

# **Synthesis and Characterization of Pillared Graphene and Holey Graphene**

**By**

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## DECLARATION

I, Rinae Makhado, hereby declare that the dissertation for Master's degree in Chemistry at the University of Venda, hereby submitted by me, has not been submitted for any other degree at any other university or tertiary institution. The dissertation does not contain any other persons' writing unless specifically acknowledged and referenced accordingly.

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Dr M.A. Legodi

## DEDICATION

This dissertation is dedicated to my mother, Gangashe T.S.; thank you for your prayers, support, guidance, and words of encouragement for me to finish this research. To my late dad (Makhado Rudzani Robert), my siblings (Makhado Rudzani and Makhado Ndamulelo), my little man who joined us along the way (Tshikovha Nduvho), and Mr Tshikovha T., thank you for your emotional and financial support, your guidance and your advice throughout this study, thank you for making me see this adventure through to the end

Finally, I dedicate this dissertation to my supervisor, Prof. T. van Ree. Thank you for your guidance, support, comments you shared that were beneficial in the completion of this study, and patience throughout this study. Thank you so much.

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## ACRONYMS AND ABBREVIATIONS

|             |                                                |
|-------------|------------------------------------------------|
| <b>BET</b>  | <b>Brunauer-Emmett-Teller</b>                  |
| <b>CV</b>   | <b>Cyclic voltammetry</b>                      |
| <b>DEC</b>  | <b>Diethyl carbonate</b>                       |
| <b>DMC</b>  | <b>Dimethyl carbonate</b>                      |
| <b>EC</b>   | <b>Ethylene carbonate</b>                      |
| <b>EIS</b>  | <b>Electrochemical impedance spectroscopy</b>  |
| <b>EV</b>   | <b>Electric vehicle</b>                        |
| <b>FTIR</b> | <b>Fourier-transform infrared spectroscopy</b> |
| <b>GO</b>   | <b>Graphene oxide</b>                          |
| <b>HEV</b>  | <b>Hybrid electric vehicle</b>                 |
| <b>hGO</b>  | <b>Holey graphene oxide</b>                    |
| <b>IR</b>   | <b>Infrared spectroscopy</b>                   |
| <b>LIB</b>  | <b>Lithium-ion battery</b>                     |
| <b>PC</b>   | <b>Propylene carbonate</b>                     |
| <b>hGO</b>  | <b>Holey graphene oxide</b>                    |
| <b>pGO</b>  | <b>Pillared graphene oxide</b>                 |
| <b>rGO</b>  | <b>Reduced graphene oxide</b>                  |
| <b>SEM</b>  | <b>Scanning electron microscopy</b>            |
| <b>TEM</b>  | <b>Transmission electron microscopy</b>        |
| <b>XRD</b>  | <b>X-ray diffraction analysis</b>              |

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## ABSTRACT

Pillared graphene (pG) and holey graphene (hG) are derivatives of graphene designed to overcome issues with agglomeration and restacking between graphene sheets, which limit surface area and ion diffusion. These two types of graphenes have enhanced catalytic properties due to holes and pillars between the sheets. Graphene oxide (GO) is synthesized from graphite using Tour's method and then reduced to reduced graphene oxide (rGO) with ascorbic acid as a reducing agent. Pillaring agents (maleoyl chloride, fumaryl chloride, oxalyl chloride) are inserted using Friedel–Crafts acylation, and holes are created using gradual thermal annealing. The infrared spectroscopic data confirmed the presence of polar groups such as hydroxyl and carboxyl groups on GO and rGO indicating that both GO and rGO were synthesized successfully. On IR analysis of the pillared graphenes synthesized using the three pillaring agents (maleoyl chloride, fumaryl chloride, oxalyl chloride) and the holey graphenes, it reveals the various vibrational stretches such as C-H, C=O, C=C, and C-O stretches at specific wavenumbers. The functionalized holey graphenes also showed similar vibrational bands. Overall, the results indicate successful synthesis of both pillared and holey graphenes using three different pillaring agents. XRD confirms the reduction of GO to rGO, this is evidenced by a decrease in interlayer spacing and the absence of an OH functional group in the IR spectra. It also reveals that the pillared graphene and holey graphene materials are fairly crystalline and also shows that the materials are amorphous. SEM showed that the holey graphenes comprise grains that are very tightly packed and compact. The low-resolution SEM micrographs confirm the XRD results, that the materials are amorphous. TEM analysis confirmed the presence of pores in the holey graphene - **hrGOFC0.15**, **hGOMC0.15**, and **hrGOOC0.15** layers; therefore, the holey graphenes were successfully synthesized.

**Keywords:** Graphene, graphene oxide, reduced graphene oxide, anode material, lithium-ion batteries.

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## CHAPTER 1: INTRODUCTION

Pillared graphene and holey graphene are innovative structural derivatives of graphene or graphene oxide that have gained a lot of attention due to their unique properties and their uses in a variety of scientific and technological fields. These two structural derivatives of graphene were designed to minimize the agglomeration and restacking of graphene nanosheets that occurs during electrode assembly by modifying the physicochemical properties of reduced graphene oxide (rGO). Graphene is a highly promising candidate for electrochemical energy storage applications due to its fascinating physicochemical properties, particularly in lithium-ion batteries due to their remarkable properties. However, they suffer from unsatisfactory areal or volumetric energy density and relatively poor rate performance, which results in a limited accessible surface area and poor ion diffusion capacity caused by the agglomeration and restacking of graphene nanosheets during electrode assembly (Liu, Zhang, *et al.*, 2020).

Graphene is made up of a single layer of atoms arranged in a planar honeycomb pattern, while pillared graphene (pG) is a graphene that consists of parallel graphene sheets separated by spacers, such as carbon nanotubes (CNTs) that act like pillars and support the graphene sheets. The insertion of pillars creates efficient pathways for ions while expanding the electrochemically active surface area. On the other hand, holey graphene is a graphene with holes created at the basal plane of graphene sheets; the creation of holes on graphene sheets increases the specific surface area, improves ion transport channels, and boosts chemical, mechanical, and thermal stability (Zhang, Wan and Yang, 2019). This structural modification facilitates ionic diffusion and boosts ion access across the whole surface, leading to superior electrochemical performance of the energy storage devices. Thus, these materials represent a significant advancement in the development of high-performance energy storage devices. However, in this study, the pillared graphene and holey graphene materials will be prepared for application in lithium-ion batteries.

Ever since Sony first launched lithium-ion batteries (LIBs) in the early 1990s, they have been used widely in many electronic devices such as smartphones, laptops, toys, and home appliances, as well as in electric cars and energy storage systems. This fast growth of lithium-ion batteries can be ascribed to advantages like higher output voltage, greater energy density, lower weight, no memory effects, longer life cycles, and a smaller environmental impact than conventional rechargeable batteries. A lithium-ion battery is a battery that uses lithium ions to store energy. Most of these batteries use carbon-based materials like graphene oxide or rGO as

their negative electrode material because of their excellent electrical conductivity, large surface area, high electron mobility, and exceptional ability to conduct electricity. This material has proved to be a fascinating electrode material for electrochemical energy storage devices.

## 1.1 ENERGY STORAGE DEVICES

Although energy production from renewable sources is becoming important, reliable and safe energy storage devices are important. High-capacity batteries are key to supporting the growth of renewable energy. Today, the lithium-ion battery (LIB) is a popular form of storage device, because of many advantages such as high energy density and good environmental impacts, with the expectations that LIBs will continue to dominate portable energy storage systems for many years to come. Most lithium-ion batteries use carbon-based or graphitic negative electrode materials; this is because of the carbon's low electrode potential. Graphene is a carbon allotrope that is widely used because of its superior electrical conductivity, high surface area (theoretical value of  $2630 \text{ m}^2 \text{ g}^{-1}$ ), high thermal conductivity of  $5000 \text{ W m}^{-1} \text{ K}^{-1}$ , and excellent carrier mobility.

## 1.2 COMPONENTS OF Li-ION BATTERIES

### 1.2.1 The Electrolyte

The electrolyte, an essential LIB component, acts as a medium that allows ions to be transported between the anode and the cathode during the charging and discharging processes. It can be in the form of a liquid, gel, solid, or polymer. Because of the close interaction between the cathode, anode, and separator, the electrolyte not only transports lithium ions via the internal circuit but also influences the battery capacity, cycle stability, and safety. The performance of Li-ion batteries, especially lifetime and power capabilities, depends a lot on the type of electrolyte used. The electrolyte's ionic conductivity influences how quickly a battery can be charged or discharged. While the electrolyte plays a background role in the battery, it also interfaces (Fig. 1) with both electrodes; therefore, the electrolyte must remain stable in its interactions with both the anode and the cathode surfaces during operation of the battery.

Most commercial LIBs use electrolytes made from non-aqueous solutions that contain lithium salts like  $\text{LiClO}_4$ ,  $\text{LiFePO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiBOB}$ , or  $\text{LiPF}_6$ . These salts are dissolved in a mixed solvent

mixture with high ionic and electronic conductivity (Balbuena and Wang, 2004), such as the organic carbonates diethyl carbonate (DEC), dimethyl carbonate (DMC), ethylene carbonate (EC), ethyl methyl carbonate (EMC), and propylene carbonate (PC). These electrolytes allow a battery to charge and discharge many times.

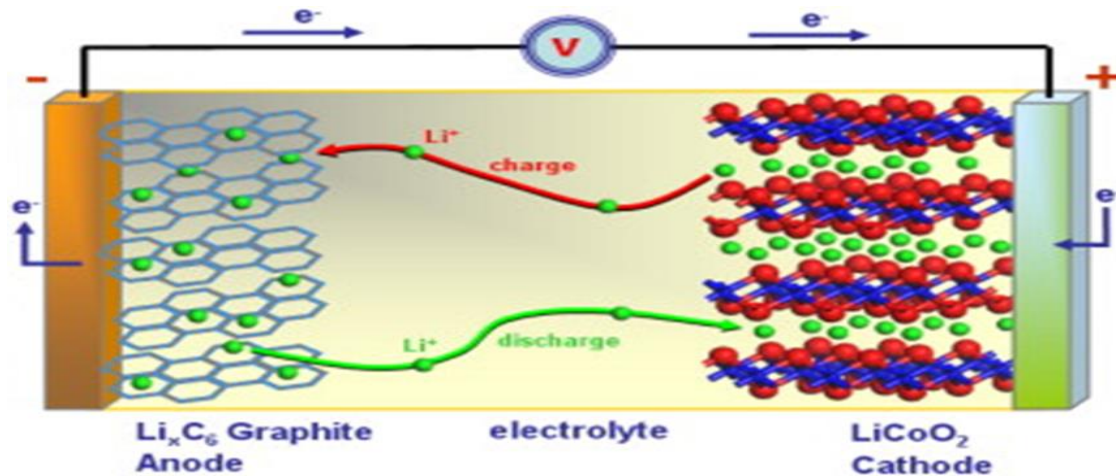


**Figure 1:** Charge/discharge processes in LIBs (Bruce *et al.*, 2008).

### 1.2.2 The Cathode

The positive electrode consists of a host network storing lithium ions that are then reversibly withdrawn when charging, as illustrated in Fig. 1. A good cathode material should have: a large storage capacity, a low resistance to lithium movement, a low chemical potential for lithium, good electrical conductivity and high stability to avoid structural changes during the charge or discharge process (Kotal *et al.*, 2022; Koech *et al.*, 2024; Stallard *et al.*, 2022; Gopalakrishnan *et al.*, 2025)

### 1.2.3 Anode Materials

The anode is the most important element of the LIB because it significantly affects the battery's performance. Rechargeable LIBs typically use carbonaceous materials such as graphene as anode material; this material acts as a structure that stores lithium ions during intercalation. Anode characteristics, such as its physical and chemical properties, ability to store energy, crystalline or amorphous states, and structural changes during the charge and discharge processes, can impact the performance of the battery (Lu, 2024; Su *et al.*, 2024).

### 1.3 GRAPHENE AS ELECTRODE MATERIAL

Graphene has attracted a lot of interest as a new electrode material because it conducts electricity very well, is very flexible, has a large theoretical surface area of  $2630 \text{ m}^2\text{g}^{-1}$  and can store about  $550 \text{ F g}^{-1}$  of electric charge (Zhu *et al.*, 2010; Sun *et al.*, 2011).

This material can accept and store lithium ions between its carbon layers and can maintain stable phases of up to  $\text{LiC}_6$  stoichiometry when intercalating lithium ions. Many researchers believe that graphene's unique properties can enhance the performance of various energy storage systems. This includes improving the mobility and driving range of EVs and HEVs, as well as making consumer electronics more efficient.

Scientists have studied graphene as a material with potential for a variety of uses, they have discovered carbon-based nanostructures like buckyball ( $\text{C}_{60}$ ), carbon nanotubes (CNTs), and different forms of graphene as potential materials for electronic, energy storage systems (supercapacitors and batteries), sensing and optical applications. Why is GO and its reduced product gaining traction among researchers? The answer is that both materials are useful in many applications where pristine graphene cannot be used, such as water filtration. Currently, the applications of graphene are primarily focused on the storage and conversion of electric and light energy to provide alternative energy sources that can replace fossil fuels, with examples including supercapacitors and lithium batteries, as well as photocatalysis applications to provide environmentally friendly devices (Fig. 2) (Askeland and Wright, 2015). In this study, the graphene materials are to be used on the anode electrode in the LIBs.

Graphene and its hybrids are a promising material for energy storage systems because of their interesting physicochemical features. However, these materials have an inferior areal or volumetric energy density and somewhat leads to a weak rate performance of the electrode. These limitations are caused by the agglomeration and restacking of graphene nanosheets during electrode assembly, which results in a limited accessible surface area, poor ion diffusion capability, and relatively poor rate performance (Liu, Zhang, *et al.*, 2020). This happens because of the strong  $\pi$ - $\pi$  interaction between graphene sheets which causes the graphene flakes to restack and form graphite-like powders and as a result the surface area reduces, subsequently, the movement of ions slows down and lowers the overall energy storage capacity. During the reduction process of GO to rGO, the number of sheets per stack increases meanwhile the surface area of reduced GO is reduced (Guo *et al.*, 2014).

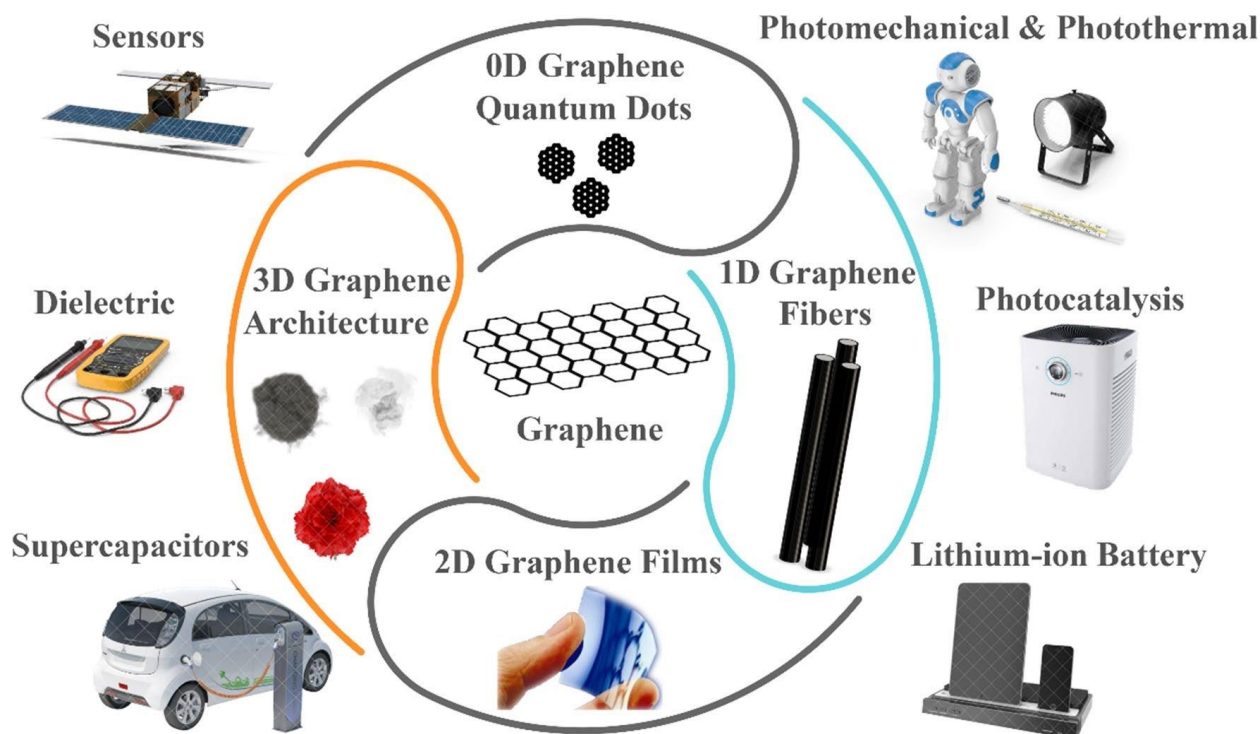


**Figure 2:** Schematic diagram of the classification of graphene and its derivatives based on dimension and application in specific energy storage (Askeland and Wright, 2015).

To solve the problems mentioned above, two novel graphene developments emerged: holey graphene and pillared graphene. These innovations aim to further decrease graphene sheet restacking and agglomeration by making holes in the GO or rGO sheets and inserting spacers or pillars (by cross-linking) between the graphene sheets with a bifunctional molecule to form cross-linked graphene stacks. The increased formation of holes and edges improves the catalytic properties of holey graphene over those of regular GO and rGO.

### 1.3.1 Holey Graphene

Holey graphene (hG) is a graphene derivative with many holes in its basal plane, with pore diameters varying from nanometers to microns. This special structural derivative has gained a lot of attention over the years due to its unique properties and versatility. Between 2010 and 2020 the number of articles focusing on hG has increased steadily (Figure 3) and this trend is expected to continue (Askeland and Wright, 2015; Rajput *et al.*, 2021). A stack of graphene layers with randomly spread holes is shown schematically in Figure 4.

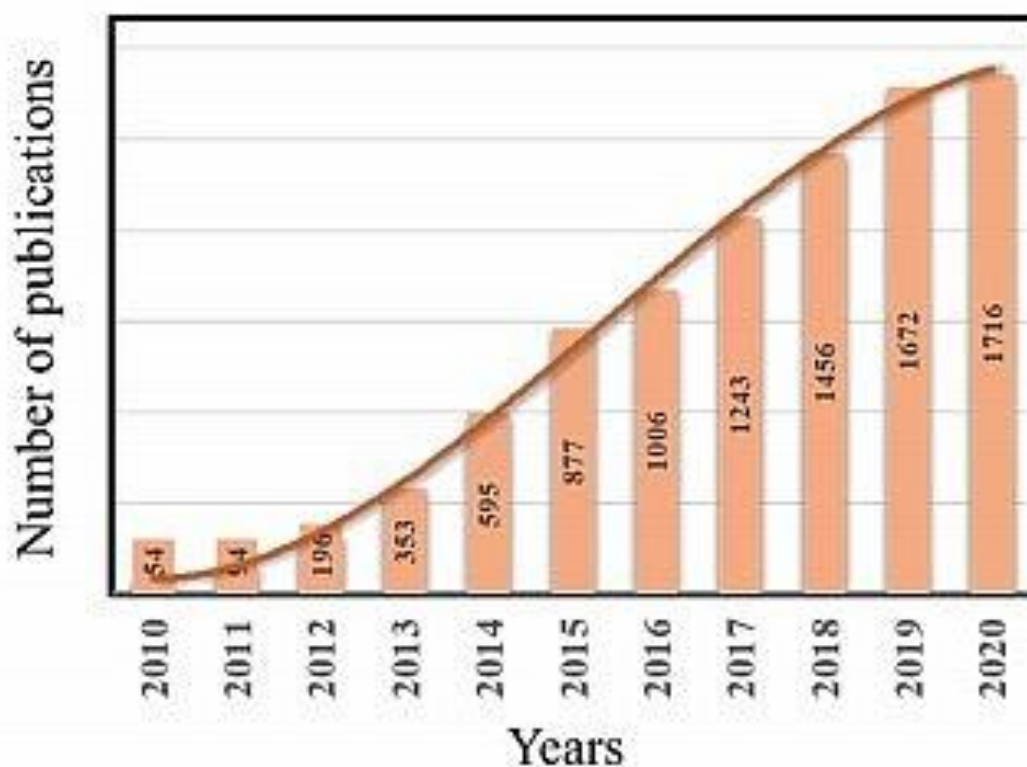


**Figure 3:** The steady increase in articles dedicated to holey or porous graphene from 2010 to 2020 (Rajput *et al.*, 2021).

Holey graphene has pores that create 3D channels, allowing ions and small molecules to move around freely throughout the material (Fig. 4). In contrast, graphite or graphene sheets without holes allow only movement in two dimensions. Thus, holey graphene sheets show the advantages of efficient ion transportation even when the sheets are stacked, better access of ions to electrode surfaces, and greater specific surface area. Furthermore, van der Waals forces between the sheets are weaker, so that the sheets' interlayer distances increase. The larger spacing between the sheets and the presence of many pores enhances the mass transport and ion mobility (Wang *et al.*, 2009; Xu, Lin, *et al.*, 2015). Holey graphene has already been applied in water desalination and purification (Boretti *et al.*, 2018; Cohen-Tanugi and Grossman, 2012; Surwade *et al.*, 2015; Wang *et al.*, 2018; Fa, 2020).



**Figure 4:** Schematic illustration of graphene and holey graphene forms. Initial 3D macroporous (a) graphene foam and (b) holey graphene foam. Compressed films of the (c) graphene foam and (d) holey graphene foam. Close-up views of (e) graphene and (f) holey graphene films. The arrows highlight the ion transport pathway (Xu, Lin, *et al.*, 2015).

### 1.3.2 Pillared Graphene

Pillared graphene (pG) consists of parallel graphene sheets separated by spacers, such as carbon nanotubes (CNTs) that act like pillars and support the graphene sheets. The entire structure (Fig. 5) can be compared to a skyscraper in its early phases, the floors represent graphene sheets, and the pillars are represented by CNTs, which do not enter from top to bottom, as demonstrated in Figure 6. Instead, they alternately go up and down, so that no two neighbouring CNTs on the same level face the same way. In addition, the structure has no expanding limits, and this is shown by the unfinished CNTs on the top and bottom of the structure (Fig. 5). Naturally, the length and intertube spacing of the CNTs can be changed at will to produce a material with tunable porosity.

The pillar molecule forms cross-linked graphene sheets with defined inter-sheet spacing. Using an optimal number of spacers, the pillared graphene materials show greatly enhanced active

surface areas, having a major impact on anode performance, especially the power capability (Burke and Miller, 2011; Pan *et al.*, 2017; Banda *et al.*, 2019).

