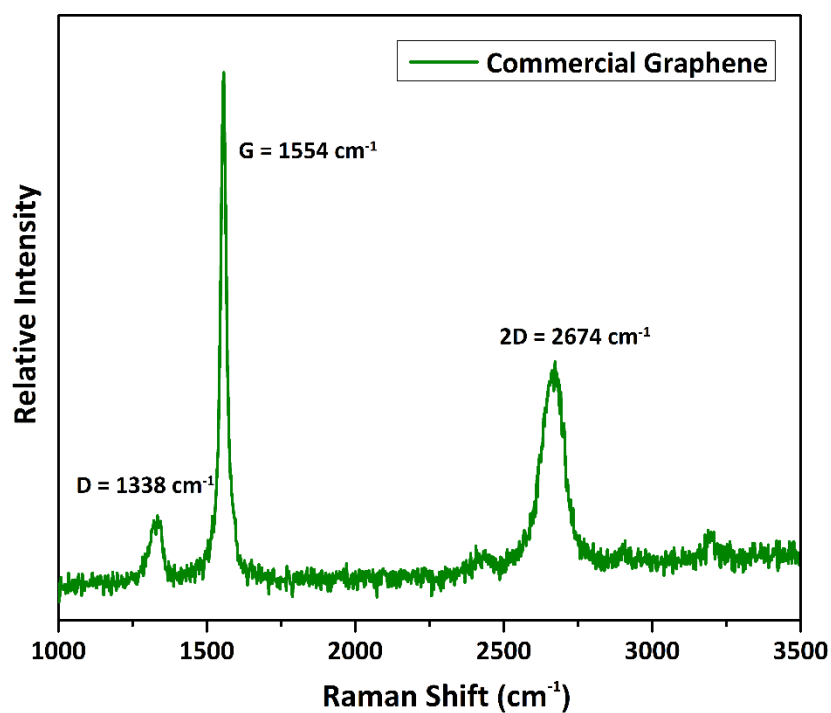


Figure 05. S4 The Raman spectrum of commercial graphene. ($I_D/I_G = 0.81$, $I_{2D}/I_G = 0.87$)