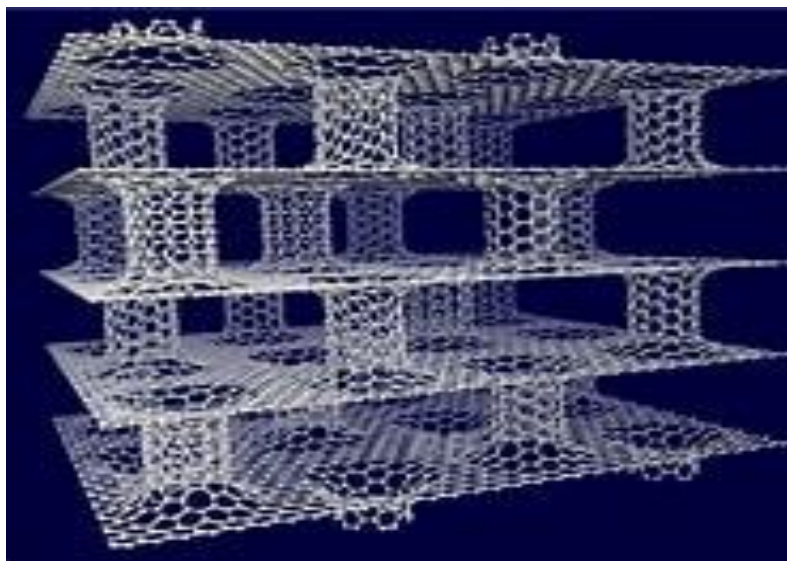


**Figure 5:** Schematic diagram of a pillared graphene (Banda *et al.*, 2018).

## 1.4 THE SIGNIFICANCE OF THE STUDY

The main aim of this study is to synthesize holey graphene and pillared graphene for use as anode materials in lithium-ion batteries to improve the performance and durability of lithium-ion batteries. A reproducible and scalable synthesis method for holey and pillared graphene materials is desirable because these modifications have been shown to enhance the material's properties, provides consistency in applications, and would support large scale production of electrode materials (Wang *et al.*, 2024; Zhou *et al.*, 2025). As technology advances, many regions in the world are experiencing rapid depletion of fossil fuels and significant environmental pollution. Because of this, more sustainable and renewable energy storage sources are required. Therefore, electrochemical energy storage systems such as fuel cells, supercapacitors, and batteries have been considered interesting candidates for energy storage. However, these electrochemical energy storage systems must be eco-friendly, reliable, and safe high-capacity energy storage devices. Batteries and supercapacitors are considered the primary electrochemical energy storage technologies on the market today (Peng *et al.*, 2018; Zhang, Shi, *et al.*, 2019; Choi *et al.*, 2020; Jia *et al.*, 2020.; Wang *et al.*, 2020).

Rechargeable Li-ion batteries have attracted a lot of attention among the rechargeable battery options because of their advantages like low weight, small size, and high voltage of lithium ions (Goodenough and Park, 2013; Hossain *et al.*, 2023). The modified and improved anode electrode materials in this study will be applied in LIBs, whereby these batteries will help not only store renewable energy for future use but they can also power the portable electronic devices that we use in our daily lives such as laptops, digital cameras, cell phone, smartwatch, and electric vehicles.

## 1.5 PROBLEM STATEMENT, AIMS AND OBJECTIVES

LIBs are of great interest because lithium is the lightest metal of all metallic elements; it is highly reactive and delivers a maximum capacity of 3860 mAh g<sup>-1</sup>. Compared to other battery technologies, they can last over 500 cycles of charge and discharge, and they have good stability. Each battery consists of four components: the electrolyte, a cathode (positive electrode), an anode (negative electrode), and a separator. The anode is usually made of carbon (graphite or graphene), and the cathode is composed of lithium metal oxides, such as lithium iron(II) phosphate (LiFePO<sub>4</sub>), lithium cobalt(III) oxide (LiCoO<sub>2</sub>), and lithium manganese(III/IV) oxide (LiMn<sub>2</sub>O<sub>4</sub>); hence, the electrolyte varies depending on the electrode materials used. A lithium-ion battery works on the principle of reversible storage and moving of lithium ions between the anode and the cathode of the cell (Lai and Ciucci, 2010). During the discharge process, lithium ions are transported from the anode through the electrolyte to the cathode, while electrons flow in the external circuit in the opposite direction, as shown in Figure 1. This movement converts chemical energy into electrical energy and the process reverses when charging.

### 1.5.1 Problem Statement

Graphene is commonly used as anode material for Li-ion batteries. However, graphene sheets tend to agglomerate and restack during electrode assembly, resulting in a decreased specific surface area, causing decreased accessibility for lithium ions and making it harder for them to move quickly; as a result, the battery energy density and performance become poor. This restacking is caused by the strong  $\pi$ - $\pi$  interactions between graphene sheets which causes the GO or rGO sheets to restack. Today, LIBs are popular storage devices because they have high energy density and are environmentally friendly. These rechargeable LIBs use carbonaceous materials such as graphene as anode material (negative electrode); this material acts as a host structure for lithium ions and can maintain a stable structure even when they store a lot of

lithium ions. Large crystallites with open porous structures present a higher surface area and allow more ions to access the outer surface (Yang *et al.*, 1998).

This tendency of graphene flakes to restack results in the formation of graphite-like powders or films, which reduces the accessible surface area and slows down the movement of lithium ions, and as a result the charge and discharge rates will be low leading to unsatisfactory energy storage.

Then, to address this problem, researchers developed new electrode materials that can significantly increase the energy density without losing the power density or cycle life (Simon and Gogotsi, 2008; Burke, 2007; Zhang and Zhao, 2009; Wang *et al.*, 2012). To reduce the graphitic restacking and agglomeration, the properties of GO/rGO are to be modified by creating holes in the graphene sheets because these holes increase the number of edges that can enhance the catalytic properties of holey graphene oxide (hGO) or holey reduced graphene oxide (hrGO) compared to regular GO/rGO. Additionally, inserting pillars between graphene sheets by cross-linking will highly enhance the electrochemically active surface area for the electrochemical reactions and an increased ion transportation effect which will enable the ions to access new active sites. The 2D layered materials with large spaces between the layers can facilitate ion diffusion and lead to a small diffusion barrier, which allows ions to be easily transported during the charging and discharging process (Tan, Lai & Zhang, 2017; Ji *et al.*, 2019). Holey graphene's large surface area and channels that facilitate ionic and molecular movement are distinctive properties of holey graphene. These features make it suitable for use in lithium-ion batteries as anode materials. Hence, using holey graphene as an anode in batteries or capacitors, the efficiency of the device is enhanced significantly, as shown by several research groups (Xu *et al.*, 2014; Xu, Lin *et al.*, 2015; Hu *et al.*, 2017; Lin *et al.*, 2017; Zhu *et al.*, 2019; Jeong *et al.*, 2019; Liu, Zhang *et al.*, 2020; Yang *et al.*, 2020).

Therefore, finding novel types of electrode materials and constructing a highly permeable durable carbon-negative electrode is important. These kinds of anode materials should allow ions and other molecules to move easily, they should have a high surface area which increases access for ions and leads to better energy storage and conversion. In general, a high-performance carbon electrode needs to have high electrical conductivity, a large surface area that's accessible to ions, a high ionic transport rate, and strong electrochemical stability. These features help ensure battery safety and an increased cycle performance. If battery safety is not ensured, this will result in an explosion or a fire, as shown by incidents (Crawford, 2013; Woo, 2020; Tweed, 2013) such as ignition of a Samsung Galaxy Note 7, fire of a Tesla Model S,

laptops, and other electronic devices, probably caused by faulty wiring causing short circuits, cell defects caused by lithium dendrite formation, or overcharging resulting in thermal runaway (Fig. 6). These carbonaceous anode materials have some other major shortcomings. They expand and contract a lot during the charging and discharging processes, causing internal stress and shortening the life cycle of these negative electrodes. The continuous expansion and contraction would lead to constant deposition of lithium ions, resulting in the formation of tree-like structures known as dendrites. As they continue to grow, the dendrites cause internal short-circuits between the electrodes, which may lead to thermal runaway and may cause an explosion or fire. Therefore, it is crucial to ensure that battery safety is a priority.



**Figure 6:** Incidents resulting from faults with LIBs (Crawford, 2013; Woo, 2020; Tweed, 2013).

### 1.5.2 Aims and Objectives of the Study

This study aims to synthesize holey graphene and pillared graphene for use as anode materials in lithium-ion batteries for improved performance and durability of LIBs, providing improved storage devices for commercial portable electronics.

Hence, this research seeks to achieve the following objectives:

- Synthesis of pillared and holey graphenes using low-cost efficient methods.
- Characterize the prepared samples using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), TEM, and X-ray diffraction (XRD) crystallography.
- To further investigate the morphology and electrochemical characteristics of reduced graphene oxides.
- Synthesis and characterization of novel electrode materials.

## CHAPTER 2: LITERATURE REVIEW

Graphene, a single-layer carbon atom arranged in a two-dimensional honeycomb pattern, it has many important applications because of its special mechanical, electrical, thermal, and chemical characteristics (Liu, Wang *et al.*, 2020; Ji *et al.*, 2019). Researchers believe that these unique qualities can enhance the efficiency of power storage applications. For example, to improve the mobility and driving range of EVs and HEVs, as well as to create efficient emerging consumer electronics, such as better battery systems. After the commercial introduction of the LIB in the late 20<sup>th</sup> Century, the early 21<sup>st</sup> Century has seen significant growth and improvements in electronic devices, along with the introduction of electric and hybrid vehicles. All these applications have become possible by the rapid development of power storage devices, most of them depending on carbon-based anode materials. Graphene is an excellent component for batteries due to its high surface area with a theoretical value of  $2630 \text{ m}^2 \text{ g}^{-1}$ , the high thermal conductivity of  $5000 \text{ W m}^{-1} \text{ K}^{-1}$ , excellent carrier mobility, good chemical, and thermal stability (Du *et al.*, 2008; Rao *et al.*, 2009; Edwards and Coleman, 2013). However, in the assembly of electrodes, the graphene sheets often restack; this self-restacking reduces the active surface area and slows down the movement of lithium ions, a major disadvantage in constructing high-performance batteries during electrode assembly. The graphene sheets tend to self-restack, causing a lower active surface area and lower ion transport kinetics, a major drawback in fabrication of high-performance batteries. This restacking is caused by the  $\pi$ - $\pi$  interactions between the sheets, which results in a decrease of the surface area, and reduced ion on diffusion rate resulting in unsatisfactory gravimetric capacitances (typically  $180 \text{ F g}^{-1}$  in organic electrolytes) and relatively low charge/discharge rates (Zhu *et al.*, 2010; Sun *et al.*, 2011; Miller *et al.*, 2010; Stoller *et al.*, 2008; Liu *et al.*, 2010).

To solve these problems, the characteristics of GO/rGO can be altered, primarily by adjusting the material's porosity and by preventing re-stacking of the graphene sheets by insertion of bifunctional spacer molecules. This approach will increase the interlayer spacing between sheets. 2D layered materials with large spacing between the layers can facilitate ion diffusion and lead to a lower diffusion barrier. As a result, lithium ions can be easily transported during the charge/discharge process (Ji *et al.*, 2019; Tan *et al.*, 2017) because the  $\text{Li}^+$  diffusion rate between graphene layers is mainly dependent on interlayer spacing (Han *et al.*, 2019).

Providing holes and pillars in graphene sheets enlarges the specific surface area, yields more ion transport channels, and improves chemical, mechanical, and thermal stability (Zhang, Shi *et al.*, 2019).

## 2.1 SYNTHESIS OF GRAPHENE OXIDE AND REDUCED GRAPHENE OXIDE

Many methods can be used to synthesize graphene oxide, but the most used method is the modified Hummers method. The Hummers method involves mixing graphite powder with sodium nitrate, potassium permanganate, and sulphuric acid (Hummers and Offeman, 1958). The main advantage of this method is that it is relatively inexpensive and highly scalable. It's a standard method for producing substantial quantities of graphene oxide and can be adjusted to create a thinner version of the material called few-layer graphene oxide.

However, there are certain drawbacks to using this method, such as the irreversible creation of defects on the graphene sheets. Other methods can be used to synthesize GO, like graphite exfoliation by pyrolysis (Lu *et al.*, 1999; Fredriksson *et al.*, 2009; Tang and Hu, 2012), using chemical vapor deposition (CVD) and reduction of graphene oxide. The graphene produced by micromechanical exfoliation and chemical vapor deposition has a good single-layer structure, but these methods are complex and only yield small amounts of graphene, which makes them unsuitable for large production and use. Therefore, this has led to finding an alternative method to synthesize GO and rGO, which is Tour's method (Marcano *et al.*, 2010), which was demonstrated to be more efficient, less hazardous, and environmentally friendly, for oxidizing graphite (Hirata *et al.*, 2004; Nakajima and Matsuo, 1994).

Ascorbic acid (L-AA) was used to reduce GO to rGO (Fernández-Merino *et al.*, 2010), because it is a mild reductant, is nontoxic and environmentally friendly. Originally, GO was reduced with hydrazine or hydrazine hydrate, but since these reductants are poisonous with high explosive potential (Furst *et al.*, 1965), they require careful handling especially when large quantities are used. For that reason, the focus has shifted to milder reaction conditions (Park and Ruoff, 2009), using natural, non-toxic, and environmentally friendly reducing agents like L-ascorbic acid that gives a good yield (Kumar and Kandelwal, 2014; Ding *et al.*, 2015). Therefore, direct reduction using ascorbic acid was implemented in this study.

Ambrosi *et al.* (2006) and Wang *et al.* (2008) used L-AA successfully as a preferred reductant for conversion of GO to rGO, and achieved a C/O ratio of about 12.5 and a conductivity of 77 S/cm.

## 2.2 PILLARED GRAPHENE

Pillared graphene is a type of graphene that consists of parallel graphene sheets that are separated by pillars and support the graphene sheets (Figure 7). This interesting kind of graphene oxide derivative was introduced some 20 years ago and was easily prepared by reacting the surface oxygen-containing functional groups with nucleophiles, such as primary amines (Bourlinos *et al.*, 2003). Pillared graphene aims to decrease graphene sheet restacking and thus provides extra sites for ion absorption. Positioning pillars between graphene sheets provides better ion transport and highly enhanced electrochemically active surface areas. The number of pillars in the galleries has a significant impact on anode performance, especially power capability.

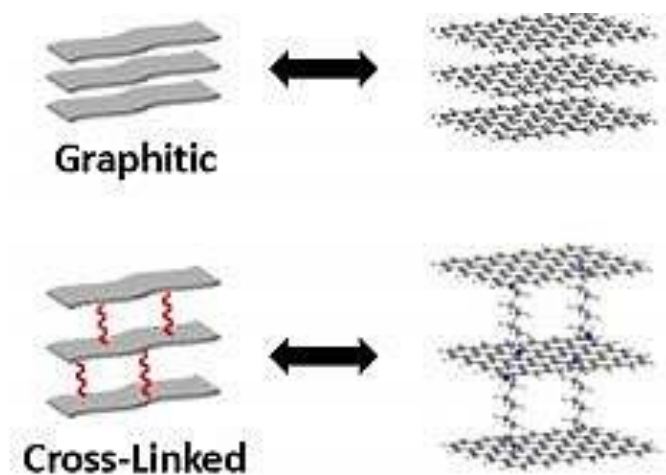
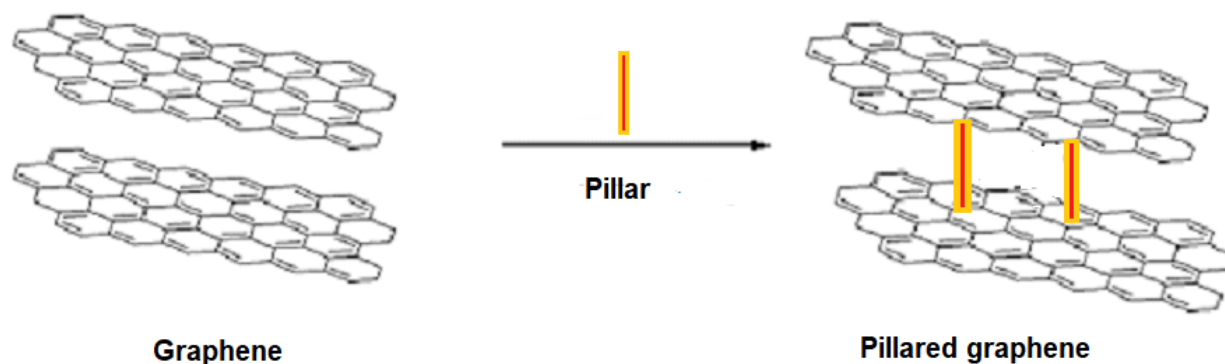


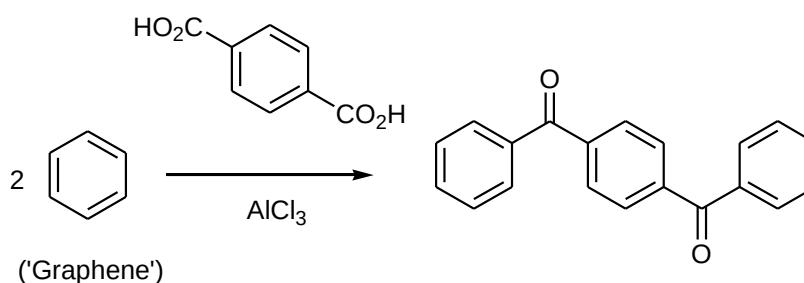
**Figure 7:** Schematic representation of graphitic and cross-linked domains (Banda *et al.*, 2019).

In this study, Friedel-Crafts acylation of the graphene aromatic rings with dioic acid chlorides was the method decided upon to insert pillars between graphene sheets. In this reaction, Lewis acid catalysts like  $\text{AlCl}_3$  are often used together with acid anhydrides, but acyl chlorides are more commonly used. Rearrangements do not occur, because the carbonium ion formed is stabilized by several resonance structures. It is also a simple procedure, the reagents used, such as  $\text{AlCl}_3$ , are inexpensive, achieving high yields of the desired product and can be

conducted under moderate conditions. In this study, different rigid and flexible pillar materials were reacted with rGO (Scheme 1) (e.g., Chua and Pumera, 2012).



#### Friedel-Crafts acylation (schematic):



**Scheme 1** Pillar insertion: (a) Schematic; (b) Example C-C bond forming reaction.

## 2.3 HOLEY GRAPHENE

Holey graphene has excellent electrical conductivity ( $>1\,000\text{ S m}^{-1}$ ), about one to two orders of magnitude higher than that of activated carbon ( $10\text{--}100\text{ S m}^{-1}$ ) (Chandrasekaran *et al.*, 2008) and also two times better than activated graphene which has a conductivity of  $500\text{ S m}^{-1}$  (Zhu *et al.*, 2019). The carbon-based electrode materials can be improved by creating pores in the materials such as graphene oxide (GO) or reduced graphene oxide (rGO), resulting in holey graphene oxide (hGO) or holey reduced graphene oxide (hrGO). These pores provide ions and molecules more freedom to move within the holey graphene material even when the sheets are stacked; the holes allow effective ion transport and enhanced mass transport, thanks to the pores and large spacings between the layers. In materials like graphite and multilayer graphene, the sheets have a tendency of restacking caused by the van der Waals interactions amongst the graphene sheets.

Holey graphene sheets with randomly spread holes over their surfaces (Fig. 8) can create a three-dimensional porous material, which is then called 'porous graphene' (Walsh *et al.*, 2016; Tao *et al.*, 2020). These pores form three-dimensional channels that allow ions to move freely throughout the material. Adding many pores increases the ions' access to the surface and boosts the specific surface area while minimizing restacking of the sheets. This will result in electrodes with large capacity for energy storage and conversion compared to the regular carbon-based anodes, because of the improved conductivity and stability.

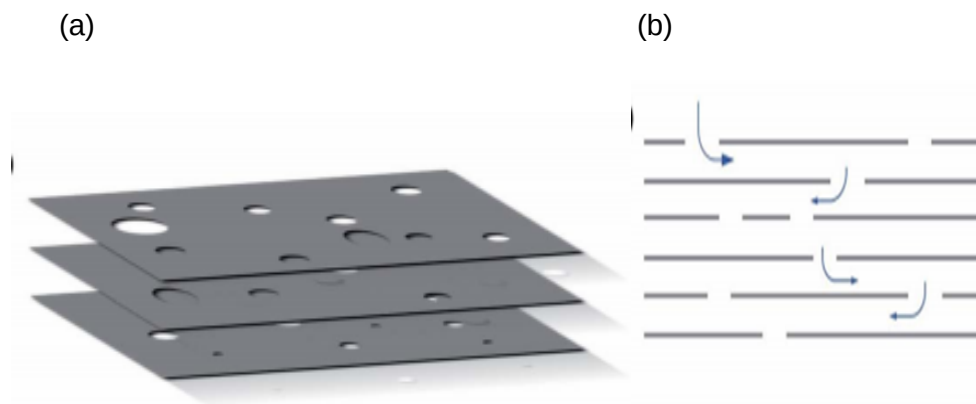


**Figure 8:** Schematic images showing (a) graphene sheets with nanopores; and (b) a stack of graphene sheets with randomly distributed nanopores forming interlayer channels, allowing smaller ions to pass through the graphene sheets (Rajput *et al.*, 2021).

There are various ways for creating holes in bulk graphene materials or sheets, such as physical, thermal, and chemical approaches and each can produce pores of different sizes, but all have their own advantages and disadvantages. The pores in graphene can be categorized into three types based on size: as microporous (<2 nm), mesoporous (2–50 nm), and macroporous (>50 nm) according to IUPAC definitions (Zdravkov *et al.*, 2007; Rouquerol *et al.*, 1994). The synthesis methods are discussed briefly below:

**(i) Physical: electron or ion beam irradiation:** Fischbein and Drndić (2008) showed that an electron beam (such as a 200 kV TEM source) passing energetic electrons or ions through a graphene layer can generate nanopores in the graphene sheet (Figure 9).

Similarly, a focused ion beam (FIB) will also produce pores in a graphene sheet. Because any ions are more massive than electrons, the transfer of momentum is easier with an ion beam. For example, Wang *et al.* (2016) were able to make nanometer-sized holes through a single graphene layer with a 30 kV gallium ion beam.

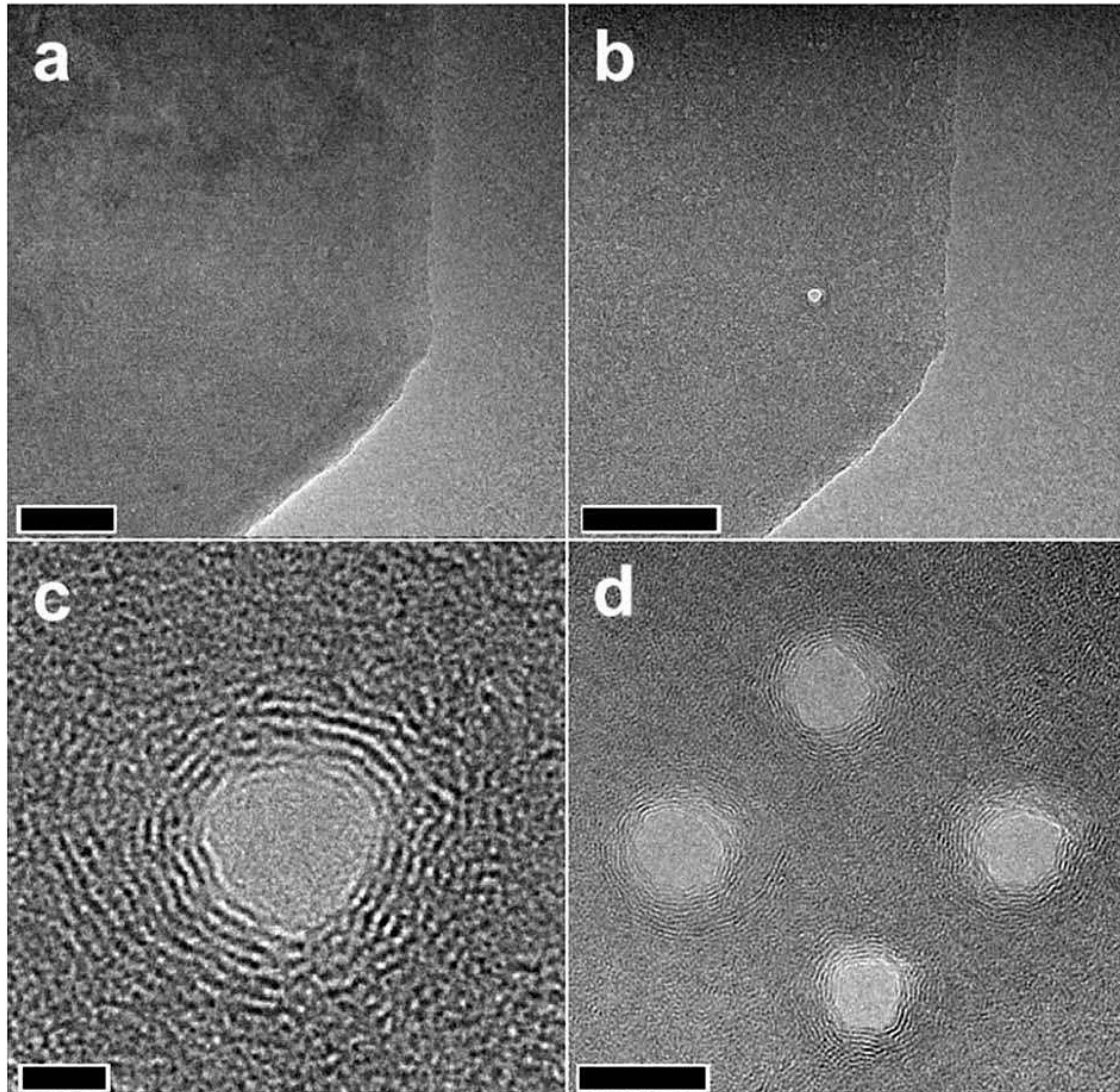


**Figure 9:** TEM images show a graphene sheet (a) before and (b,c,d) after creation of a nanopore by an electron beam. Scale bars are 50, 50, 2, and 10 nm, respectively. (Fischbein and Drndić, 2008).

**(ii) Thermal annealing method:** Holey graphene can be formed by heat treatment of GO or rGO (Peng *et al.*, 2015; Wu *et al.*, 2017; Su *et al.*, 2021).

- **Rapid thermal annealing (RTA):** Certain functional groups are destroyed by heating of GO or rGO at a suitable temperature, and gases such as  $\text{CO}_2$  are formed (Yang *et al.*, 2015). As  $\text{CO}_2$  is released, pressure builds up between the layers, resulting in a high pressure that can blow holes through the graphene sheets (Fig. 10).
- **Gradual thermal annealing (GTA):** Walsh *et al.* (2016) created hG from graphene sheets by heating graphene in the air at a specified temperature and time.

Both techniques can be used to produce promising hG materials for application in energy storage devices.

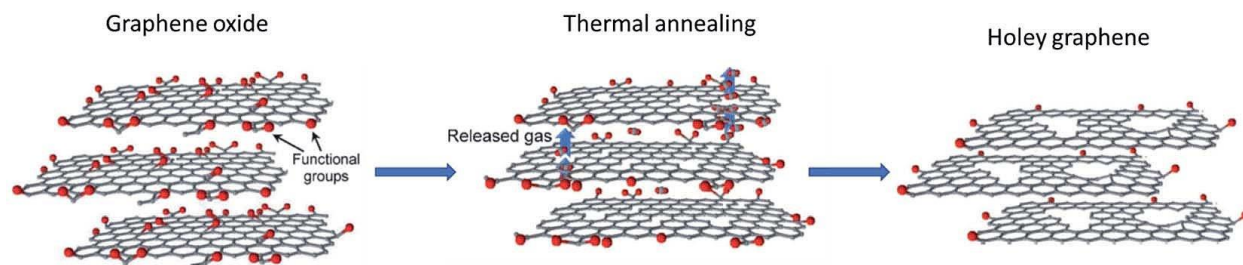


**Figure 10:** Holey graphene is synthesized from graphene oxide by rapid thermal annealing (Yang *et al.*, 2015).

**(iii) Chemical methods:** It is also possible to create pores by chemical etching with reagents such as  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ , and  $\text{KOH}$  to directly generate pores in graphene sheets ranging from nm to a few microns.

**(iv) Nanoparticle-assisted oxidation (catalytic oxidation):** Seo *et al.* (2017) proposed a chemical patterning method using a covalent organic framework of  $\text{Fe(III)}$  complexed with porphyrin as a template.

**(vii) Chemical etching:** Zhao *et al.* (2011) synthesized hGO from a dispersion of GO in  $\text{HNO}_3$ ; in the process carbon atoms are removed from the GO sheet, resulting in the formation of nanopores 7 to 600 nm in diameter. Chang *et al.* (2016) also used  $\text{HNO}_3$  (Figure 11) to prepare holey graphene electrodes using self-assembled 3D graphene consisting of nanoporous graphene flakes (2.5 nm) for use in a high-performance supercapacitor. Xu, Chen, *et al.* (2015) used  $\text{H}_2\text{O}_2$  as an etching agent by heating it for 4 h with GO at  $100^\circ\text{C}$  and stirring to produce hGO (Fig. 12).

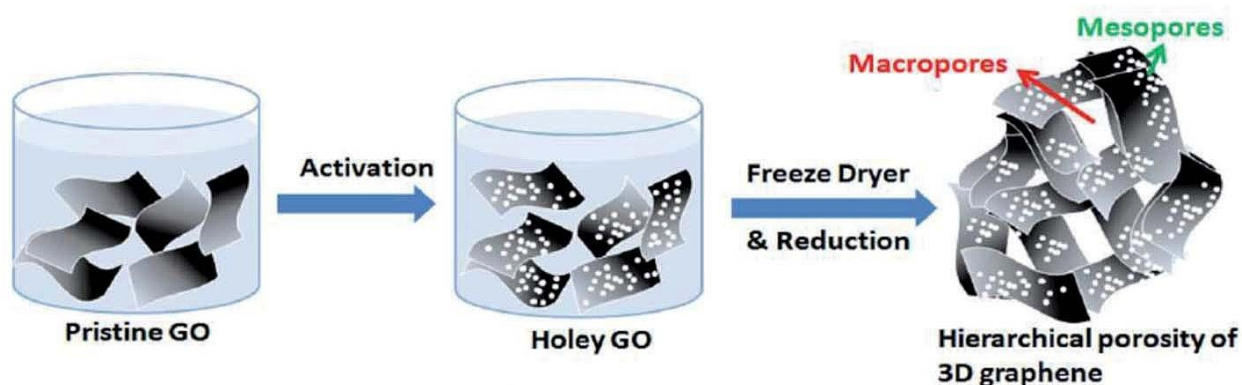


**Figure 11:** Obtaining porous 3D graphene (Chang *et al.*, 2016).

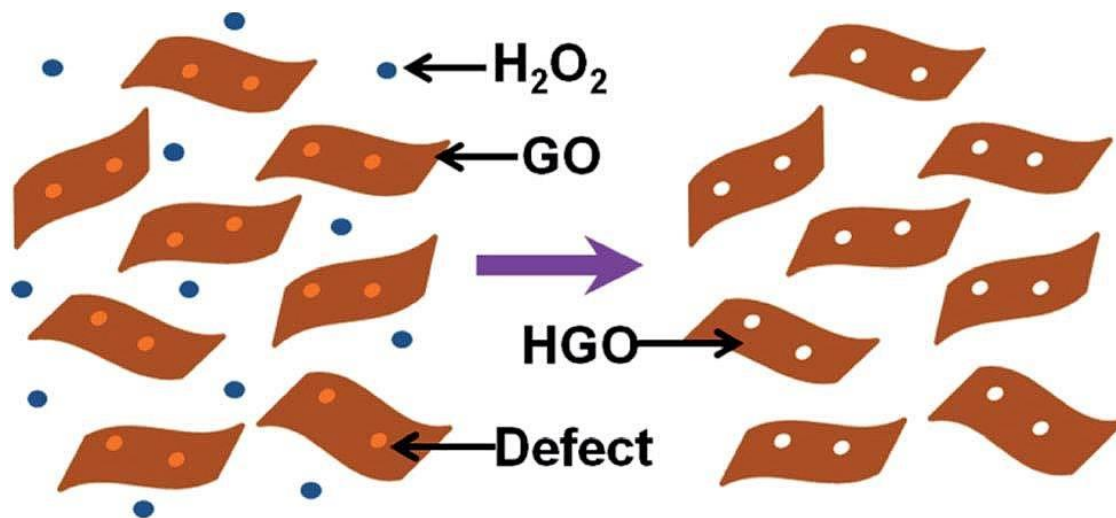


**Figure 12:** Synthesis of holey GO (Xu, Chen *et al.*, 2015).

## CHAPTER 3: RESULTS AND DISCUSSION

The following objectives are achieved in the analysis of results:

- Synthesis of pillared and holey graphene using low-cost efficient methods.
- Characterize the prepared samples using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), TEM, and X-ray diffraction (XRD) spectroscopy.
- Synthesis and characterization of novel electrode materials.

FTIR spectra, XRD spectra, SEM micrographs and TEM images were recorded for all GO and rGO samples, pillared graphene and holey graphene samples. The sample codes were derived as follows:

FC    fumaryl pillars  
GO    graphene oxide  
h     holey  
MC    maleoyl pillars  
OC    oxalyl pillars  
r      reduced

0.15, 0.20, 0.30 = the number of millimoles of the dichloride reacted with 80 mg GO or rGO.

Therefore, for example, **hrGOOC0.20** represents holey reduced graphene oxide with 0.20 mmol added oxalyl pillars.

### 3.1 IR SPECTROSCOPY

FTIR spectroscopy is an important tool used to study and identify chemical compounds and functional groups in materials. In this study, FTIR was used to determine the efficacy of introducing oxygen-containing functional groups into the carbon lattice, as well as to explore the structure and functional groups in graphite, GO, rGO, pillared graphene, and holey graphene. When infrared light passes through a sample, some of the light is absorbed by the sample's molecular vibrations while the rest goes through the sample. The FTIR detects the molecular vibration mode and generates a unique signal for each molecule in the fingerprint region, allowing researchers to explore the functional groups on the surface of these materials. IR signals for graphite, GO, and rGO appeared between  $3400\text{ cm}^{-1}$  and  $3200\text{ cm}^{-1}$ ,  $1700\text{ cm}^{-1}$ - $1600$

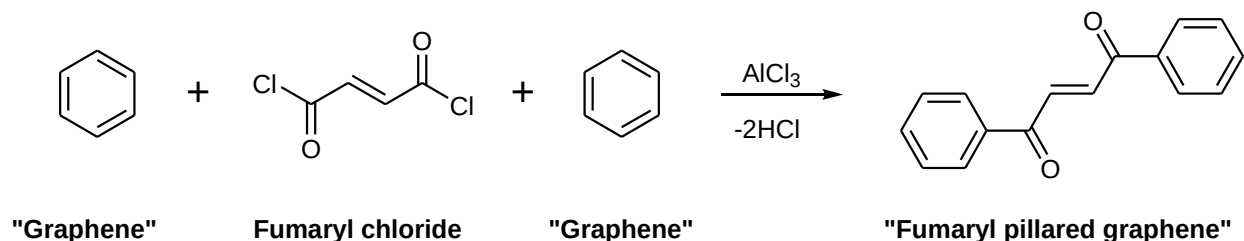
$\text{cm}^{-1}$ , and around  $1200\text{ cm}^{-1}$ , respectively, corresponding to the stretching vibrations of the O-H, carboxylic C=O, and epoxide or ester C-O-C bonds.

### 3.1.1 IR analysis of GO and rGO synthesized from commercial graphite flakes.

IR spectroscopy was performed on graphite powder prior to the application of Tour's method, as well as after the oxidation of graphite powder, and reduction of graphene oxide to rGO. The IR analysis revealed the presence of oxygen-containing functional groups in the GO spectrum, as evidenced by the presence of a broad band at  $3312\text{ cm}^{-1}$  in the high-frequency area which corresponds to a O-H stretching vibration, and this is confirmed because water molecules were adsorbed on GO during the application of Tour's method, which indicates that the sample has strong hydrophilicity. A second band occurs at  $1716\text{ cm}^{-1}$ , corresponding to a C=O stretching vibration, and a third band at  $1137\text{ cm}^{-1}$  represents a C-O stretching vibration. When GO was chemically reduced to rGO, some of the functional groups in the structure were eliminated (Fig. 13). The broad OH stretch of GO is absent in rGO after chemical reduction, indicating that some of the oxygen-containing functional groups have been reduced. However, there is still a band that occurs at  $1716\text{ cm}^{-1}$  corresponding to a C=O stretching vibration. These results confirm that both GO and rGO were synthesized successfully.

### 3.1.2 IR analysis of GO/rGO functionalized with fumaryl chloride

Fumaryl chloride is an acylating agent; in the Friedel-Crafts acylation, it introduces the fumaryl group onto the GO/rGO surface. It also acts as an electrophile, which means that it can react with the aromatic rings or GO/rGO, creating a covalent bond, and as a result, pillars will be introduced on the reactive sites (Scheme 2).



**Scheme 2** Formation of fumaryl pillared GO or rGO

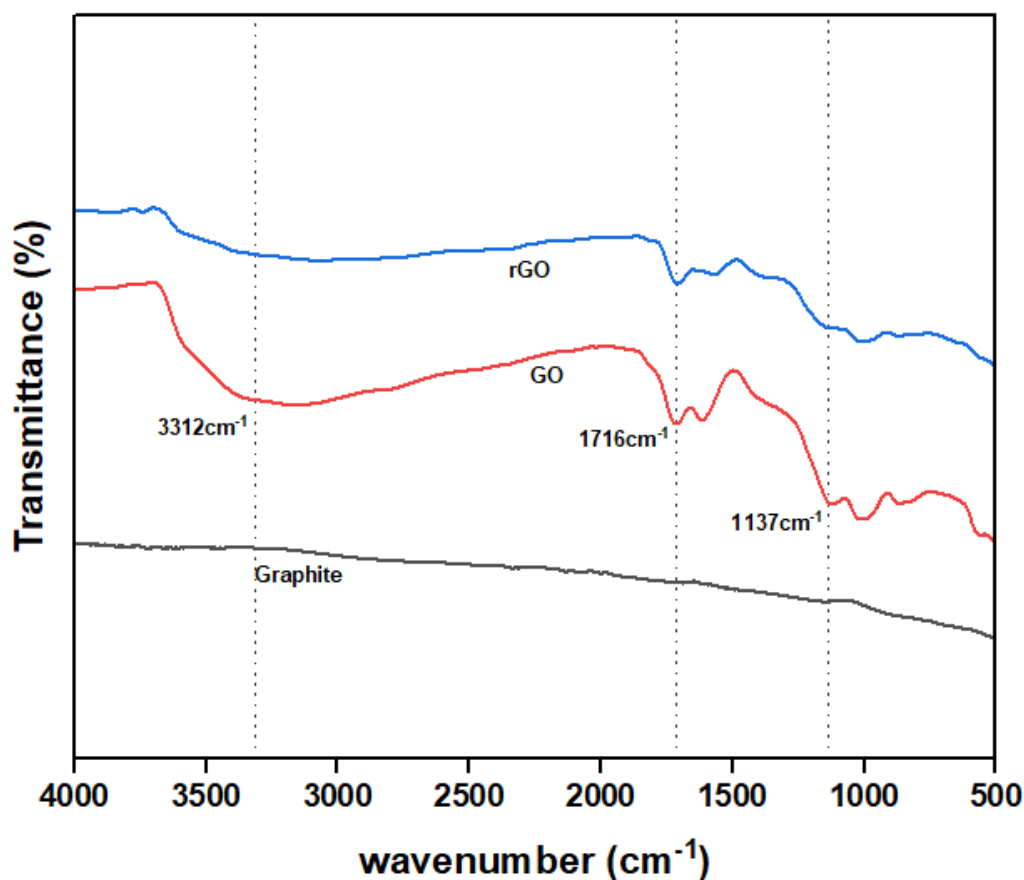


**Figure 13:** IR spectra of graphite flakes (black), GO (red), and rGO (blue)

### 3.1.2.1 *IR analysis of GO functionalized with fumaryl chloride (GOFC)*

Infrared spectroscopy was performed on the graphene oxide treated with fumaryl chloride at 0.15 mmol, 0.20 mmol, and 0.30 mmol concentration (**GOFC0.15**, **GOFC0.20**, and **GOFC0.30**), and also on the holey graphene which was functionalized with fumaryl chloride at 0.15 mmol concentration (**hGOFC0.15**). The IR analysis of GO as a starting material (Figure 14) revealed the presence of oxygen-containing functional groups in the spectrum, as shown by the presence of a broad band at  $3312\text{ cm}^{-1}$  in the high-frequency area which corresponds to O-H stretching vibration. A second band occurs at  $1716\text{ cm}^{-1}$ , corresponding to a C=O stretching vibration, and a third band at  $1128\text{ cm}^{-1}$  represents a C-O stretching vibration. The broad OH stretching vibration is absent in the spectra of the pillared graphenes (**GOFC0.15**, **GOFC0.20**, and **GOFC0.30**) and also in the spectrum of holey graphene oxide (**hGOFC0.15**), which means that the OH has been reduced. For the pillared graphenes - **GOFC0.15**, **GOFC0.20**, and **GOFC0.30** - and holey graphene **hGOFC0.15**, a first band is occurring  $2348\text{ cm}^{-1}$  corresponding to C-H

stretch; meanwhile, the peak does not appear in the GO spectrum. A second band appears at  $1716\text{ cm}^{-1}$  (C=O stretch) and a third band appears at  $1200\text{ cm}^{-1}$  (C-O stretch). Incidentally, the C-O stretching band has shifted due to the insertion of pillars. These results show that the pillared graphene and holey graphene were successfully synthesized.

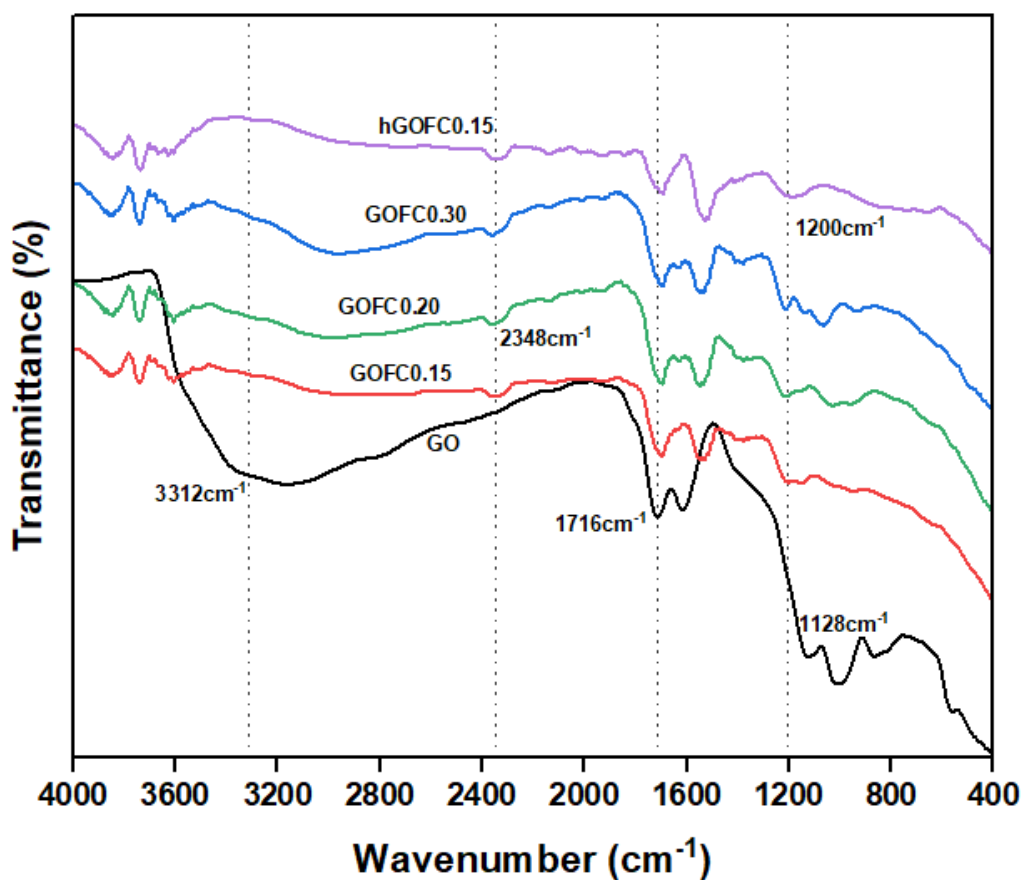


**Figure 14:** IR spectra of GO (black), GOFC0.15 (red), GOFC0.20 (green), GOFC0.30 (blue), and hGOFC0.15 (purple)

### 3.1.2.2 IR analysis of rGO functionalized with fumaryl chloride (rGOFC)

Infrared spectroscopy was performed on the reduced graphene oxide functionalized with fumaryl chloride at 0.15 mmol and 0.20 mmol acid chloride per 80 mg rGO (**rGOFC0.15** and **rGOFC0.20**), and also on the holey reduced graphene oxide functionalized with fumaryl chloride at 0.15 mmol concentration (**hrGOFC0.15**). The chemical reduction of GO to rGO eliminated some of the functional groups, as shown in the rGO IR spectrum (Figure 15). The IR analysis of rGO revealed that there is still a band occurring at  $1777\text{ cm}^{-1}$  corresponding to a C=O stretching vibration. For the IR analysis of the pillared graphenes **rGOFC0.15** and **rGOFC0.20** and the

holey graphene **hrGOFC0.15**, a C-H stretch band occurs at  $2403\text{ cm}^{-1}$ , while the C-H band is absent in the rGO spectrum. A band appearing at  $1777\text{ cm}^{-1}$  corresponds to a C=O stretching vibration, a band appearing at  $1605\text{ cm}^{-1}$  corresponds to C=C stretching, and the band appearing at  $1268\text{ cm}^{-1}$  corresponds to the C-O stretching vibration; the C-O stretch is absent in the rGO spectrum. These results show that the pillared and holey graphenes were successfully synthesized.

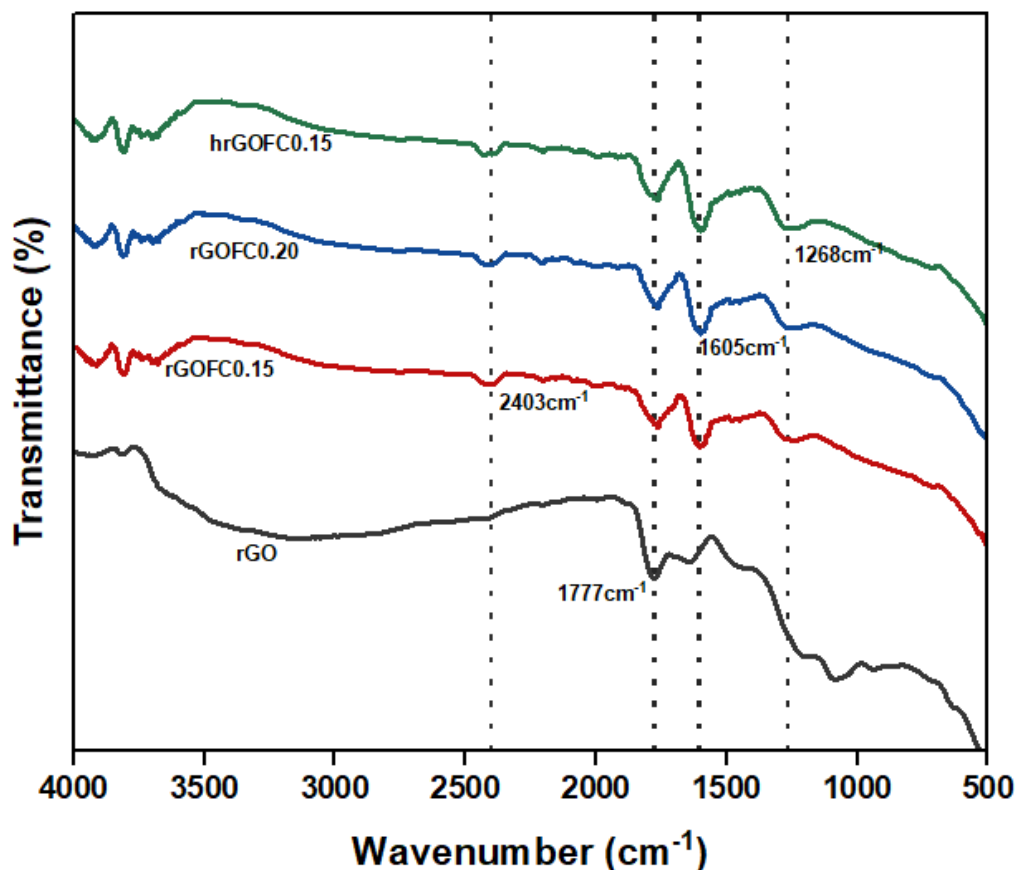
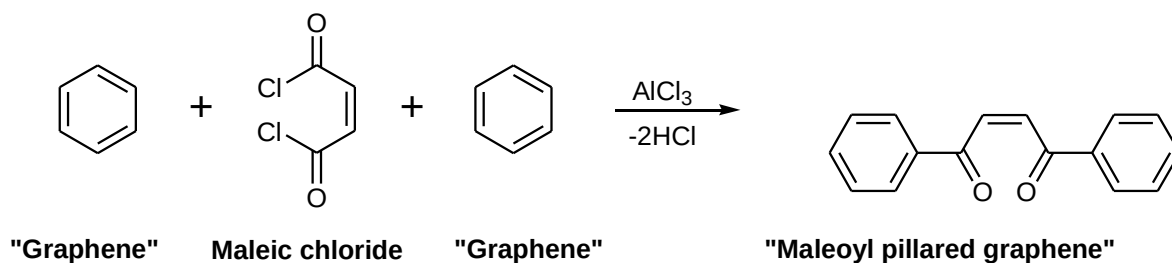


**Figure 15:** IR spectra of rGO (black), rGOFC0.15 (red), rGOFC0.20 (blue), and hrGOFC0.15 (green).

### 3.1.3 IR analysis of GO/rGO functionalized with maleoyl chloride

Maleoyl chloride is an acylating agent that introduces the maleoyl group onto the GO/rGO surface and it also acts as an electrophile, attacking the aromatic rings of GO/rGO and forming a covalent bond, functionalizing the GO/rGO surface by introducing pillars on reactive sites (Scheme 3).