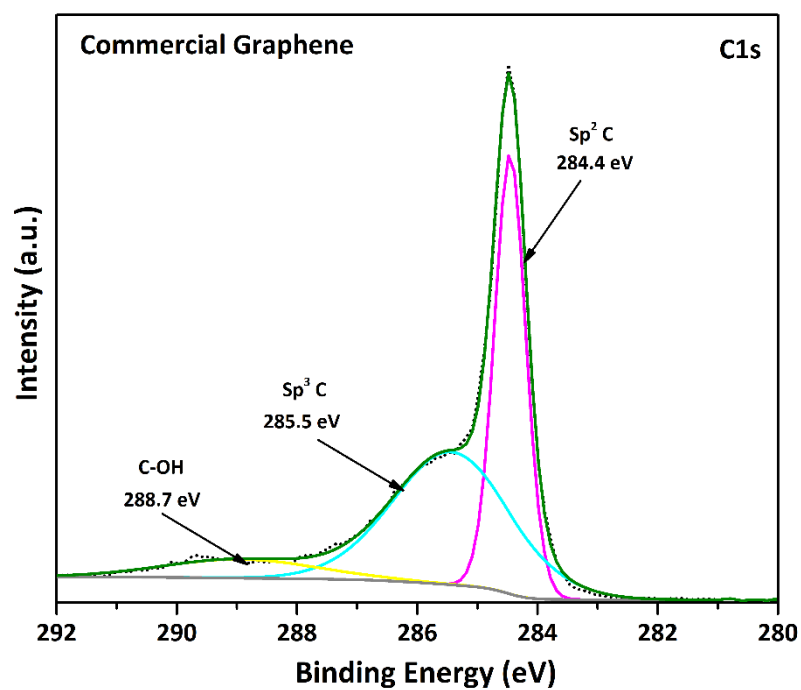


Figure 05. S5 The XPS C1s spectrum of commercial graphene

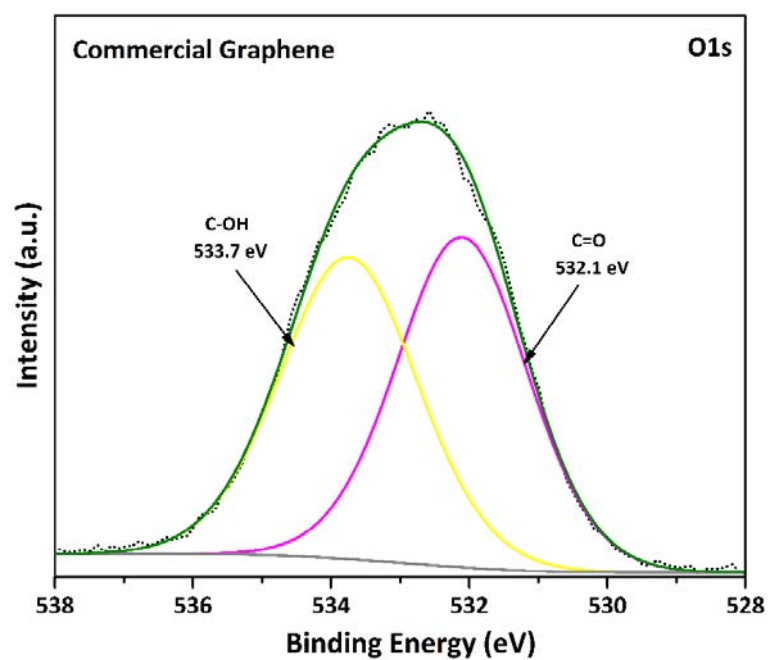


Figure 05. S6 The XPS O1s spectrum of commercial graphene.

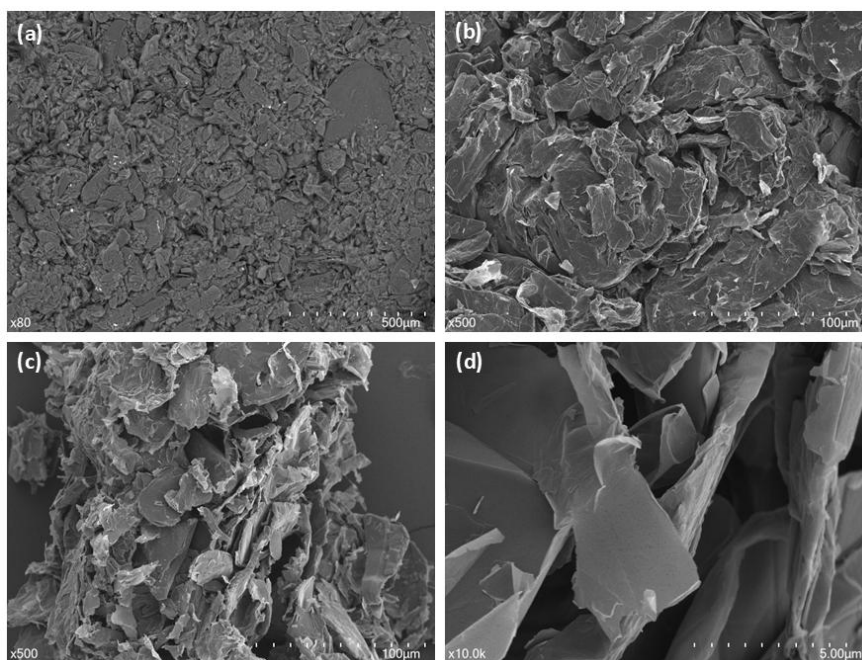


Figure 05. S7 The SEM images of commercial graphene.