**Scheme 3:** Formation of maleoyl pillared GO or rGO

### 3.1.3.1 *IR analysis of GO functionalized with maleoyl chloride (GOMC)*

IR spectroscopy was performed on the graphene oxide containing the maleoyl group at 0.15 mmol, 0.20 mmol, and 0.30 mmol concentrations (Figure 16), as explained (**GOMC0.15**, **GOMC0.20**, and **GOMC0.30**), and also on the holey graphene functionalized with maleoyl chloride (**hGOMC0.15**). For the GO spectrum, the presence of oxygen-containing functional groups is revealed in the spectrum, as evidenced by the presence of a broad band at  $3312\text{ cm}^{-1}$  in the high-frequency area which corresponds to O-H stretching vibration. A second band occurs at  $1700\text{ cm}^{-1}$ , corresponding to a C=O stretching vibration, and a third band at  $1127\text{ cm}^{-1}$  represents a C-O-C (peroxide) stretching vibration. The broad OH stretching vibration is absent in the spectra of the pillared graphenes - **GOMC0.15**, **GOMC0.20**, and **GOMC0.30**, which means that the OH functional groups have been reduced or esterified however a band appears at  $1700\text{ cm}^{-1}$  which corresponds to a C=O stretching vibration, but there is an absence of a C-O vibrational stretch at  $1127\text{ cm}^{-1}$  in the **GOMC0.15**, **GOMC0.20** and **GOMC0.30** spectra. For **hGOMC0.15**, the IR analysis also revealed the absence of a broad OH vibrational stretch. A band appearing at  $2342\text{ cm}^{-1}$  corresponds to a C-H stretch, another appears at  $1700\text{ cm}^{-1}$  corresponding to a C=O vibration and the absence of a C-O vibrational stretch is also revealed in the spectrum. These results show that GO, pillared graphene, and holey graphene were successfully synthesized.

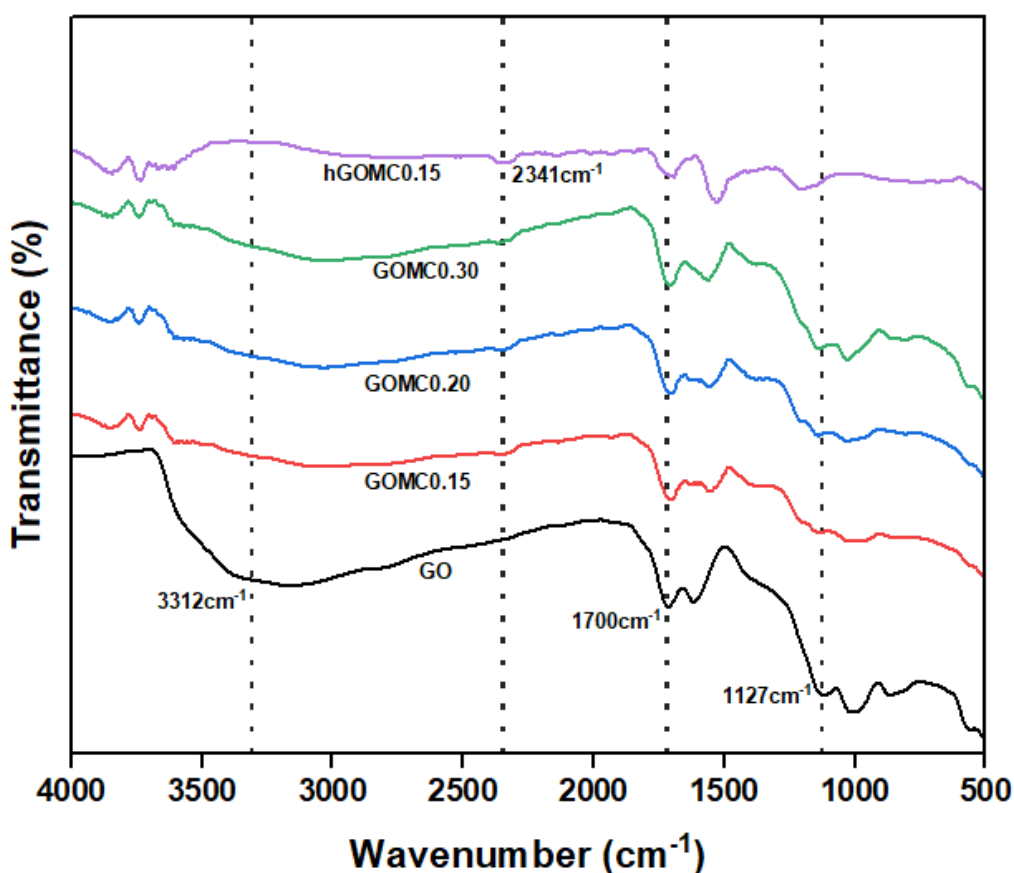


**Figure 16:** IR spectra of **GO** (black), **GOMC0.15** (red), **GOMC0.20** (blue), **GOMC0.30** (green) and **hGOMC0.15** (purple)

### 3.1.3.2 IR analysis of rGO functionalized with maleoyl chloride (rGOMC)

IR spectroscopy was performed on the reduced graphene oxide functionalized with maleoyl chloride (Figure 17) as described (**rGOMC0.15** and **rGOMC0.20**), and also on the holey graphene (**hrGOMC0.15**). The IR spectrum of rGO still revealed a band at  $1700\text{ cm}^{-1}$  consistent with C=O stretching. The spectra of the pillared graphenes are shown as **rGOMC0.15** and **rGOMC0.20**. A band at  $2441\text{ cm}^{-1}$  is consistent with a C-H stretch, while a band at  $1815\text{ cm}^{-1}$  is caused by a C=O stretching vibration. For **hrGOMC0.15**, the IR analysis also revealed a band at  $1815\text{ cm}^{-1}$  (C=O stretch). These results show that rGO, pillared graphene, and holey graphene were successfully synthesized.

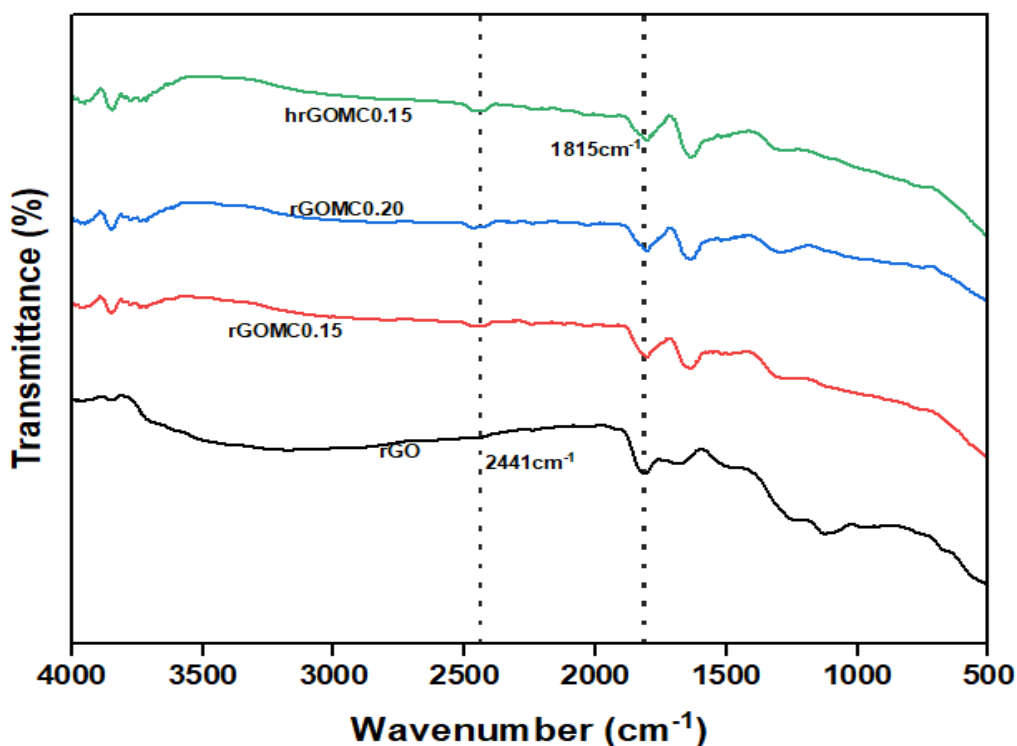
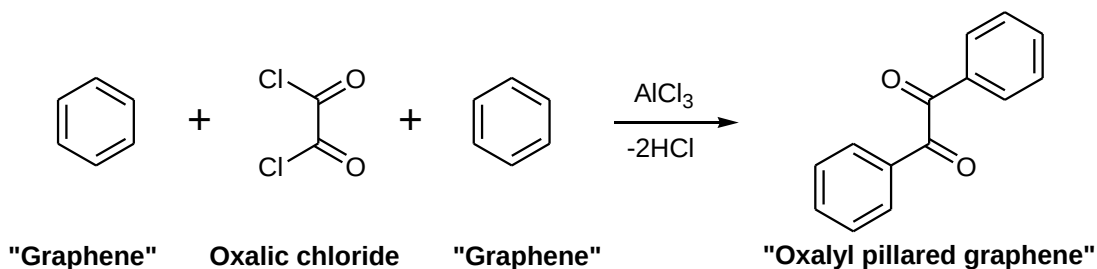


**Figure 17:** IR spectra of rGO (black), rGOMC0.15 (red), rGOMC0.20 (blue), and hrGOMC0.15 (green).

### 3.1.4 IR analysis of GO/rGO functionalized with oxalyl chloride

Oxalyl chloride introduces the oxalyl group onto the GO/rGO surface and acts as an electrophile that attacks the aromatic rings of GO/rGO forming a covalent bond, which then introduces pillars onto the reactive sites (Scheme 4). This acylating agent can also reduce the GO/rGO surface area by reacting with oxygen-containing groups.



**Scheme 4** Formation of oxalyl pillared GO or rGO

### 3.1.4.1 IR analysis of GO functionalized with oxalyl chloride (GOOC)

IR spectroscopy was performed on the graphene oxide functionalized by reaction with oxalyl chloride as described (**GOOC0.15**, **GOOC0.20**, and **GOOC0.30**), and also on the corresponding holey graphene (**hGOOC0.15**). In the GO spectrum, the oxygen-containing functional groups are revealed (Figure 18), as evidenced by the presence of a broad band at  $3312\text{ cm}^{-1}$  in the high-frequency area consistent with an O-H stretching vibration. Another band occurs at  $1740\text{ cm}^{-1}$  (C=O stretch), and a third band at  $1216\text{ cm}^{-1}$  represents a C-O-C (epoxide) stretching vibration. The broad O-H stretching vibration is absent in the spectra of the pillared graphenes **GOMC0.15**, **GOMC0.20**, and **GOMC0.30**, which means that the OH functional groups have been removed or esterified. A band appears at  $1740\text{ cm}^{-1}$  (C=O stretch), but the C-O stretching vibration at  $1216\text{ cm}^{-1}$  is absent in the **GOMC0.15**, **GOMC0.20**, and **GOMC0.30** spectra. For **hGOOC0.15**, the IR analysis also revealed the absence of a broad O-H stretch. A C=O stretching band appears at  $1740\text{ cm}^{-1}$ . These results show that GO, pillared graphene, and holey graphene were successfully synthesized.

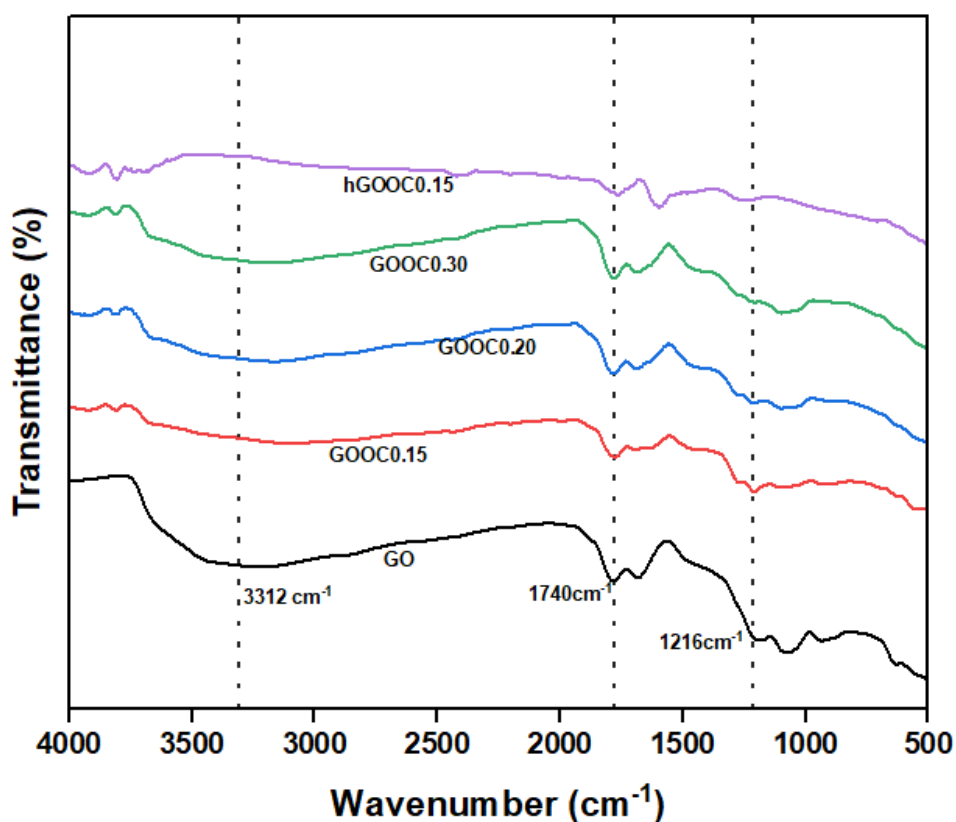


**Figure 18:** IR spectra of GO (black), **GOOC0.15** (red), **GOOC0.20** (blue), **GOOC0.30** (green), and **hGOOC0.15** (purple).

### 3.1.4.2 IR analysis of rGO functionalized with oxalyl chloride (rGOOC)

IR spectroscopy was performed on the reduced graphene oxide reacted with oxalyl chloride (Figure 19) as described (**rGOOC0.15** and **rGOOC0.20**), and also on the acylated holey graphene (**hrGOOC0.15**). The IR spectrum still has a band at  $1700\text{ cm}^{-1}$  consistent with a C=O stretching vibration. In the spectra of the pillared graphenes **rGOMC0.15** and **rGOMC0.20**, a C=O band appears at  $1706\text{ cm}^{-1}$ . For **hrGOOC0.15**, the IR analysis revealed the presence of a C-H stretch at  $2341\text{ cm}^{-1}$  and another band at  $1706\text{ cm}^{-1}$  (C=O stretch). These results show that rGO, pillared, and holey graphenes were successfully synthesized.

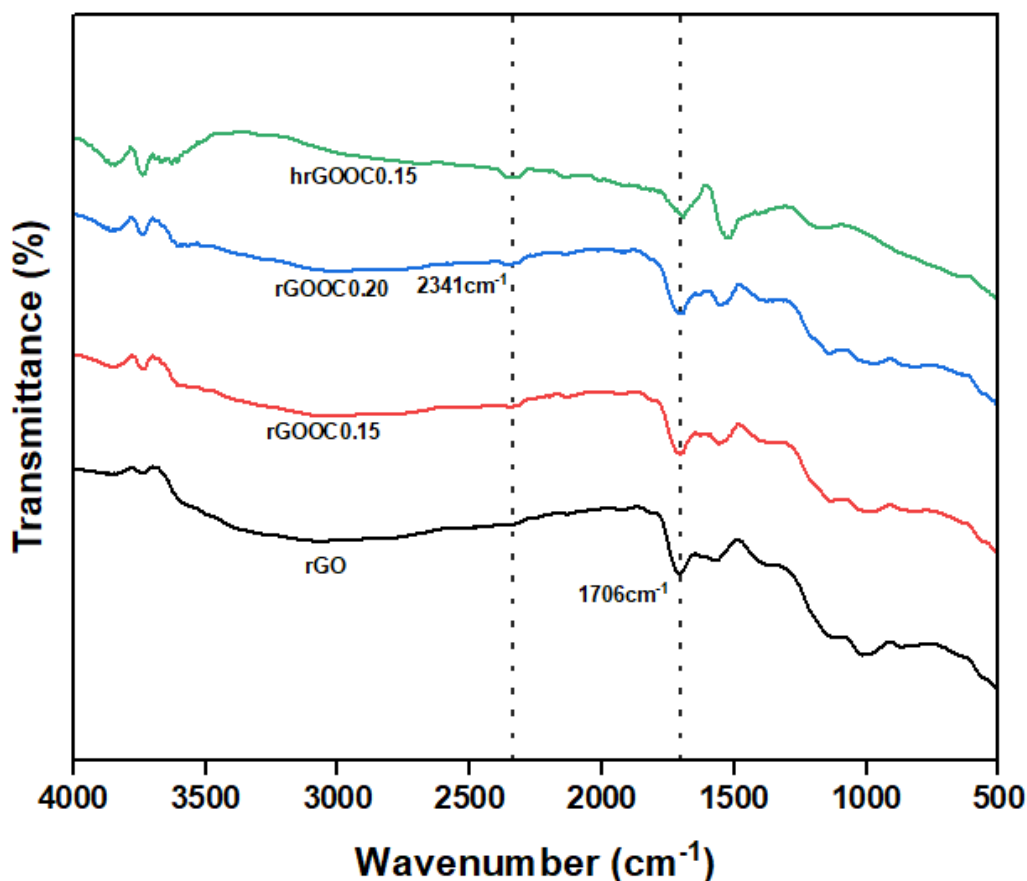


**Figure 19:** IR spectra of rGO (black), **rGOOC0.15** (red), **rGOOC0.20** (blue), and **hrGOOC0.15** (green).

## 3.2 X-RAY DIFFRACTION CRYSTALLOGRAPHY

XRD is a characterization technique that is used to analyse a material's composition, structure, and crystalline form. X-ray radiation with a wavelength similar to the spacing between atoms in

the sample is passed through the material. As a result, the rays are diffracted by collisions with the atoms, and the angle of diffraction,  $\theta$ , is affected by the distances between the atoms in the molecule. The interlayer spacings between layers in the material can therefore be calculated and correlated with the synthesis parameters, *etc.* (Jin *et al.*, 2018; Palaniselvam *et al.*, 2014; Zheng *et al.*, 2015). The structure and morphology of the materials were characterized using a Rigaku Smart Lab X-ray diffractometer. The sample is prepared on the sample holder and thereafter mounted on the sample stage. The X-ray source then generates X-rays, which are directed at the sample. The X-rays will then interact with the sample's atoms, causing diffraction. The goniometer positions the sample and detector at precise angles ( $\theta$ ) relative to the X-ray beam. The detector measures the diffracted X-rays as a function of angle ( $2\theta$ ). Then the collected data are analyzed using software to produce a diffraction pattern, which is used to identify the sample's crystalline structure, phase, and other properties. The  $2\theta$  diffraction angles of graphite, GO, rGO and the pillared samples appeared between  $9.67^\circ$  and  $45^\circ$ . The interlayer spacing between graphene layers was calculated using Bragg's law, which is stated as follows:

$$n\lambda = 2d\sin\theta$$

where:

$\lambda$  is the wavelength of the X-ray beam (usually  $\lambda = 0.15406$  nm)

$d$  is the spacing of the crystal layers

$\theta$  is the incident angle

$n$  is an integer

### 3.2.1 XRD analysis of graphite, GO, and rGO

Figure 20(a) shows the XRD spectra of graphite, GO, and rGO, but because the peaks were not showing clearly, the spectra were then drawn separately.

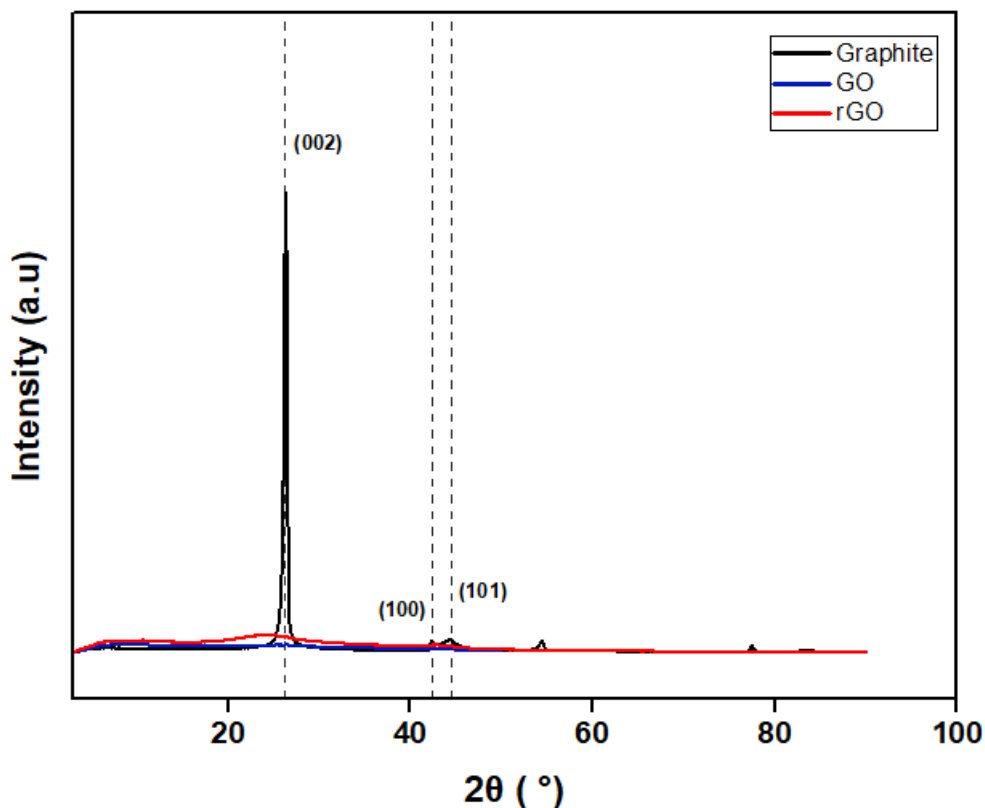


**Figure 20(a):** XRD spectra of graphite (black), GO (blue) and rGO (red).

Figure 20(b) shows the XRD pattern of natural graphite flakes before the oxidation using Tour's method, where a sharp (002) diffraction peak appears at  $2\theta = 26.11^\circ$  with a  $d$  spacing of 0.341 nm; this result corresponds well with literature data (e.g., Zhang *et al.*, 2021). Other low-intensity peaks consistent with (100) and (101) diffraction planes can also be observed in the spectrum. It can be concluded that graphite is highly crystalline and has a very sharp (002) peak.

Fig. 20(c) shows the XRD spectrum of GO synthesized using Tour's method. The (002) diffraction peak appears at  $2\theta = 26.39^\circ$  with a  $d_{(002)}$  spacing of 0.337 nm. Additionally, a broad (001) diffraction peak occurs at  $2\theta = 9.67^\circ$  with an interlayer spacing of 0.914 nm. A smaller (100) peak appears at  $2\theta = 42.50^\circ$  with an interlayer spacing of 0.213 nm; this indicates that GO exhibits turbostratic disorder (Nethravathi *et al.*, 2008), which is believed to be due to incomplete oxidation. The observed broad peak also indicates that GO has a small particle size, but it differs from that of the crystalline graphite. The pattern was also not smooth; this might be due to the irregular spacing of GO layers, which affects the quality and interpretation of XRD data (Yang *et al.*, 2020).

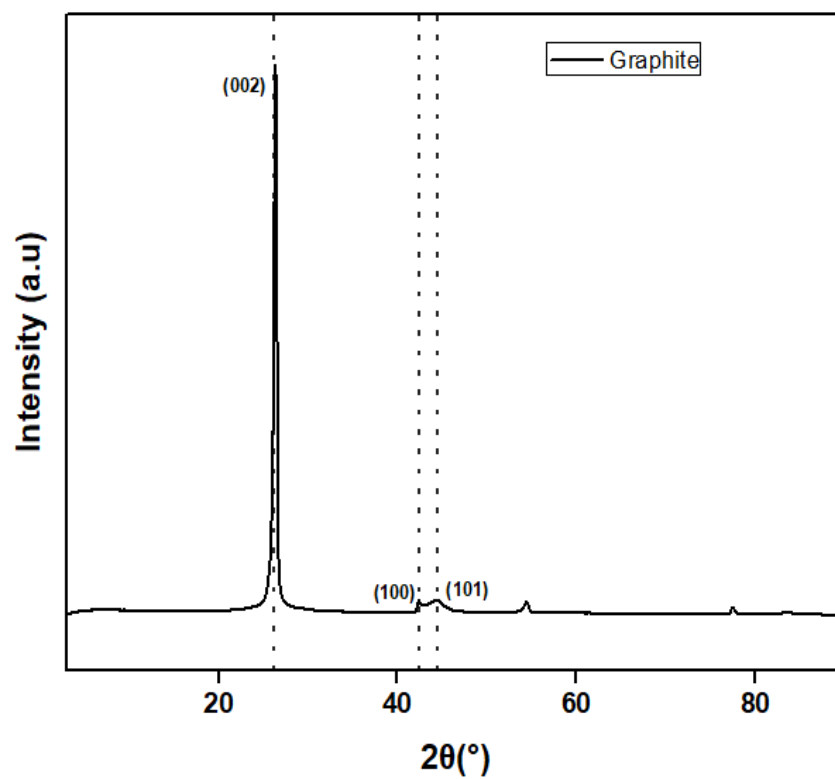


**Figure 21(b):** XRD spectrum of graphite

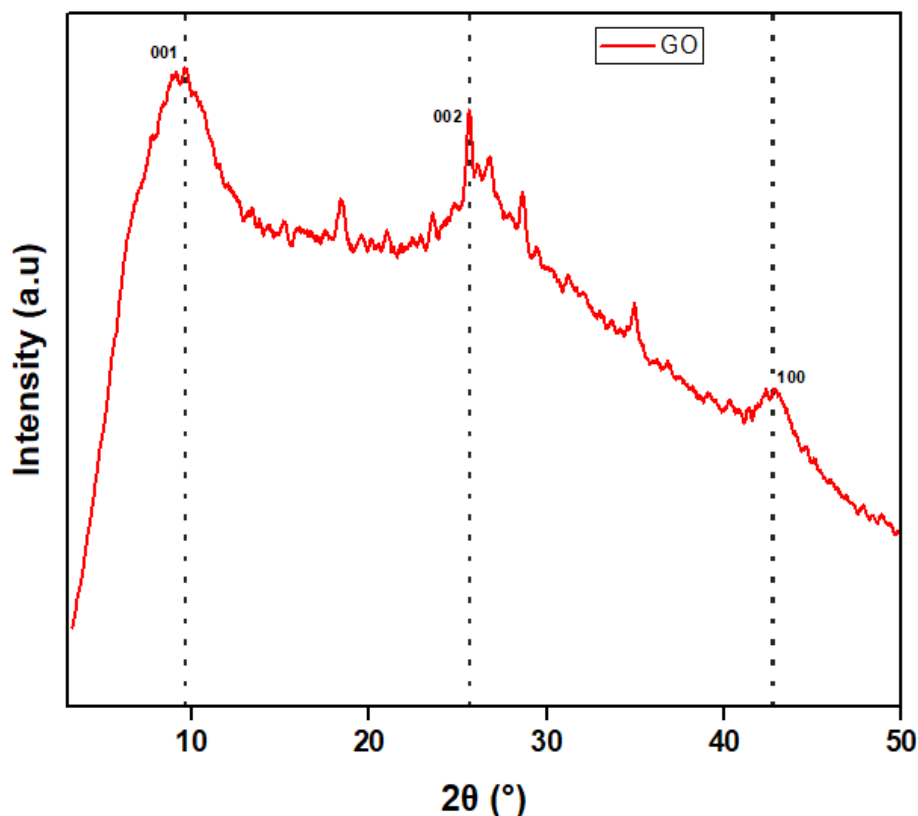


**Figure 22(c):** XRD spectrum of GO

Figure 20(d) shows the XRD spectrum of rGO obtained from GO by ascorbic acid reduction. The reduction of GO to rGO results in structural change as evidenced by the comparison of the X-ray diffraction patterns of GO and rGO. Figure 20(d) shows a major sharp diffraction peak at  $2\theta = 24.92^\circ$  consistent with the (002) diffraction plane and 0.357 nm interlayer spacing, which is an increase over that of GO. On the other hand, the (100) interlayer spacing remained approximately the same, with  $d_{(100)} = 0.213$  nm in the case of GO and  $d_{(100)} = 0.211$  nm for rGO, with  $2\theta = 42.88^\circ$ . Compared to the GO spectrum in Figure 20(c), rGO has broader peaks but a relatively smooth spectrum; this means that the material is fairly crystalline, has structural order, and contains fewer defects.

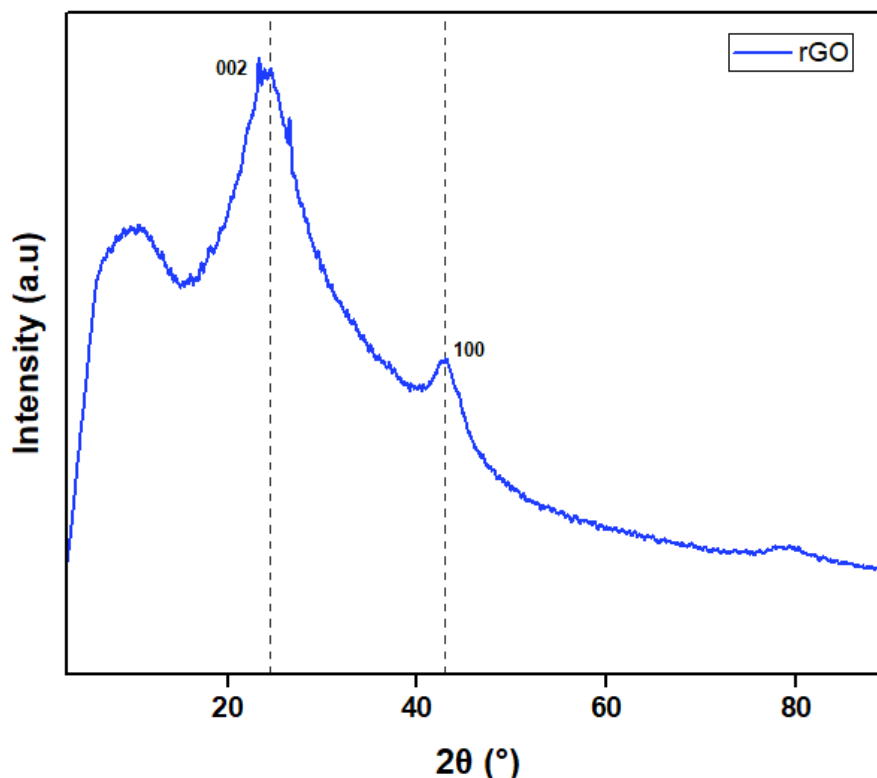


Figure 23(d): XRD spectrum of rGO

### 3.2.2 XRD analysis of GO functionalized with fumaryl chloride

For the fumaryl functionalized graphene oxides (Figure 21), at  $2\theta = 10.66^\circ$  the pillared GO samples display a broad (001) diffraction peak with a corresponding interlayer  $d_{(001)}$  spacing of 0.829 nm, minor reflective (101) peaks appearing at  $2\theta = 18^\circ$  with a  $d_{(101)}$  spacing of 0.492 nm, and a faint broad (201) peak at  $2\theta = 25.25^\circ$  corresponding to  $d_{(201)} = 0.352$  nm. Another low-intensity reflective peak (100) appears at  $2\theta = 42.71^\circ$  corresponding to  $d = 0.212$  nm. For holey graphene oxide functionalized with 0.15 mmol fumaryl chloride (**hGOFC0.15**), the sharp diffraction peak (002) is at  $2\theta = 25.25^\circ$  with the interlayer  $d_{(002)}$  spacing of 0.352 nm and the low-intensity reflective peaks are appearing at  $2\theta = 18^\circ$  (101) with the  $d$  spacing of 0.492 nm and another reflective peak (100) at  $2\theta = 42.71^\circ$  with  $d = 0.212$  nm. The interlayer spacing  $d_{(002)}$  increased from 0.337 nm in graphite to 0.352 nm in GO and **hGOFC0.15**; this is due to the replacement of hydroxyl and carboxyl functional groups after fumaryl insertion. As for the reflective peaks, they indicate that GO exhibits turbostratic disorder (Nethravathi *et al.*, 2008), probably caused by incomplete oxidation.

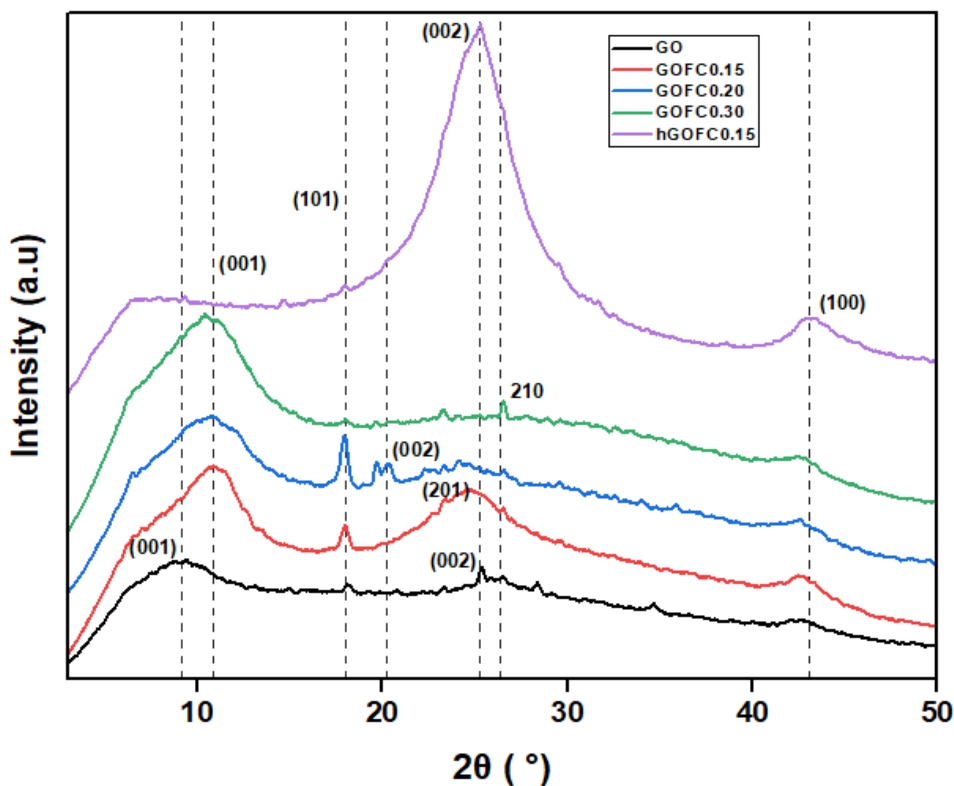


**Figure 24:** XRD spectra of GO functionalized with fumaryl chloride: GO (black), **GOFC0.15** (red), **GOFC0.20** (blue), **GOFC 0.30** (green), and **hGOFC0.15** (purple).

With increasing amounts of fumaryl pillars, the intensity of the XRD spectra gradually decreases because of the increasing interlayer spacing, which results in a reduction of the intensity. The peaks at higher  $2\theta$  correspond to GO stacking and indicate a reduction degree close to that of rGO. The peaks below  $20^\circ$  correspond to intercalation and cross-linking of the graphene sheets (Band *et al.*, 2019). The pillared and holey graphenes are fairly crystalline and contain few defects; increasing pillar concentrations results in additional peaks, which means the materials have more crystalline phases.

### 3.2.3 XRD analysis of rGO functionalized with fumaryl chloride

Figure 22 shows the effect of the addition of different amounts of fumaryl groups on reduced graphene oxide sheets. The rGO and functionalized rGO spectra all show a sharp (002) diffraction peak at  $2\theta = 23.49^\circ$  consistent with a 0.378 nm interlayer spacing, and a reflective peak (101) at  $2\theta = 41.88^\circ$  with an interlayer spacing of 0.216 nm. Also visible after the chemical reduction of GO to rGO, the (001) interlayer spacing  $d_{(001)}$  decreased from 0.915 nm for GO to

0.883 nm for rGO; this is the result of reduction of oxygen-containing groups on the graphene oxide sheets and aggregation. Thus, reduction of GO to rGO is confirmed by XRD analysis.

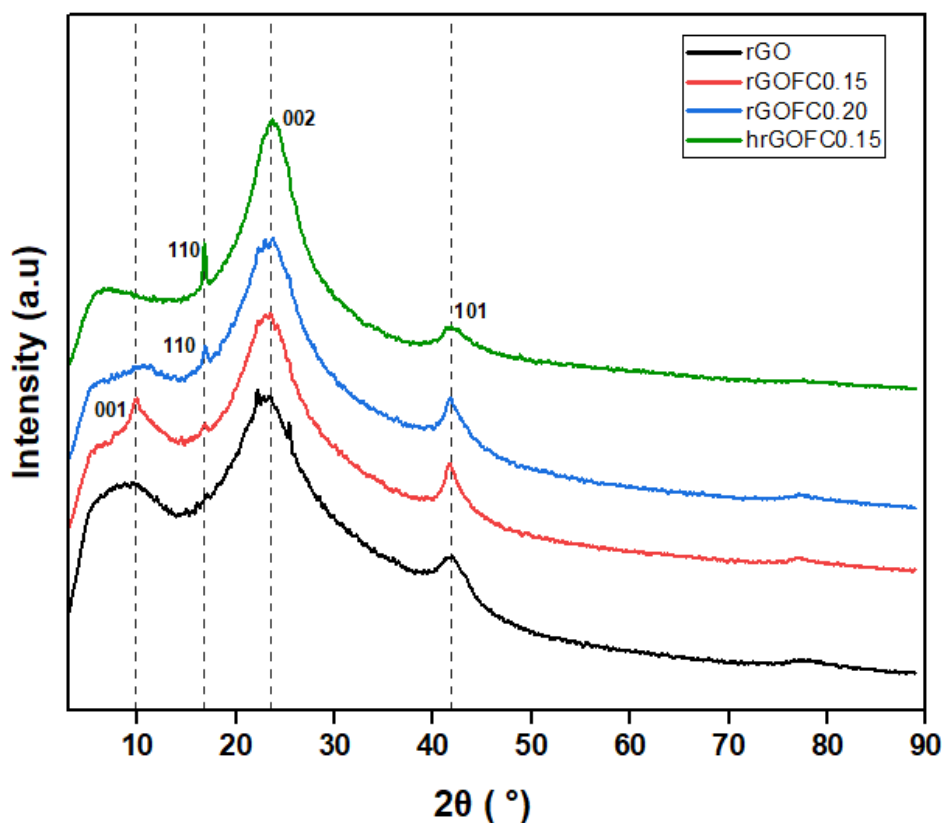


**Figure 25:** XRD spectra of rGO (black), rGOFC0.15 (red), rGOFC0.20 (blue), and hrGOFC0.15 (green).

Sample **rGOFC0.15** also shows a small sharp diffraction peak at  $2\theta = 10^\circ$  in the diffraction plane (001) with a  $d$  spacing of 0.883 nm. Samples **rGOFC0.20** and **hrGOFC0.15** show a low-intensity sharp (110) diffraction at  $2\theta = 16.7^\circ$  with 0.530 nm interlayer spacing. With increasing number of fumaryl pillars, the intensity seems to decrease. The interlayer spacing  $d_{(002)}$  of rGO, **rGOFC0.15**, **rGOFC0.20**, and **hrGOFC0.15** is the same (0.378 nm) and is greater than that of graphite and GO. The spectra (Figure 22) of the pillared and holey graphenes have relatively sharp peaks and are smooth, meaning that the materials are fairly crystalline and have high structural order and fewer defects.

### 3.2.4 XRD analysis of GO functionalized with maleoyl chloride

Figure 23 shows the effect of different amounts of maleoyl pillars on graphene oxide. The sharp (002) diffraction peak is at  $2\theta = 25.29^\circ$  with  $d_{(002)} = 0.352$  nm. A low-intensity sharp reflective

peak (110) appears at  $2\theta = 18^\circ$  with 0.492 nm spacing. The observed broad (001) peak at  $2\theta = 9.67^\circ$  with  $d_{(001)} = 0.854$  nm indicates a small particle size, and that it is not highly crystalline. The pattern is also not smooth, probably due to the irregular GO layer spacing.

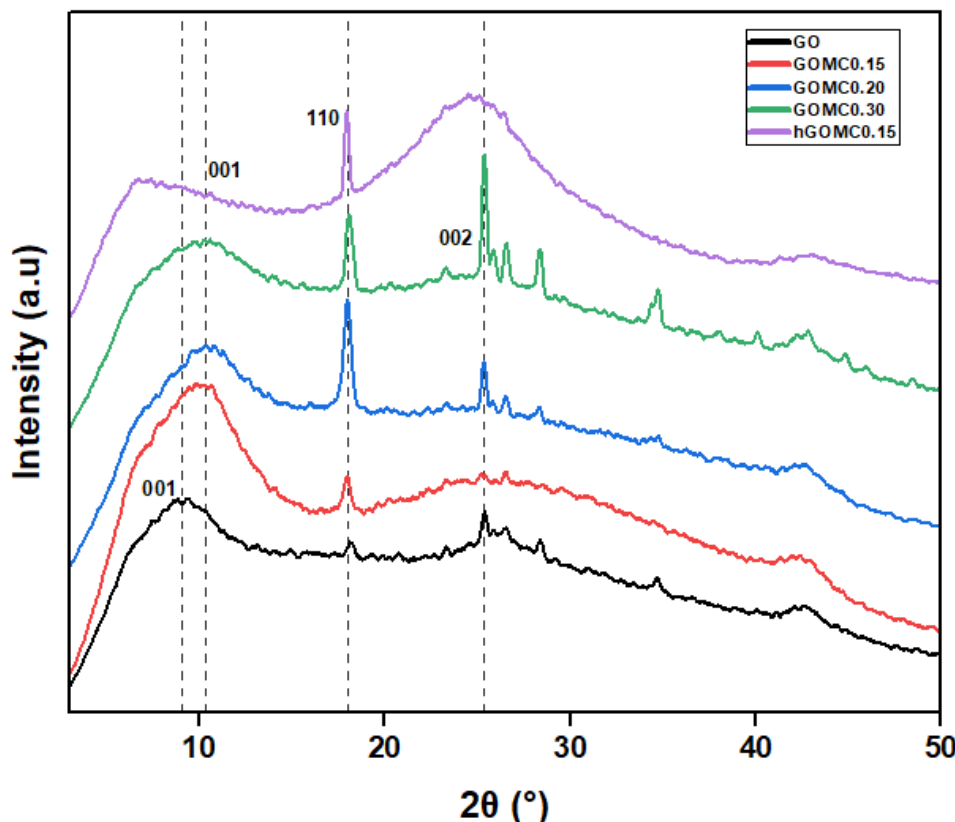


**Figure 26:** XRD patterns of GO (black), **GOMC0.15** (red), **GOMC0.20** (blue), **GOMC0.30** (green) and **hGOMC0.15** (purple).

After the insertion of maleoyl pillars on the GO sheets, the interlayer spacing  $d_{(002)} = 0.352$  nm remained the same. The maleoyl pillars replaced some oxygen-containing groups but did not significantly alter spacing; this might be due to a low degree of functionalization with maleoyl pillars on the GO sheets, or due to the restacking of GO layers. The (001) spacing  $d_{(001)}$  decreased from 0.915 nm for GO to 0.854 nm in the case of pillared GO. With increasing maleoyl pillars, the intensity decreases, and the GO peaks shift towards greater angles.

The pillared graphenes (**GOMC0.15**, **GOMC0.20** and **GOMC0.30**) are fairly crystalline and contain few defects, and an increase in pillar concentration also results in additional peaks appearing (Figure 23), which means the materials have more crystalline phases. However, **hGOMC0.15** has small size effects and contains more defects. The irregular spacing of layers affected the XRD patterns of all the pillared and holey graphenes.

### 3.2.5 XRD analysis of rGO functionalized with maleoyl chloride

Figure 24 shows the effect of different amounts of maleoyl pillars with reduced graphene oxide. Both rGO and the maleoyl pillared rGOs have a sharp (002) diffraction peak at  $2\theta = 25.00^\circ$  with  $d_{(002)} = 0.355$  nm and a low intensity (100) reflective peak at  $2\theta = 42.29^\circ$  consistent with a 0.214 nm interlayer spacing. The pillared holey rGO (**hrGOMC0.15**) shows the same XRD pattern and spacing. This might be due to rGO layers that are restacked during chemical reduction because of the strong  $\pi$ - $\pi$  interactions between graphene sheets.

Increasing pillar concentration results in additional peaks in the spectrum, and the materials are in a more aggregate phase.