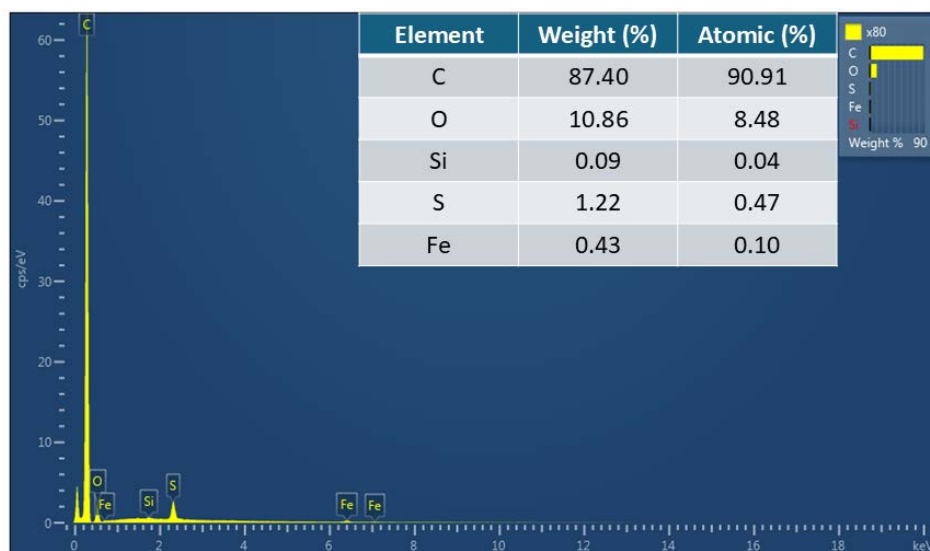


Figure 05. S8 The EDX analysis of commercial graphene.

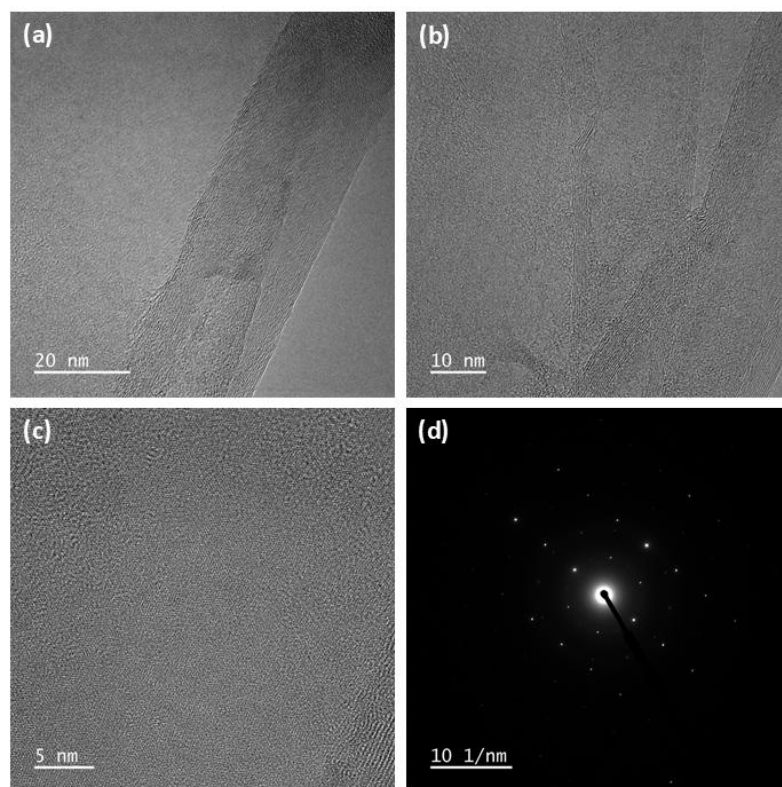


Figure 05. S9 The HRTEM images (a-c) and SAED pattern of commercial graphene (d).

In Chapter 04, to support Section 4.2.2.3: Preparation of TC & TC-GO Water Suspension, images were included to illustrate the behaviour of TC and TC-GO in water before using the ultrasonic mixer.

- Image (a) shows TC in water and PC, where TC remains floated on the water-PC mixture.
- Image (b) shows TC-GO in water and PC, where TC-GO is more dispersed compared to TC. This is due to the presence of oxygenated functional groups in TC-GO, making it more hydrophilic.
- Image (c) presents TC, TC-GO, and graphene in water and PC, highlighting that graphene does not dissolve well in water.