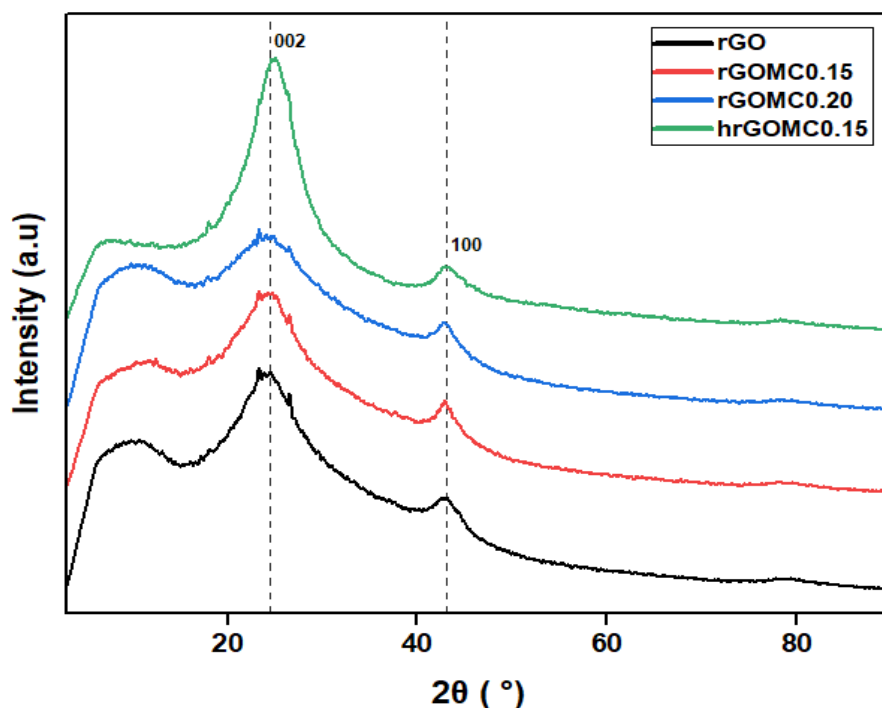


**Figure 27:** XRD patterns of rGO (black), **rGOMC0.15** (red), **rGOMC0.20** (blue), and **hrGOMC0.15** (green).

### 3.2.6 XRD analysis of GO functionalized with oxalyl chloride

Figure 25 shows the effect of different amounts of oxalyl pillars on graphene oxide. GO exhibited a (001) diffraction peak at  $2\theta = 9.47^\circ$ , with  $d_{(001)} = 0.914$  nm on an otherwise featureless spectrum. Only the holey pillared GO (**hGOOC0.15**) exhibited a broad diffraction peak at  $2\theta = 25.09^\circ$  with  $d_{(002)} = 0.355$  nm. The observed broad peak indicates that the GO has a small particle size and that it is not highly crystalline. Again, irregular spacing of the GO layers

probably affected the appearance of the spectrum. The pillared GOs show a sharp (110) diffraction peak at  $2\theta = 18^\circ$  corresponding to  $d_{(110)} = 0.492$  nm. The samples also show a weak (100) peak at  $d_{(002)} = 0.212$  nm. Samples **GOOC0.15** and **GOOC0.20** have highly crystalline phases and structural order with few defects. **GOOC0.30** is less crystalline and has a structural disorder with more defects.

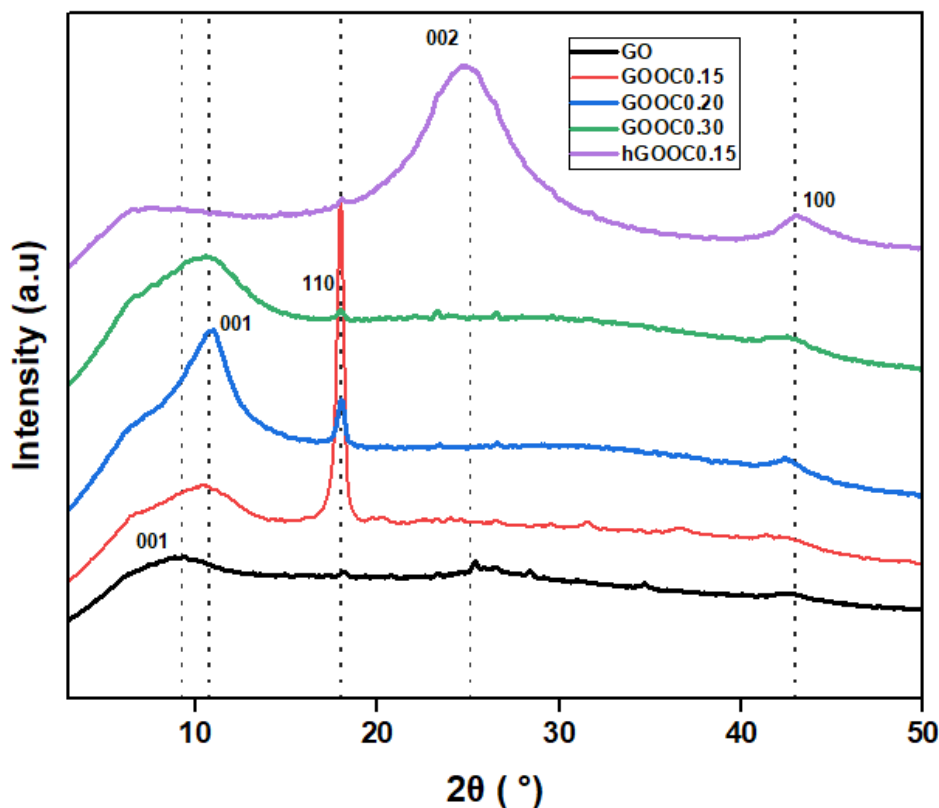


**Figure 28:** XRD of GO functionalized with oxalyl chloride: GO (black), **GOOC0.15** (red), **GOOC0.20** (blue), **GOOC0.30** (green), and **hGOOC0.15** (purple).

With increasing oxalyl pillar concentration, the intensity decreases, and the GO peaks shift towards greater angles. Sample **hGOOC0.15** is less crystalline, contains more structural disorder, and has more defects. The interlayer spacing  $d_{(002)}$  of **GOOC0.15** is 0.493 nm, but after the gradual thermal annealing, the interlayer spacing  $d_{(002)}$  of **hGOOC0.15** decreased to 0.355 nm due to some of the oxygen-containing functional groups being reduced as evidenced by Figure 13. The spectra for all the pillared and holey graphenes appeared to be smooth, meaning that there is regular spacing of layers.

### 3.2.7 XRD analysis of rGO functionalized with oxalyl chloride

Figure 26 shows the effect of different amounts of oxalyl pillars with rGO. All the samples show a sharp (002) diffraction peak at  $2\theta = 23.51^\circ$ , corresponding to  $d_{(002)} = 0.378$  nm, and a low intensity reflective (100) peak at  $2\theta = 42.10^\circ$  with an interlayer spacing of 0.214 nm. The interlayer spacing  $d_{(002)}$  of rGO, **rGOOC0.15**, **rGOOC0.20**, and **hrGOOC0.15** is the same (0.378 nm), possibly due to the restacking of the rGO layers since during chemical reduction, the GO/rGO tend to restack because of the strong  $\pi$ - $\pi$  interactions between graphene sheets and the reduction process doesn't significantly alter the layer arrangement. With increasing oxalyl concentration, the intensity decreases and as evidenced by the spectra (Figure 26), the pillared (**rGOOC0.15** and **rGOOC0.20**) and holey graphenes (**hrGOOCC0.15**) display smooth patterns, meaning that the materials are fairly crystalline and contain fewer defects.

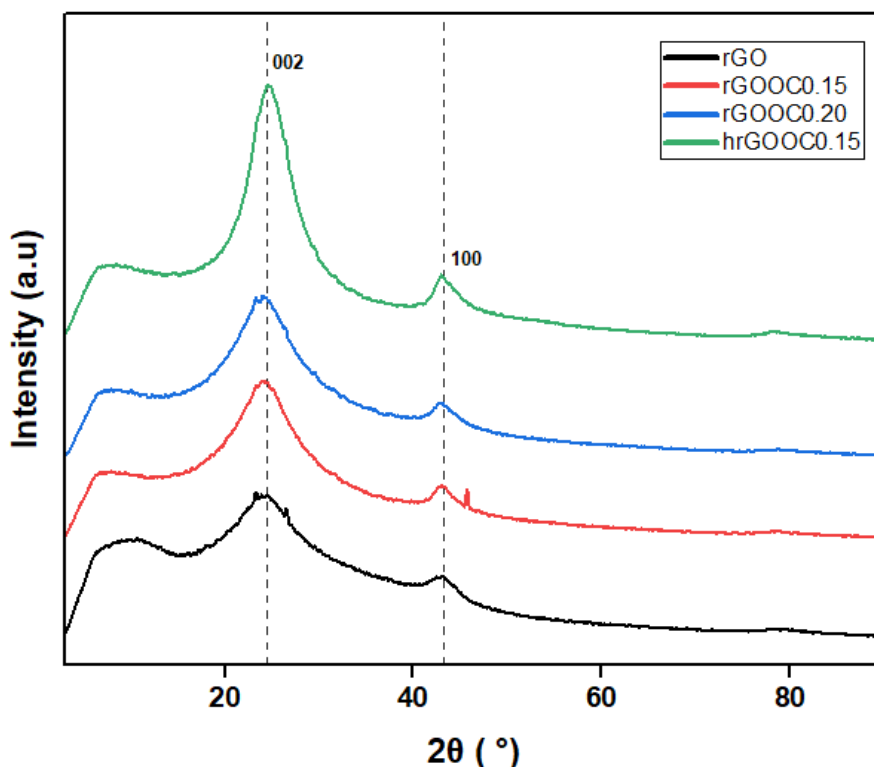


**Figure 29:** XRD of rGO functionalized with oxalyl chloride: rGO (black), **rGOOC0.15** (red), **rGOOC0.20** (blue), and **hrGOOC0.15** (green).

### 3.3 SCANNING ELECTRON MICROSCOPY (SEM)

SEM investigates the surface morphology, composition, and layout of a sample. It uses a focused electron beam to generate high-resolution images and information on the sample's

surface. The electron cannon uses either field emission or thermionic emission to produce an electron stream. The beam is then accelerated by a high voltage to reach the needed energy level. The sample then passes the condenser lenses then the beam focuses on the sample. To scan the sample, the beam moves up and down and side to side using scan coils. When the electron beam strikes a sample, it produces secondary electrons, backscattered electrons, and X-rays (in Energy-Dispersive Spectroscopy). Detectors then capture the emitted signals, which are then analyzed and amplified. After that, the image is generated by scanning the beam and detecting signals pixel-by-pixel which is then projected on a monitor. The holey graphenes comprise grains that are very tightly packed and compact. However, TEM results should provide more information. The low-resolution SEM micrographs confirm the XRD results that the materials are amorphous.

### 3.3.1 SEM analysis of Graphite, GO and rGO

Figure 27(a) is the SEM image of the as-received natural flake graphite before the application of Tour's method. SEM reveals the scattered rough flakes of graphite that spread with varying and irregular sizes as shown in Figure 27(a). After graphite undergoes oxidation the morphology of GO is as shown in Figure 27(b) which shows thick, stacked, and randomly aggregated grains. The thickness of GO morphology is due to the presence of oxygen-containing functional groups that bound to the plane, indicating that graphite has been peeled off during the oxidation process (Sobon *et al.*, 2012). Figure 27(c) shows the SEM images of rGO obtained from GO after ascorbic acid reduction; the micrograph reveals an ultrathick, folded, and aggregated grain of rGO. However, the grain of rGO is no longer as stacked as the one of GO (Figure 27(b)).

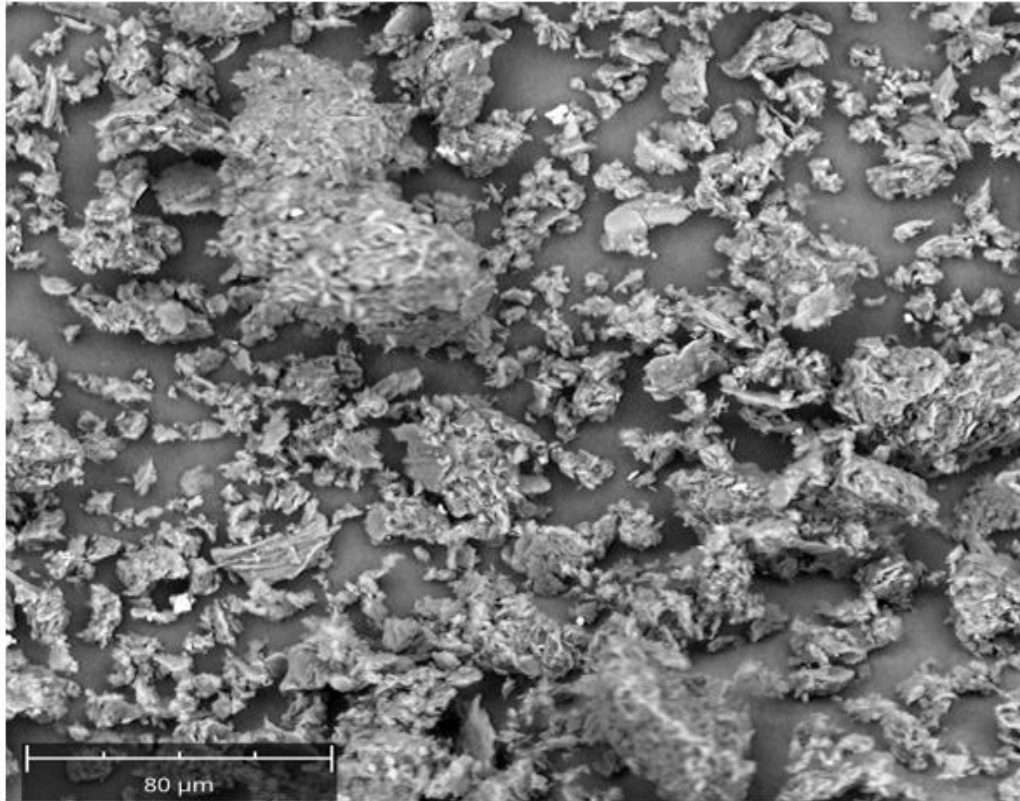


**Figure 30(a):** SEM micrograph of the as-received natural flakes of graphite at 4000X magnification

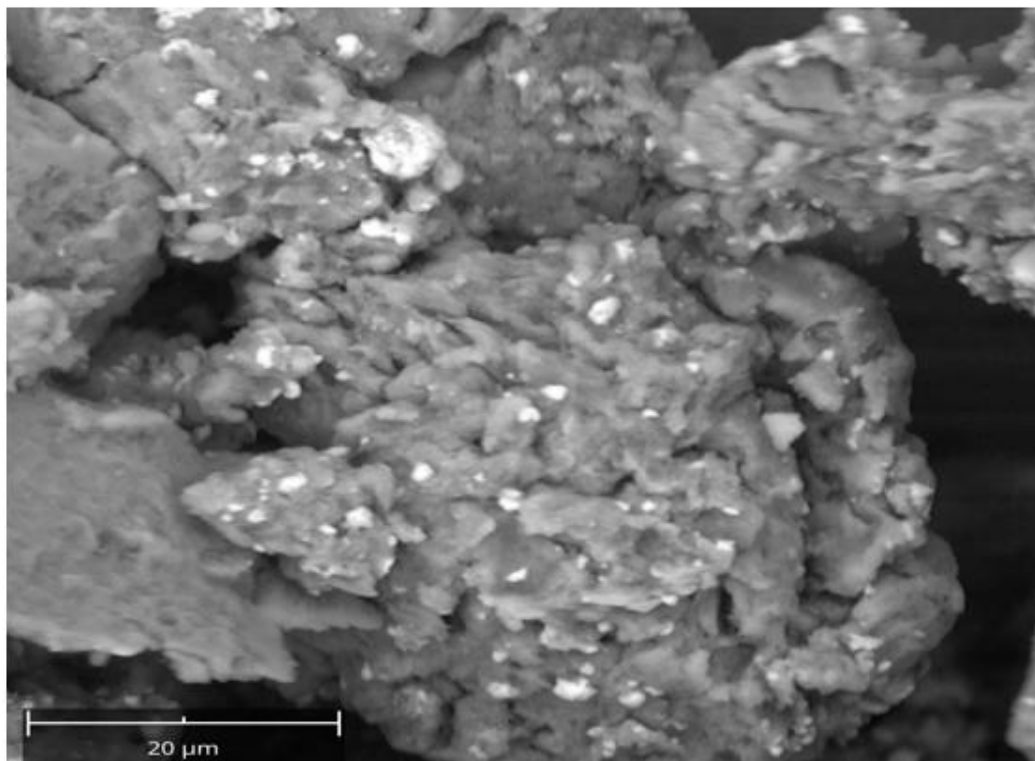


**Figure 31(b):** SEM micrograph of the graphene oxide at 4000X magnification

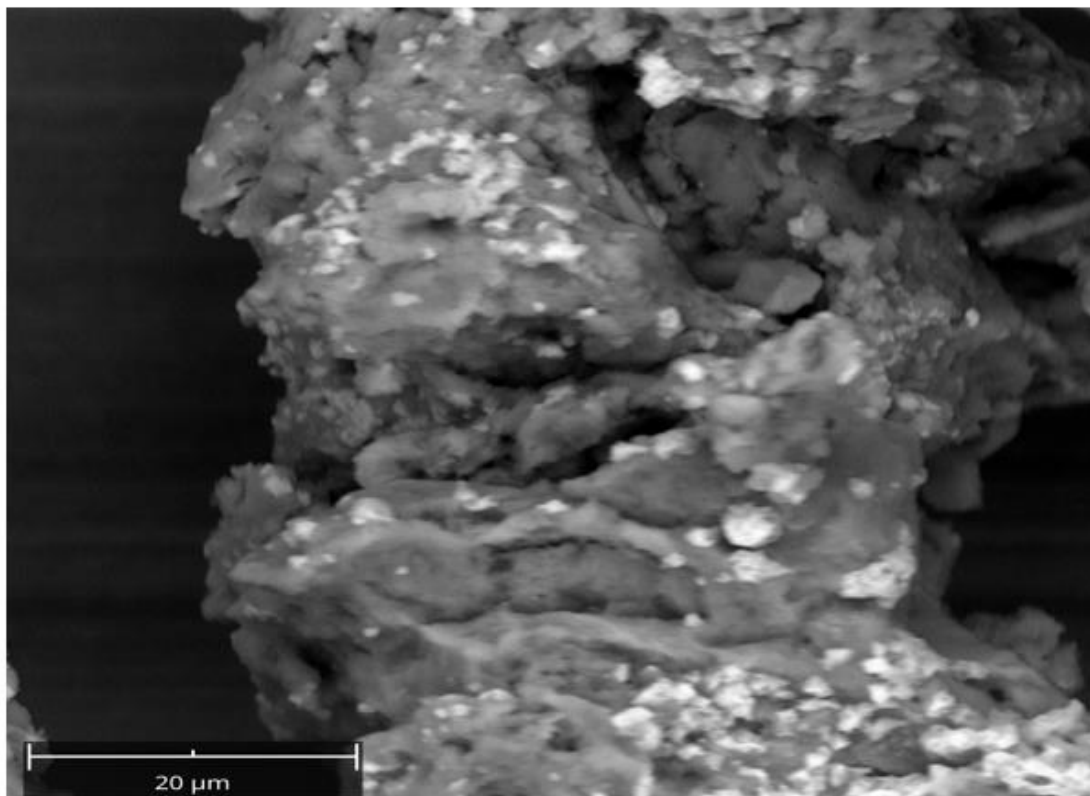


**Figure 32(c):** SEM micrograph of rGO at 4000X magnification.

### 3.3.2 SEM analysis of fumaryl pillars and holes

The fumaryl pillar acts as a spacer between the GO layers so that they can reduce the randomly stacking agglomeration of GO layers which will provide efficient transport pathways resulting in high ion accessible surface area.

#### ***3.3.2.1 SEM micrographs of holey graphene oxide functionalized with fumaryl pillars***

Figure 28 is the SEM image of **hGOFC0.15**, which was synthesized using gradual thermal annealing of GO functionalized with a fumaryl pillar as a precursor (**GOFC0.15**).

The SEM image demonstrates the thin films which are also stacked above each other, the layers are stacked because a small quantity of fumaryl chloride was inserted between the layers, and hence the films appear stacked (0.15 mmol of fumaryl chloride). The presence of

pores on the micrograph is not clearly seen at the magnification of 4000X, but TEM will provide more information.

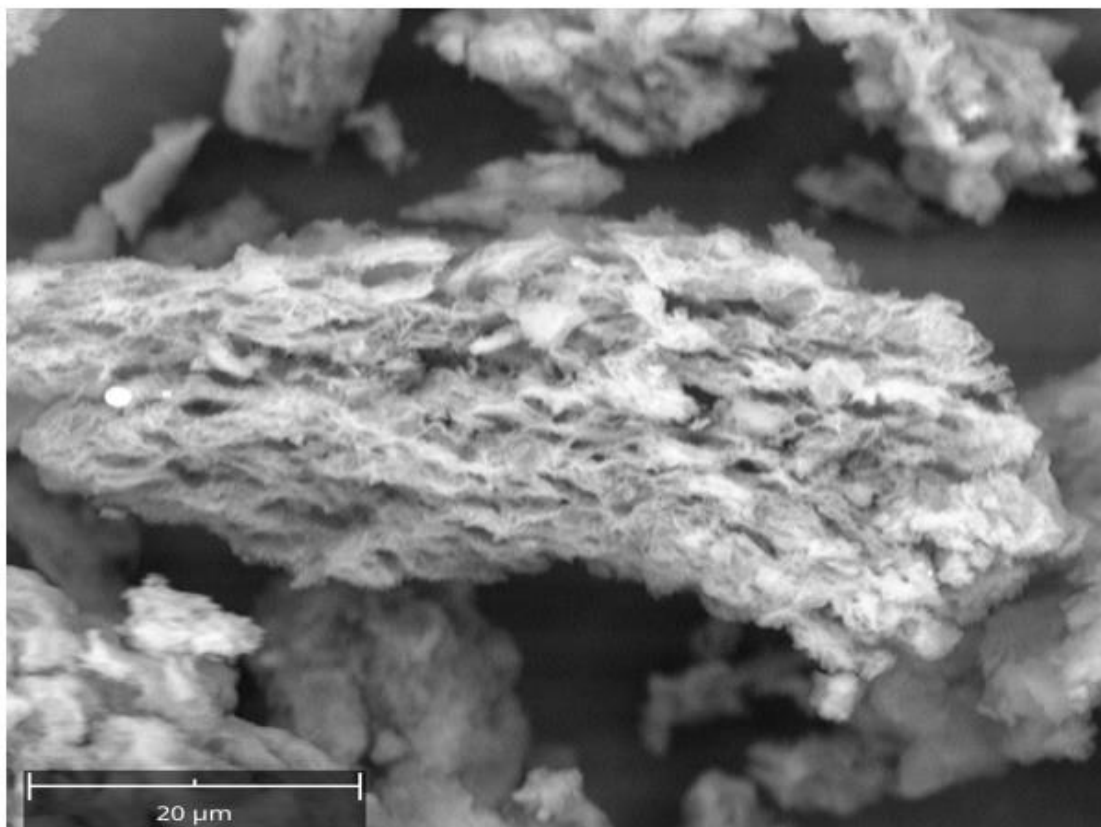


**Figure 33:** SEM micrograph of **hGOFC0.15** at 4000X magnification

### ***3.3.2.2 SEM micrographs of holey reduced graphene oxide functionalized with fumaryl pillars***

Figure 29 is the SEM image of **hrGOFC0.15**, which was synthesized using gradual thermal annealing of rGO functionalized with fumaryl pillars as a precursor (**rGOFC0.15**). The SEM image shows the thick, rough grains of **hrGOFC0.15** with small scattered agglomerated flakes, the grains appear agglomerated because a small quantity of fumaryl chloride was used, hence the films appear compact (0.15 mmol of fumaryl chloride). The presence of pores is not clearly visible in this micrograph, but TEM will reveal more information.

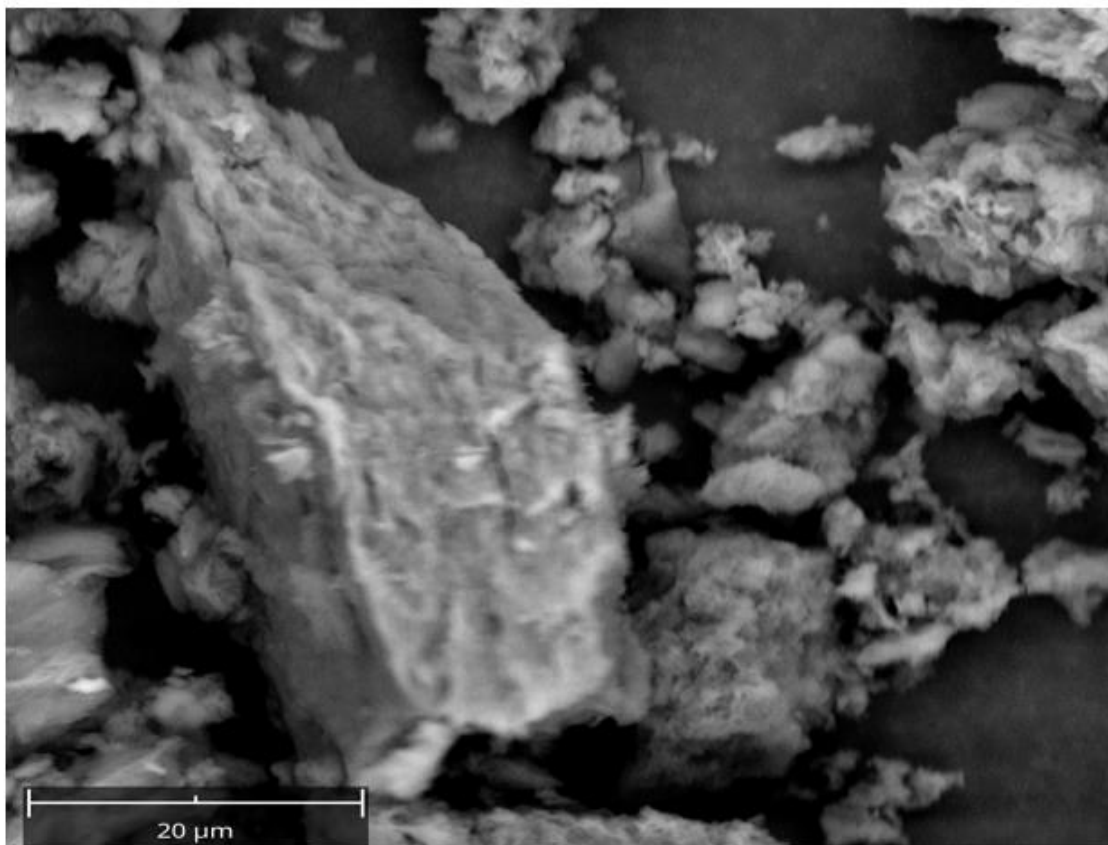


**Figure 34:** SEM micrograph of **hrGOFC0.15** at 4000X magnification.

### 3.3.3 SEM analysis of maleoyl pillars and holes

The maleoyl pillar acts as a spacer between the GO layers so that they can reduce the randomly stacking agglomeration of GO layers which will provide an efficient in transport pathways resulting in high ion accessible surface area.

#### 3.3.3.1 SEM micrographs of holey graphene oxide functionalized with maleoyl pillars

Figure 30 is the SEM image of **hGOMC0.15**, which was synthesized using a gradual thermal annealing method using a GO functionalized with a *maleoyl pillar* as a precursor (**GOMC0.15**). The SEM image shows an aggregated grain of **hGOMC0.15** and the micrograph reveals the presence of pores on the grain even though they are not clearly seen at the magnification of 4000X, but TEM will provide more information.

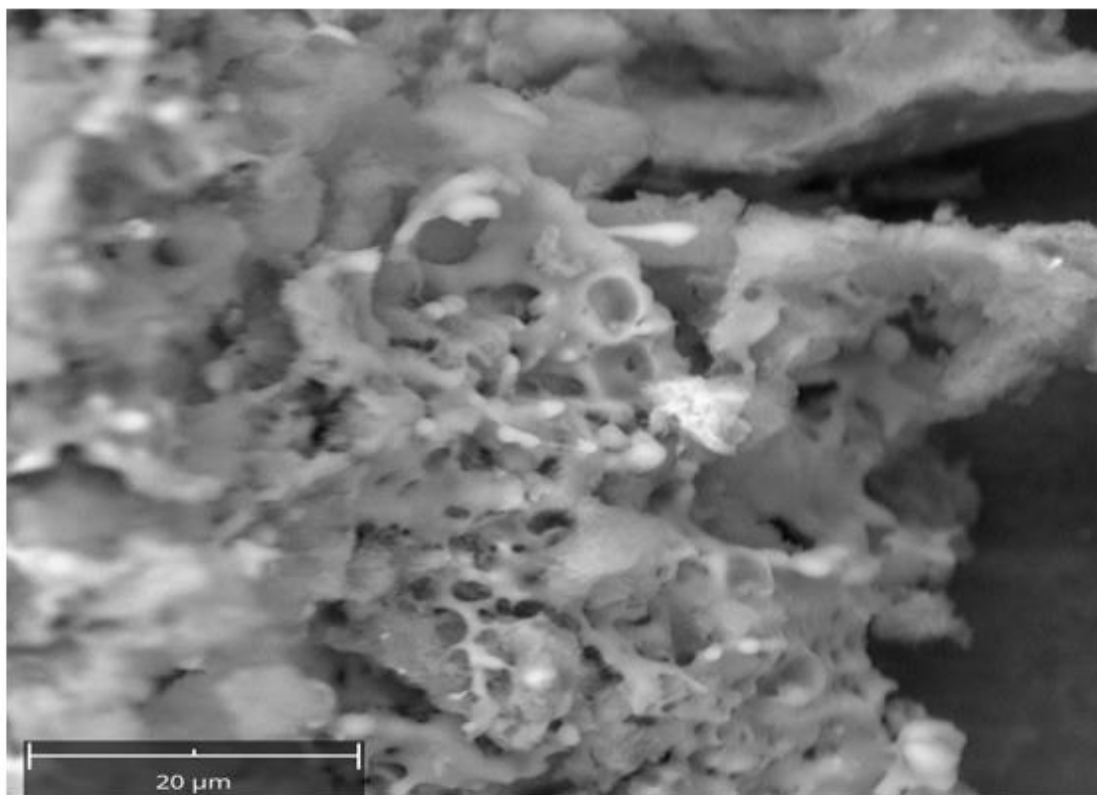


**Figure 35:** SEM micrograph of **hGOMC0.15** at 4000X magnification

### ***3.3.3.2 SEM micrographs of holey reduced graphene oxide functionalized with maleoyl pillars***

Figure 31 is a SEM image of **hrGOMC0.15**, which was synthesized using a gradual thermal annealing method using an rGO functionalized with maleoyl pillar as a precursor (**rGOMC0.15**), which shows thick worm-like films that are randomly aggregated. The presence of pores is not clear in this micrograph, but TEM will reveal more information.

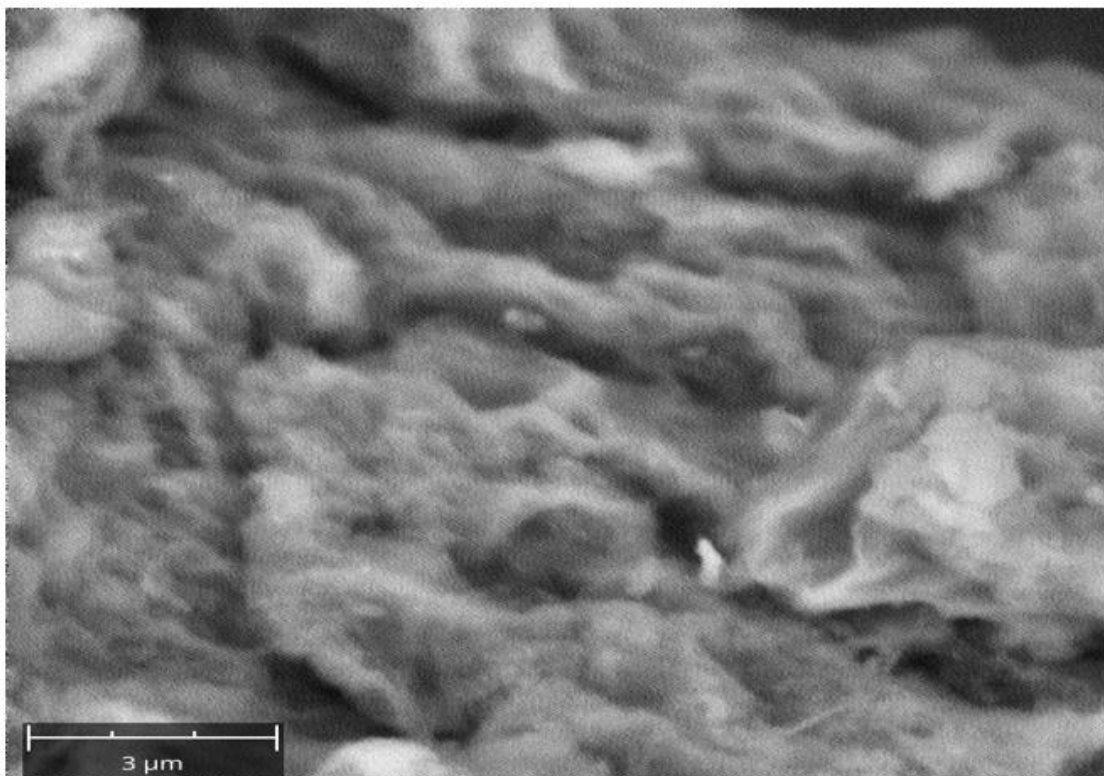


**Figure 36:** SEM micrograph of **hrGOMC0.15** at 10000X magnification

### 3.3.4 SEM analysis of oxalyl pillars and holes

The oxalyl pillar acts as a spacer between the GO layers so that they can reduce the randomly stacking agglomeration of GO layers which will provide efficient transport pathways resulting in high ion-accessible surface area.

#### 3.3.4.1 SEM micrographs of holey graphene oxide functionalized with oxalyl pillars

Figure 32 is the SEM image of **hGOOC0.15**, which was synthesized using a gradual thermal annealing method using a GO functionalized with oxalyl pillars as a precursor (**GOOC0.15**). The SEM image shows the scattered rough grains of **hGOOC0.15** at the magnification of 2000X as shown in the micrograph, the presence of pores on the grains is not clearly seen at this magnification but TEM will provide more information.

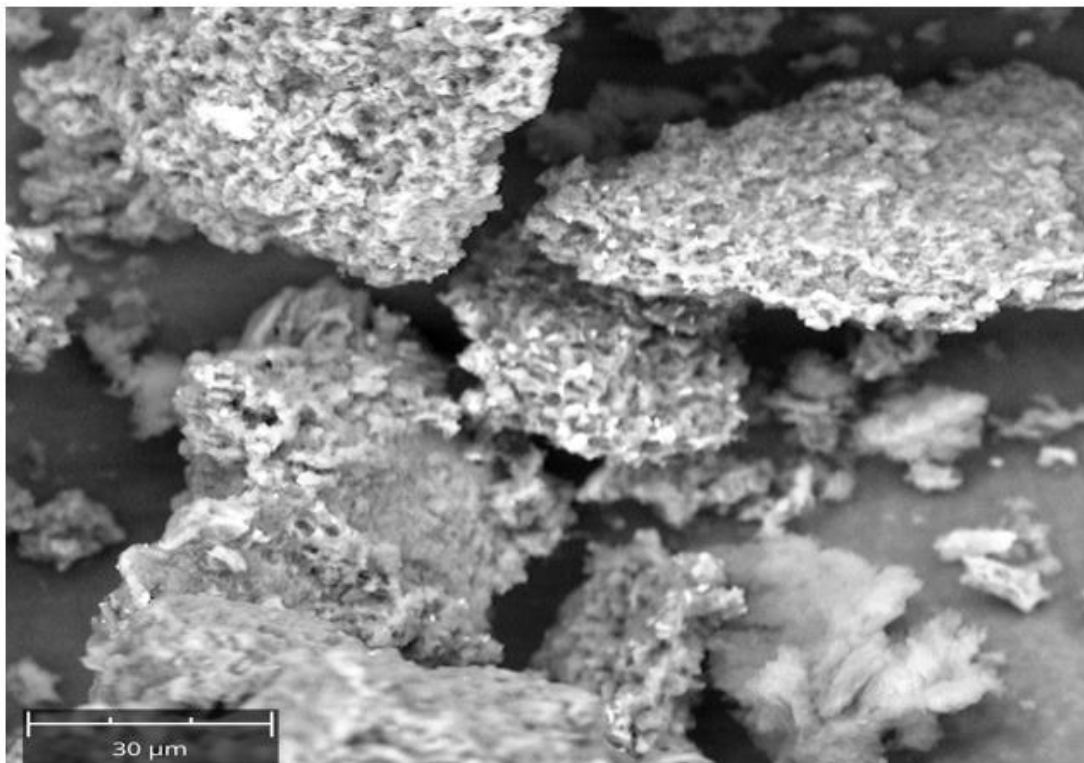


**Figure 37:** SEM micrograph of **hGOOC0.15** at 2000X magnification.

#### **3.3.4.2 SEM micrographs of holey reduced graphene oxide functionalized with oxalyl pillars**

Figure 33 is a SEM image of **hrGOOC0.15**, which was synthesized using a gradual thermal annealing using a rGO functionalized with *oxalyl pillars* as a precursor (**rGOOC0.15**). The SEM micrograph shows a wrinkled-like structure which is having thin films which are randomly aggregated, the presence of pores is not clear on this micrograph, but TEM will reveal more information.

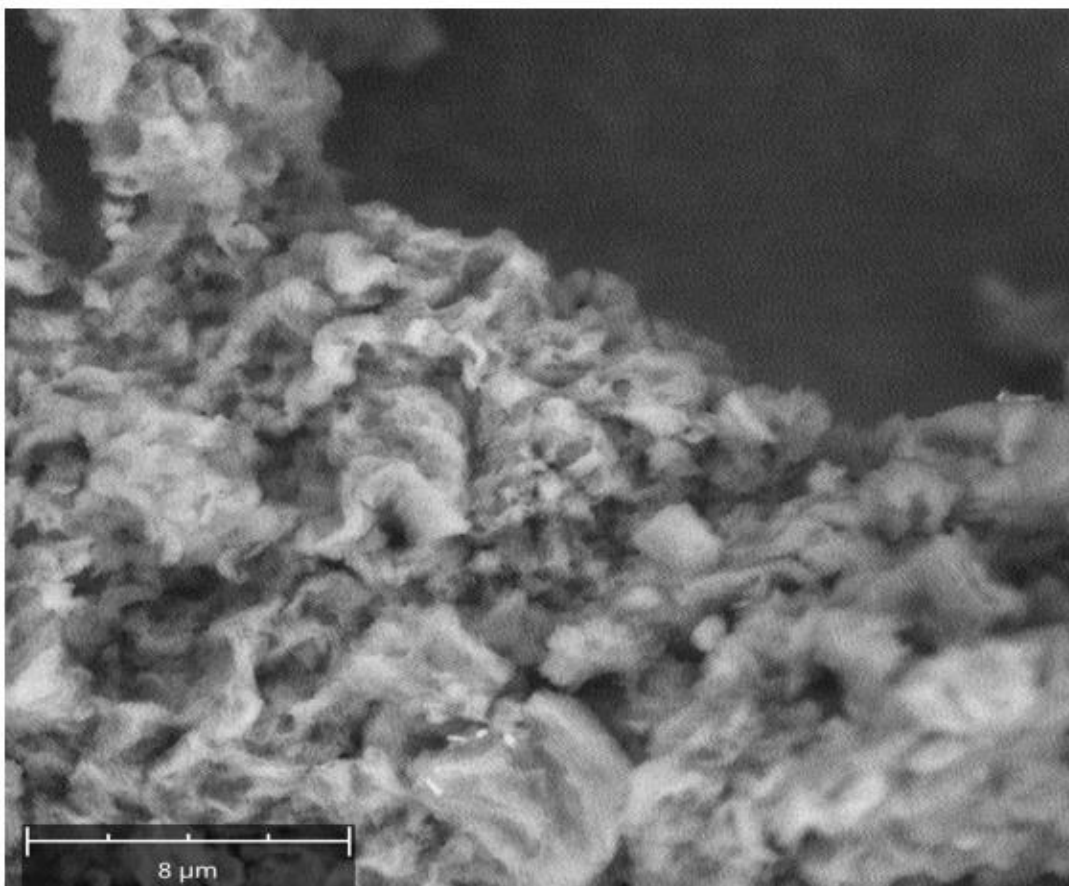


**Figure 38:** SEM micrograph of **hrGOOC0.15** at 10000X magnification.

### 3.4 TRANSMISSION ELECTRON MICROSCOPY (TEM)

Transmission electron microscopy (TEM) is an analytical technique used to investigate the smallest structures in matter. TEM can magnify nanoscale structures up to 50 million times, revealing astonishing detail at the atomic scale, unlike optical microscopes that use visible light. This is because electrons have a significantly shorter wavelength (about 100 000 times shorter) than that of visible light when accelerated through a strong electromagnetic field, thus increasing the microscope resolution significantly (Egerton, 2016). To create a TEM image, a high-energy electron beam passes through an extremely thin material that allows electrons to pass through usually thinner than 100 nm. The microscope uses a series of electromagnetic lenses and openings to focus on the beam on the sample, reducing distortions and increasing the resultant image on a dedicated camera or phosphor screen. TEM confirmed the presence of

pores in the holey **hrGOFC0.15**, **hGOMC0.15**, and **hrGOOC0.15** layers; therefore, these holey graphenes were successfully synthesized.

### 3.4.1 TEM micrographs of GO and rGO

The TEM images of GO and rGO (Figure 34) exhibit a sheet-like morphology with different transparencies of the investigated area. Figure 34(a) shows the TEM images of GO revealing sheet morphology with different transparencies, and dark areas which indicate the thick stacking nanostructure of several graphene oxide layers containing some oxygen functional groups. The higher transparency areas indicate much thinner films of a few layers of graphene oxide resulting from exfoliation. In Figure 34(b), rGO sheets are shown that are agglomerated and stacked with fewer wrinkles. In contrast to the graphene oxide sample (Fig. 34(a)), the surface area of the delaminated graphene layers is much greater after the chemical reduction of GO, demonstrating layer delamination due to reduction.

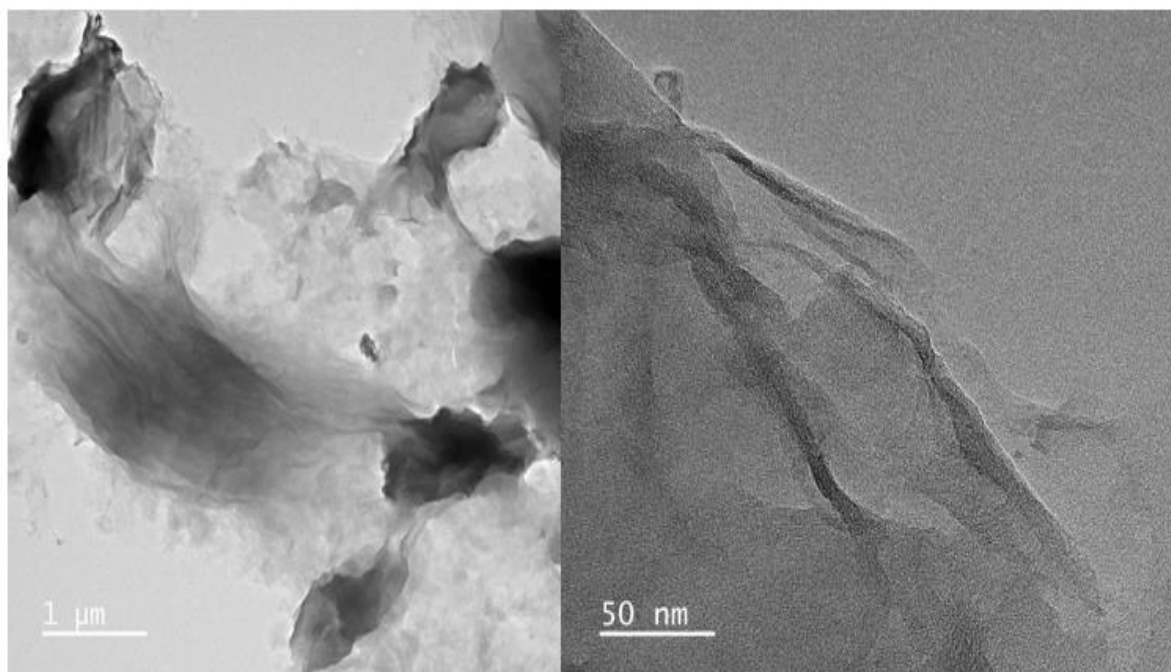


**Figure 39(a):** TEM images of GO.

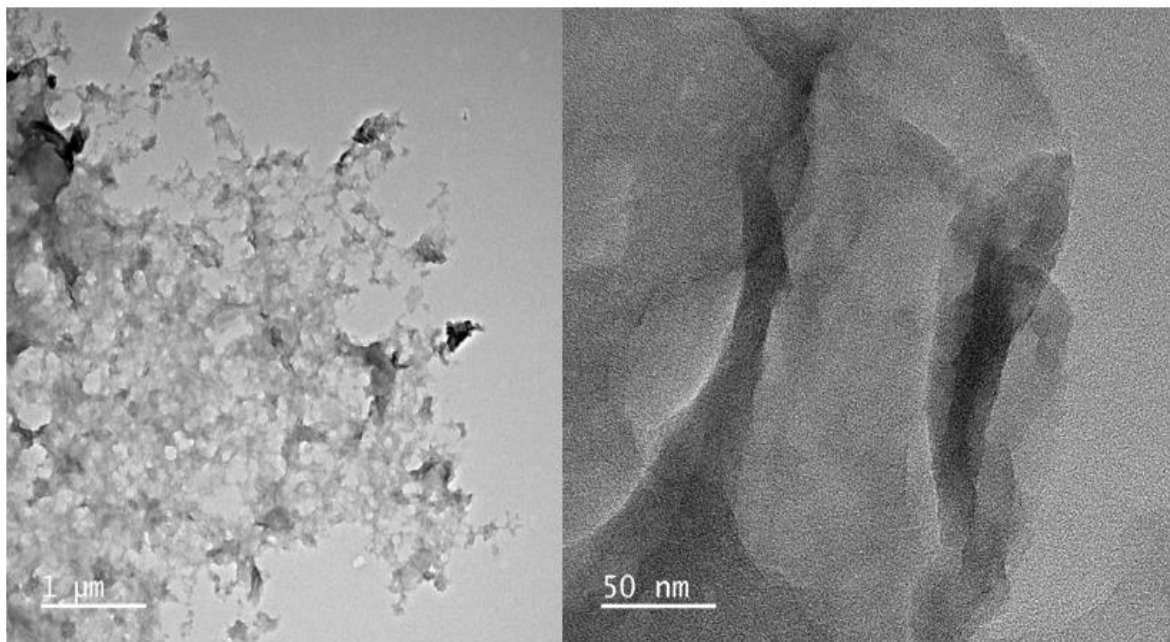


**Figure 40(b):** TEM images of rGO.

### 3.4.2 TEM analysis of GO with fumaryl pillars and holes

#### 3.4.2.1 TEM images of holey graphene oxide functionalized with fumaryl pillars (*hGOFC0.15*)

Figure 35 displays the TEM images of holey graphene oxide synthesized using **GOFC0.15** as a precursor. The image exhibits large darker areas and a transparent sheet-like structure that is aggregated; the dark areas indicate the thick stacking of several holey graphene oxide layers with some oxygen-containing functional groups. Several pores can be seen in the higher-resolution TEM image; therefore **hGOFC0.15** has been successfully synthesized.