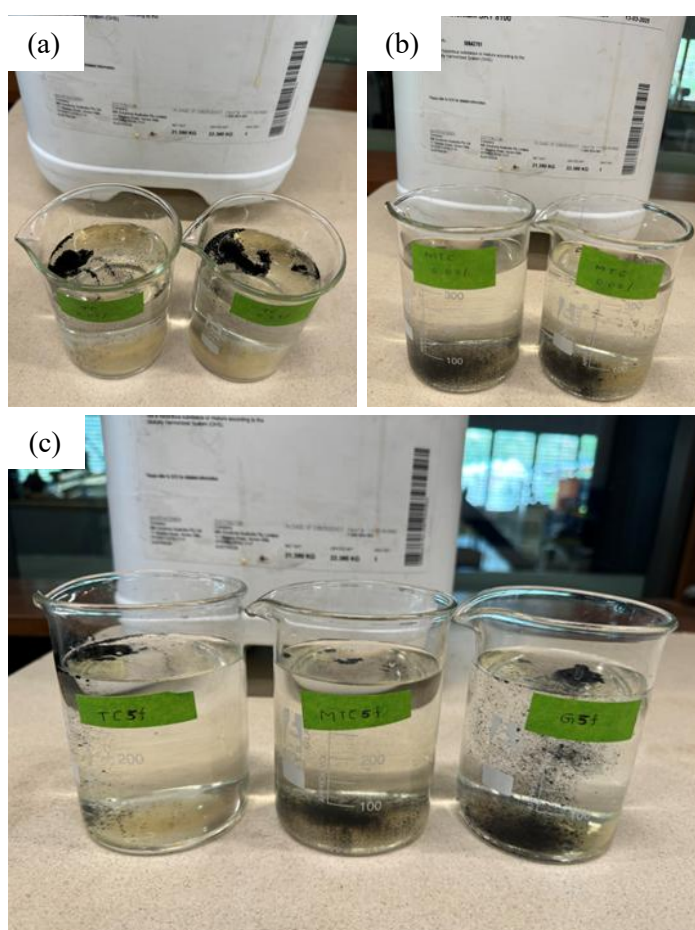


Figure 05. S10 Before dispersion process (a) TC in water-PC (b) TC-GO in water-PC (c) TC (left)/TC-GO (middle)/Graphene (right) in water-PC.

In Chapter IV, Flow table tests and strength tests were conducted for commercial graphene as well.

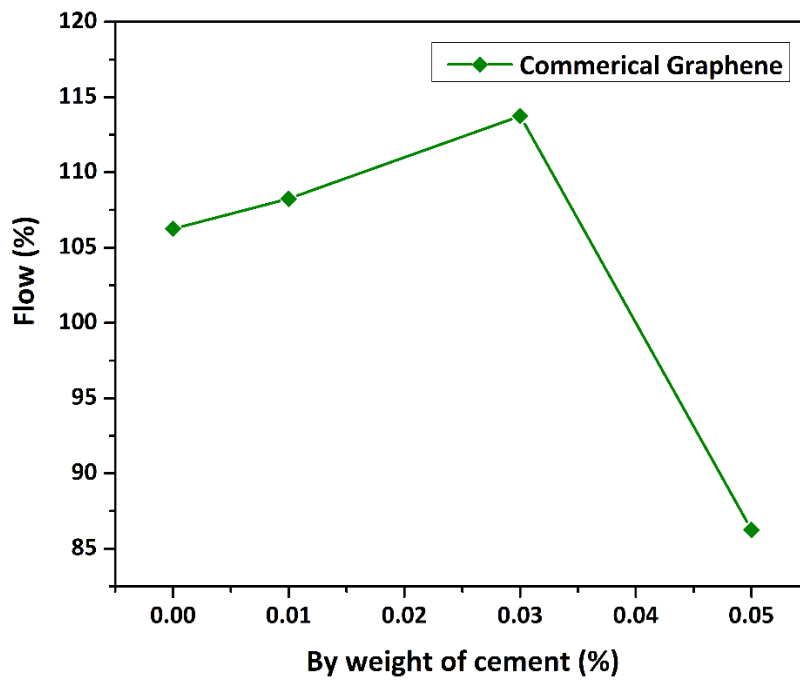


Figure 05. S11 The Flow table test results of commercial graphene.

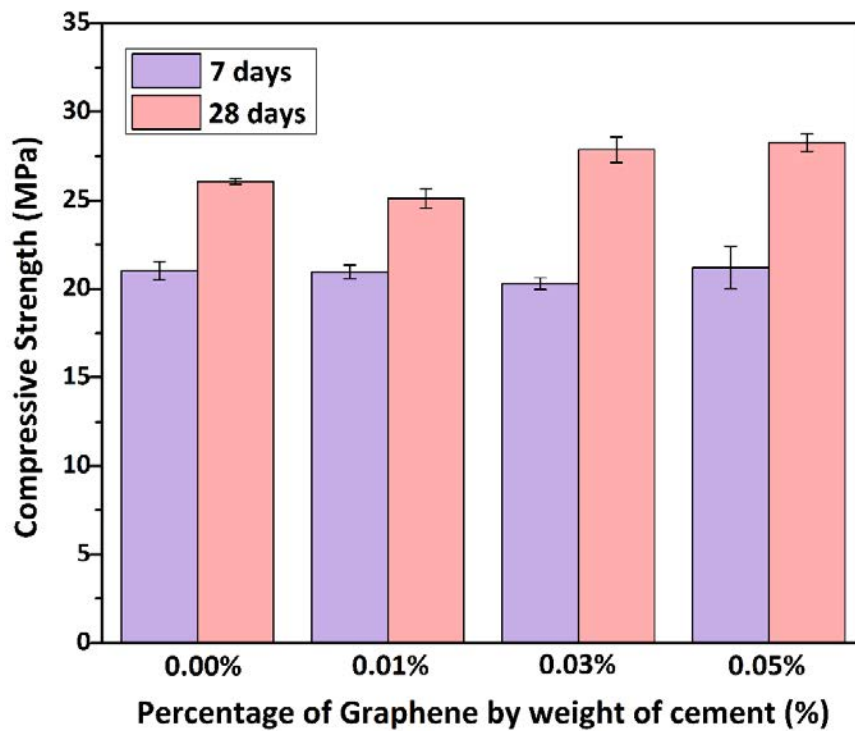


Figure 05. S12 The Compressive strength of Graphene incorporated cement mortar in 7 and 28 days.

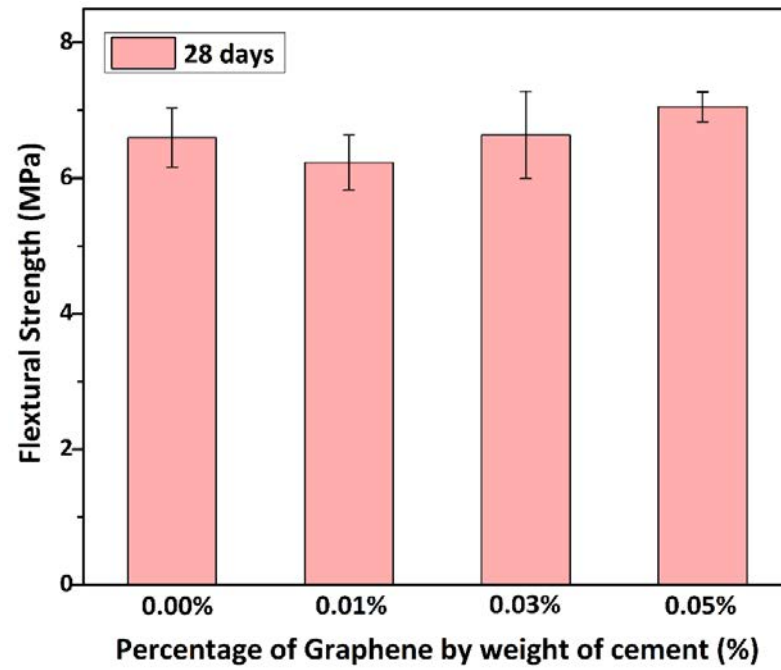


Figure 05. S13 The Flexural strength of Graphene incorporated cement mortar in 28 days.

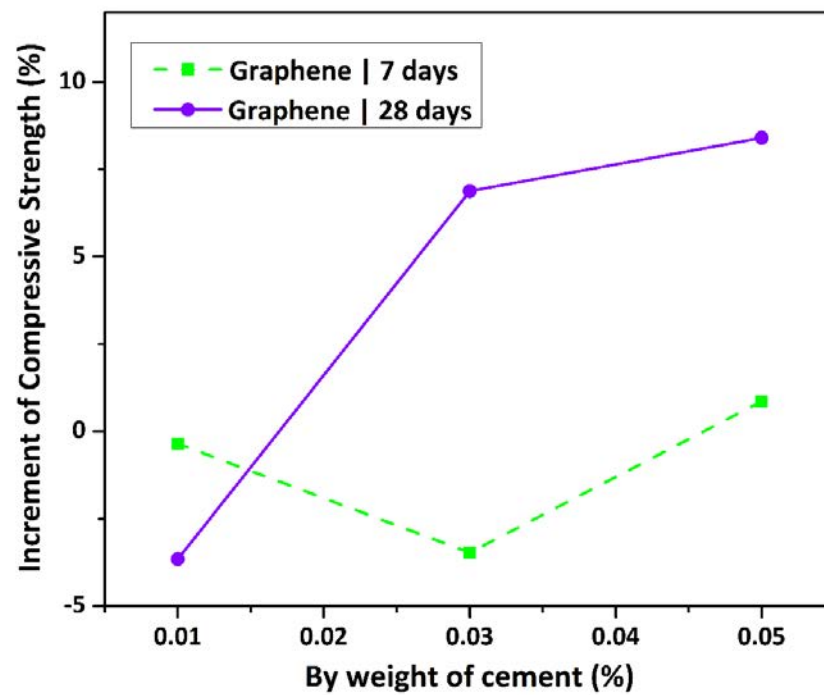


Figure 05. S14 The Compressive strength increment of Graphene added cement mortar in 7 & 28 days.

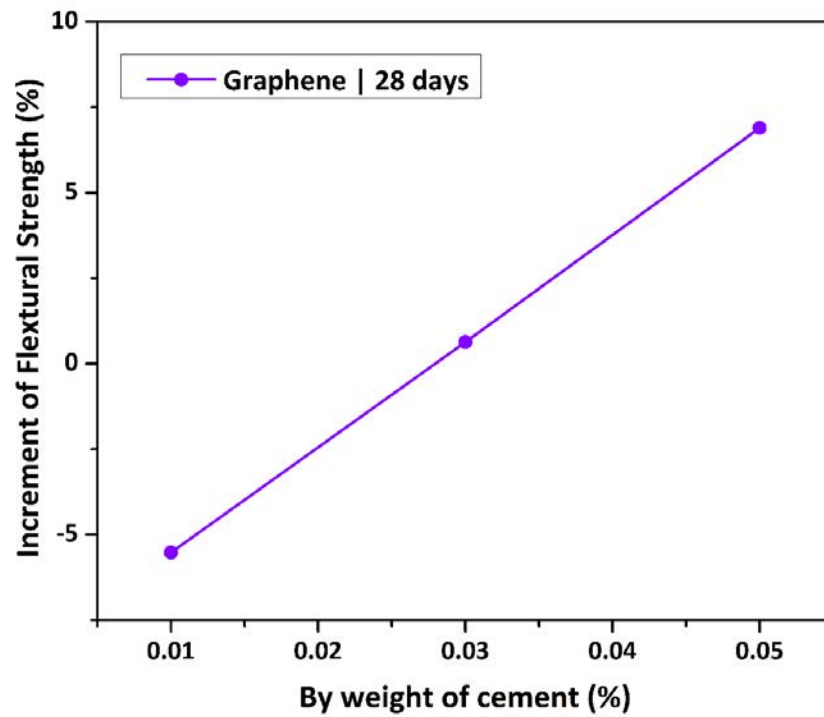


Figure 05. S15 The Flexural strength increment of TC and TC-GO added cement mortar in 28 days.

For the cement mortar preparation, the water-to-cement ratio was set at 0.75 (337.5/450). Adjustments for the water-to-cement ratio and aggregate moisture content were made accordingly. For that the Saturated surface dry (SSD) test was conducted. The following diagrams show the SSD test and its steps.

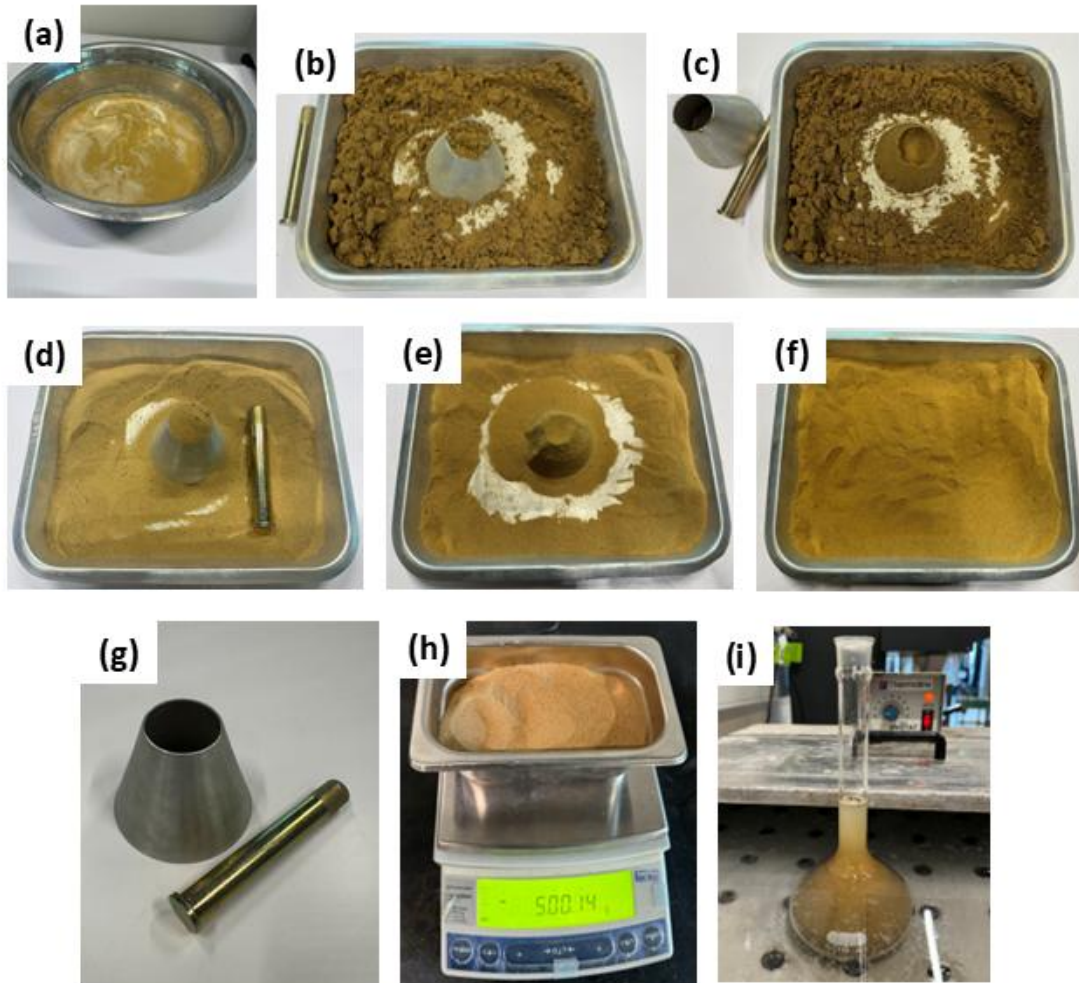


Figure 05. S16 The SSD test (a) sand immersed in water for 24 hours (b-c) Before SSD condition (d-f) SSD condition (g) Mold and tamper for SSD test (h) SSD sand for Gravimetric Procedure (i) Pycnometer and SSD sand

The calculation of Adjusting Mix Designs Based on Saturated Surface-Dry Conditions is shown below.

Water-to-Cement Ratio and Aggregate Moisture Corrections

The following information is obtained from the initial mix design:

1. Cement – 450 g
2. Water – 337.5 g
3. Fine aggregate (Sand) – 1350 g
 - Absorption – 0.945 %
 - Moisture content – 0.

Absorption Calculation

$$A = \frac{W_{SSD} - W_{OD}}{W_{OD}} \times 100\%$$

A = Absorption

W_{SSD} = Weight-saturated surface-dry aggregate

W_{OD} = Weight oven-dry aggregate

$$A = \frac{500.14 - 495.06}{495.06} \times 100\%$$

$$A = 1.026 \%$$

Moisture Content Calculation

$$MC = \frac{W_{initial} - W_{OD}}{W_{OD}} \times 100\%$$

MC = Moisture Content

$W_{initial}$ = Weight of the sample before drying

W_{OD} = Weight of the sample after drying

$$MC = \frac{250.00 - 248.99}{248.99} \times 100\%$$

$$MC = 0.405 \%$$

The moisture content is below the absorption value, the fine aggregates absorbed a portion of the mixed water.

The amount of water absorbed by the fine aggregate is calculated as:

$$\begin{aligned} \text{Water Absorbed} &= (\text{Absorption} - \text{Moisture Content}) \times \text{Weight of Fine Aggregate} \\ &= (1.026 \% - 0.405 \%) \times 1350 \text{ g} \\ &= 8.38 \text{ g} \end{aligned}$$

The adjusted water content becomes:

$$\text{Corrected Water} = 337.5 \text{ g} - 8.38 \text{ g} = 329.12 \text{ g}$$

$$\begin{aligned} \text{Corrected Water-to-Cement ratio} &= \frac{\text{Corrected Water}}{\text{Cement}} \\ &= \frac{329.12 \text{ g}}{450 \text{ g}} = 0.73 \end{aligned}$$