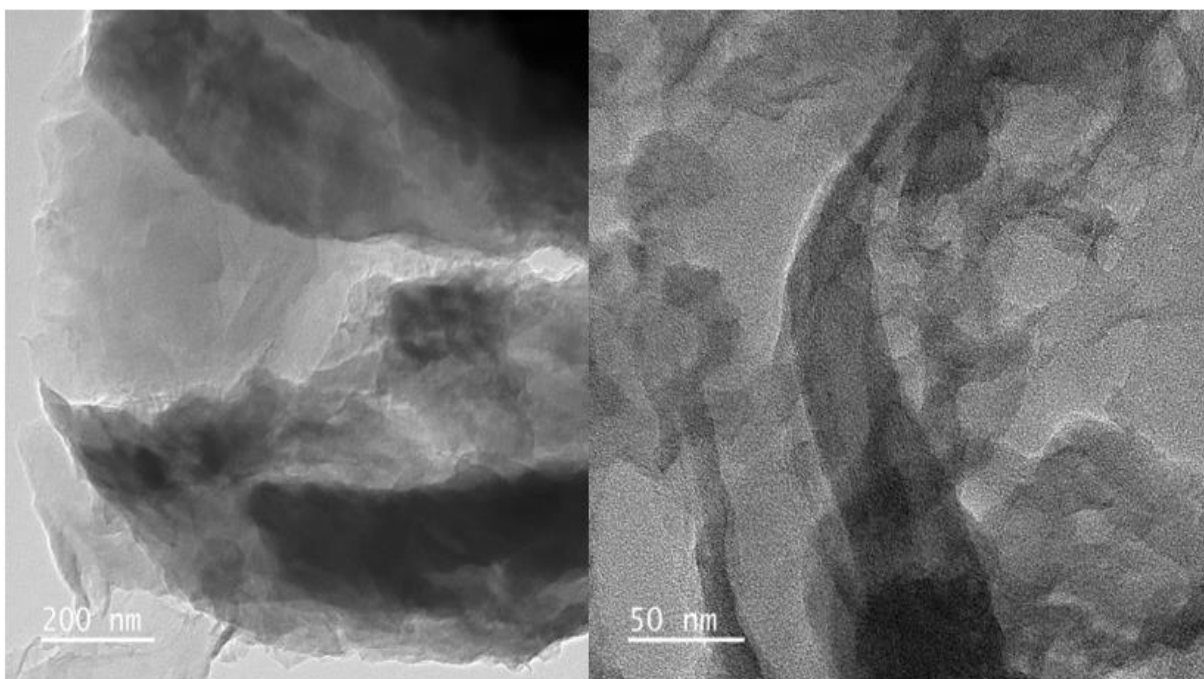


**Figure 41:** TEM images of **hGOFC0.15**

#### ***3.4.2.2 TEM image of holey reduced graphene oxide functionalized with fumaryl pillars (hrGOFC0.15)***

Figure 36 shows a TEM image of holey reduced graphene oxide synthesized using **rGOFC0.15** as a precursor. Figure 36 exhibits an aggregated transparent sheet-like structure with several pores in the **hrGOFC0.15** sheets, as evidenced by the small thick and dark circles that represent pores; therefore **hrGOFC0.15** has been successfully synthesized.

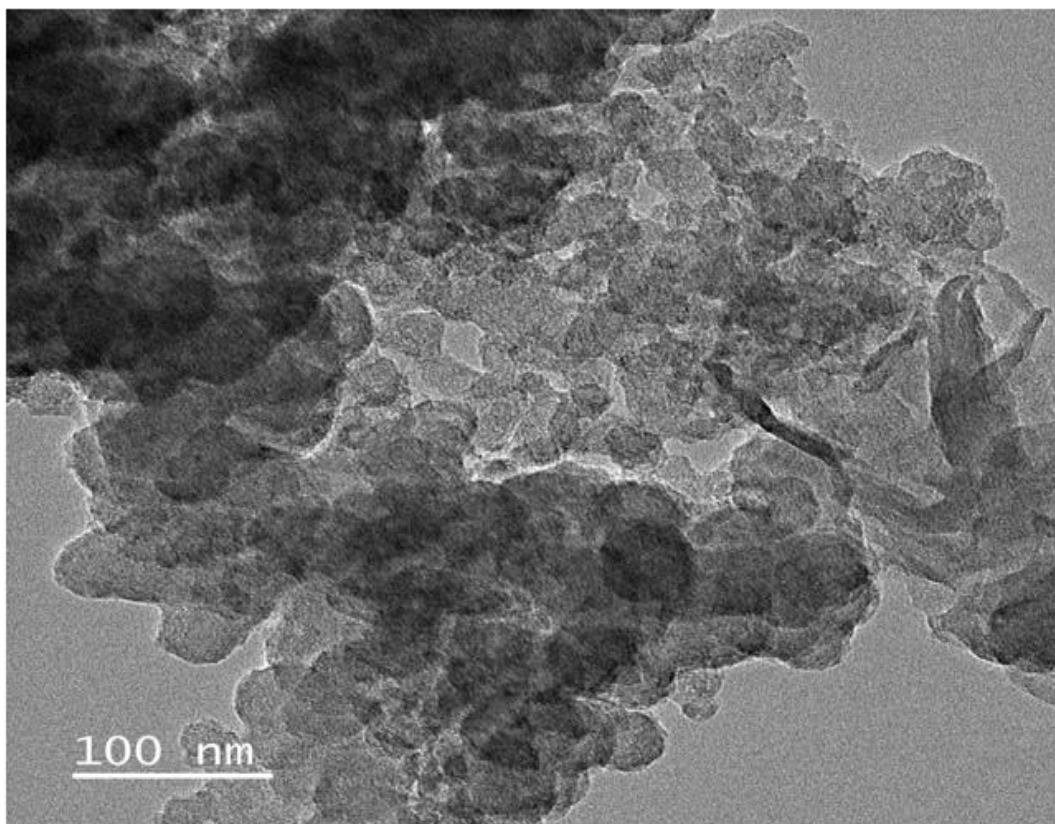


**Figure 42:** TEM image of hrGOFC0.15.

### 3.4.3 TEM analysis of maleoyl pillar and holes

#### ***4.4.3.1 TEM images of holey graphene oxide functionalized with maleoyl pillar (hGOMC0.15)***

Figure 37 shows the TEM images of holey graphene oxide synthesized using **GOMC0.15** as a precursor. The images show dark and transparent sheet-like structures. The dark areas indicate the thick stacking of several holey graphene oxide layers with some oxygen-containing functional groups; the higher transparency area indicates much thinner films of a few layers of pillared graphene oxide clearly showing pores. This is evidenced by randomly distributed small dark circles on the sheet in the transparent areas, representing holes. Therefore, **hGOMC0.15** was successfully synthesized.

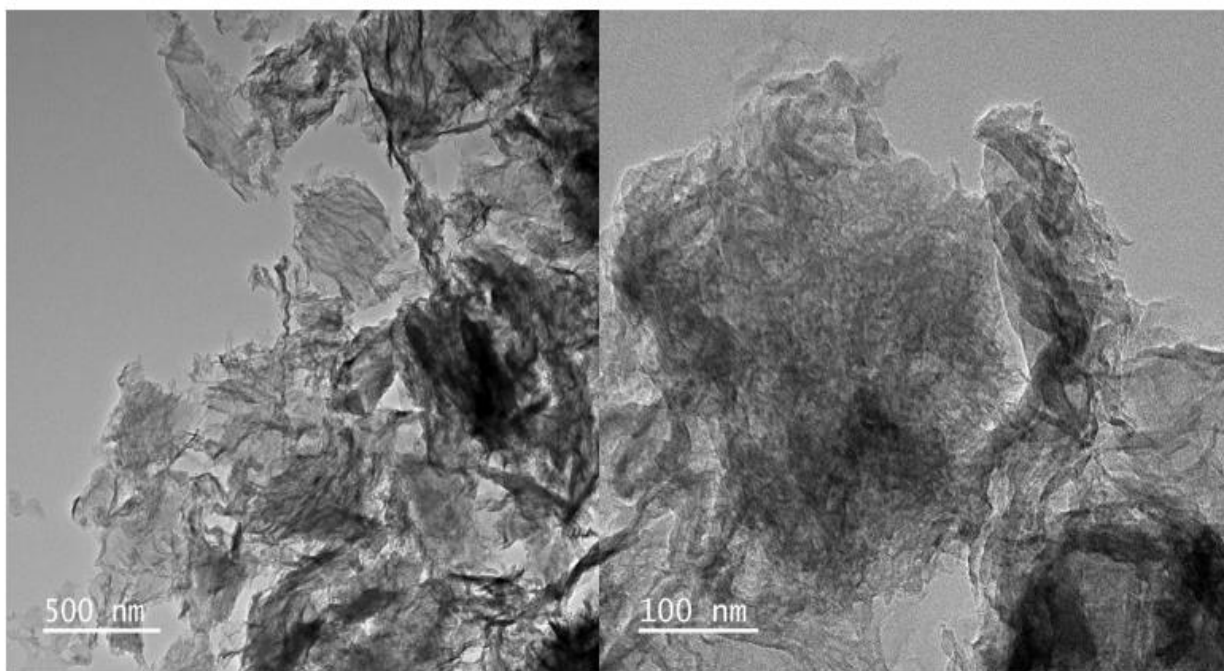


**Figure 43:** TEM images of **hGOMC0.15**.

#### **3.4.3.2 TEM images of holey reduced graphene oxide functionalized with maleoyl pillar (hrGOMC0.15)**

Figure 38 shows TEM images of holey reduced graphene oxide synthesized using **rGOMC0.15** as a precursor. The images exhibit crumpled transparent sheet-like structures with several pores and crystalline areas.

### **3.4.4 TEM analysis of oxalyl pillars and holes**

#### **3.4.4.1 TEM images of holey graphene oxide functionalized with oxalyl pillars (hGOOC0.15)**

Figure 39 shows the TEM images of holey graphene oxide synthesized using **GOOC0.15** as a precursor. The images show darker and transparent sheet-like structures wrinkles and scrolls on the surface of the **hGOOC0.15** sheets, clearly showing the stacking of hGO layers with oxygen-containing functional groups. TEM cannot confirm the fabrication of pores on the **hGOOC0.15**.

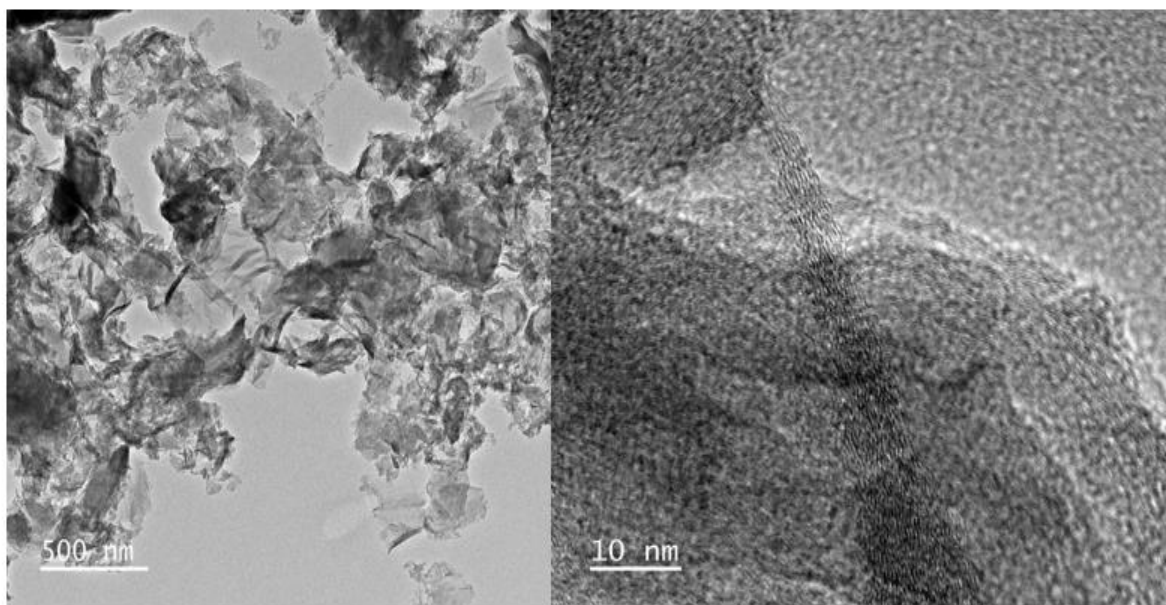


**Figure 44:** TEM images of hrGOMC0.15

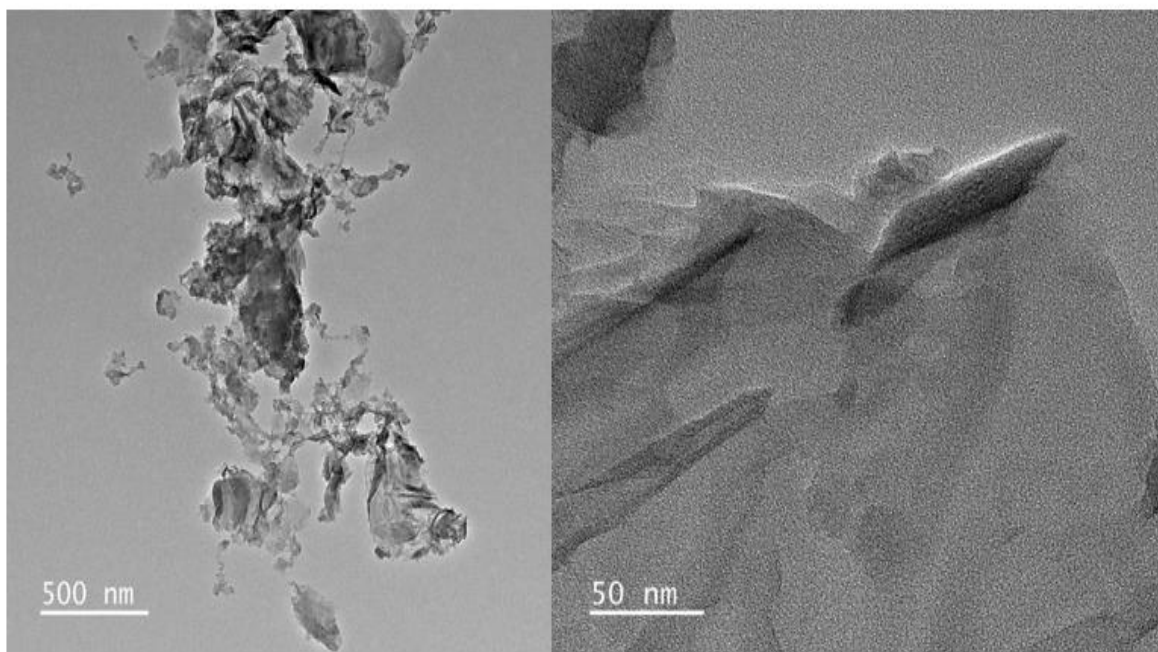


**Figure 45:** TEM images of hGOOC0.15.

#### 3.4.4.2 TEM images of holey reduced graphene oxide functionalized with oxalyl pillars (hrGOOC0.15)

Figure 40 shows TEM images of holey reduced graphene oxide synthesized using **rGOOC0.15** as a precursor. The images show transparent sheet-like structures with randomly distributed small dark circles on the sheets representing holes, meaning that **hrGOOC0.15** was successfully synthesized using the gradual thermal annealing method.

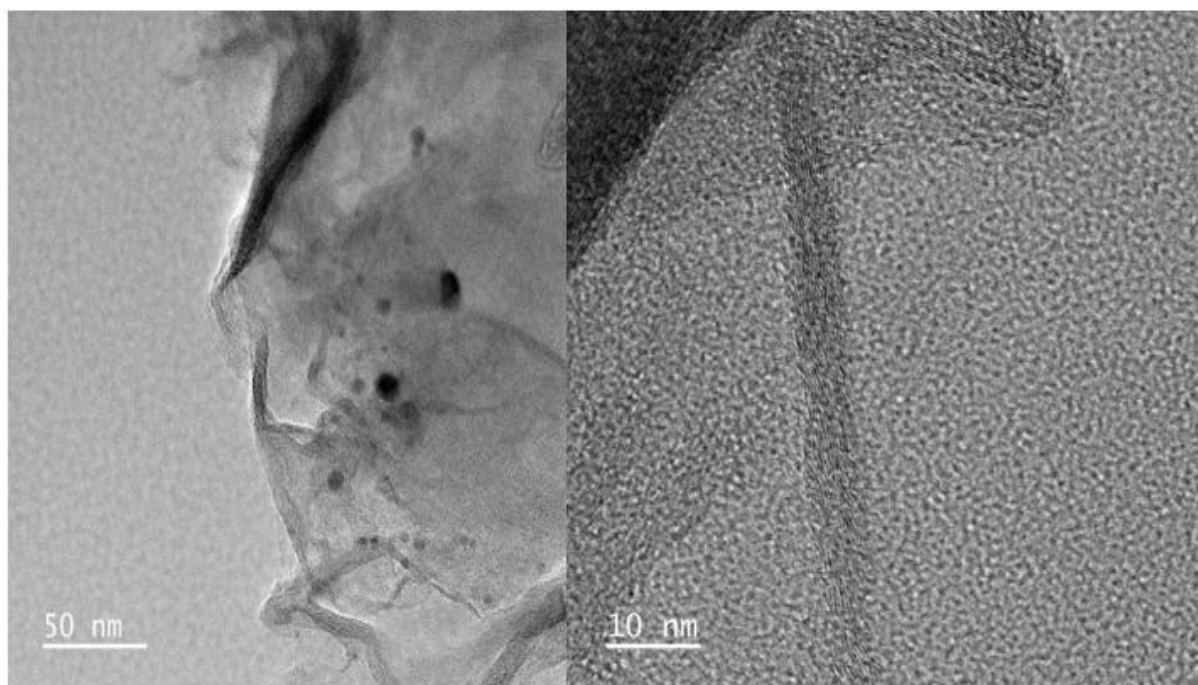


**Figure 46:** TEM images of **hrGOOC0.15**.

### 3.5 SUMMARY

To conclude this chapter, the most salient results are presented and discussed briefly.

#### 3.5.1 Graphene Oxide – $d_{(002)} = 0.337$ nm

The IR analysis (Figure 41(a)) revealed the presence of oxygen-containing functional groups in the GO spectrum, as evidenced by the presence of a broad band at  $3312\text{ cm}^{-1}$ . A second band

occurs at  $1716\text{ cm}^{-1}$ , corresponding to a C=O stretching vibration, and a third band at  $1137\text{ cm}^{-1}$  represents a C-O stretching vibration. In the XRD spectrum (Figure 41(b)), the broad (002) diffraction peak appeared at  $2\theta = 26.39^\circ$  with a  $d_{(002)}$  spacing of 0.337 nm. The observed broad peak indicates that GO has a small particle size.

SEM (Figure 41(c)) shows the morphology of GO as thick, stacked, and randomly aggregated grains, due to the presence of oxygen functional groups bound to the plane. The TEM images (Figure 41(d,e,f)) of GO exhibit a sheet-like morphology with different transparencies of the investigated area. Dark areas indicate the thick stacking nanostructure of several graphene oxide layers containing some oxygen functional groups. The higher transparency areas indicate much thinner films of a few layers of graphene oxide resulting from exfoliation.

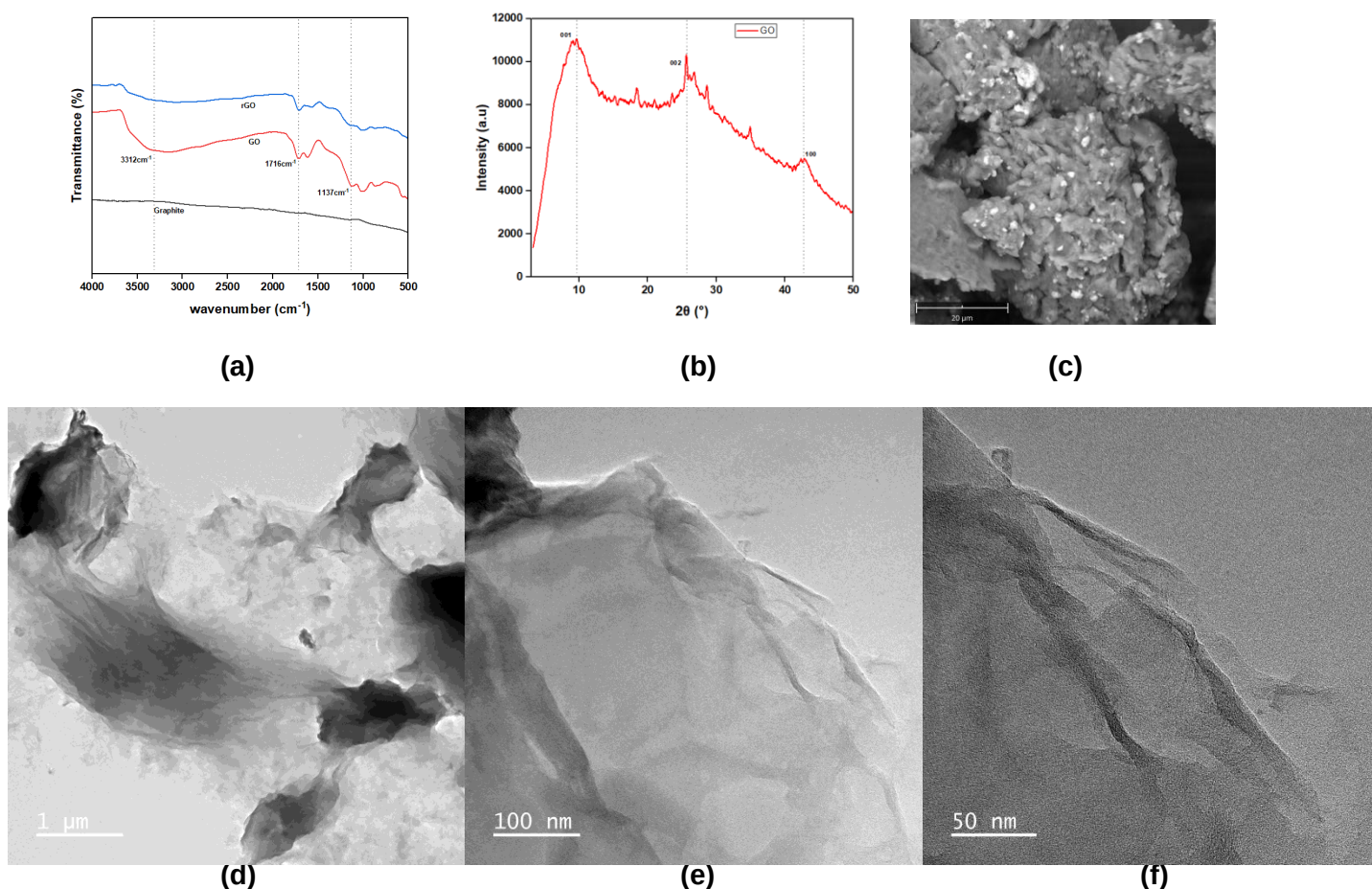


**Figure 47:** Graphene oxide: (a) IR spectrum; (b) XRD spectrum; (c) SEM; (d,e,f) TEM at different magnifications.

### 3.5.2 Reduced Graphene Oxide – $d_{(002)} = 0.355$ nm

In the IR spectrum of rGO (Figure 42(a)), the broad OH stretch is absent, indicating that some of the oxygen-containing functional groups were reduced. However, there is still a band occurring at  $1716\text{ cm}^{-1}$  corresponding to a C=O stretching vibration. The sharp diffraction peak (Figure 42(b)) at  $2\theta = 24.92^\circ$  corresponds to the interlayer spacing  $d_{(002)} = 0.357$  nm, which is an increase over that of GO. The material is fairly crystalline and has structural order.

The SEM image of rGO (Figure 42(c)) reveals an ultrathick, folded, and aggregated grain. However, the grain of rGO is no longer as aggregated as that of GO. The TEM images of rGO (Figure 42(d,e,f)) exhibit a sheet-like morphology stacked with fewer wrinkles.

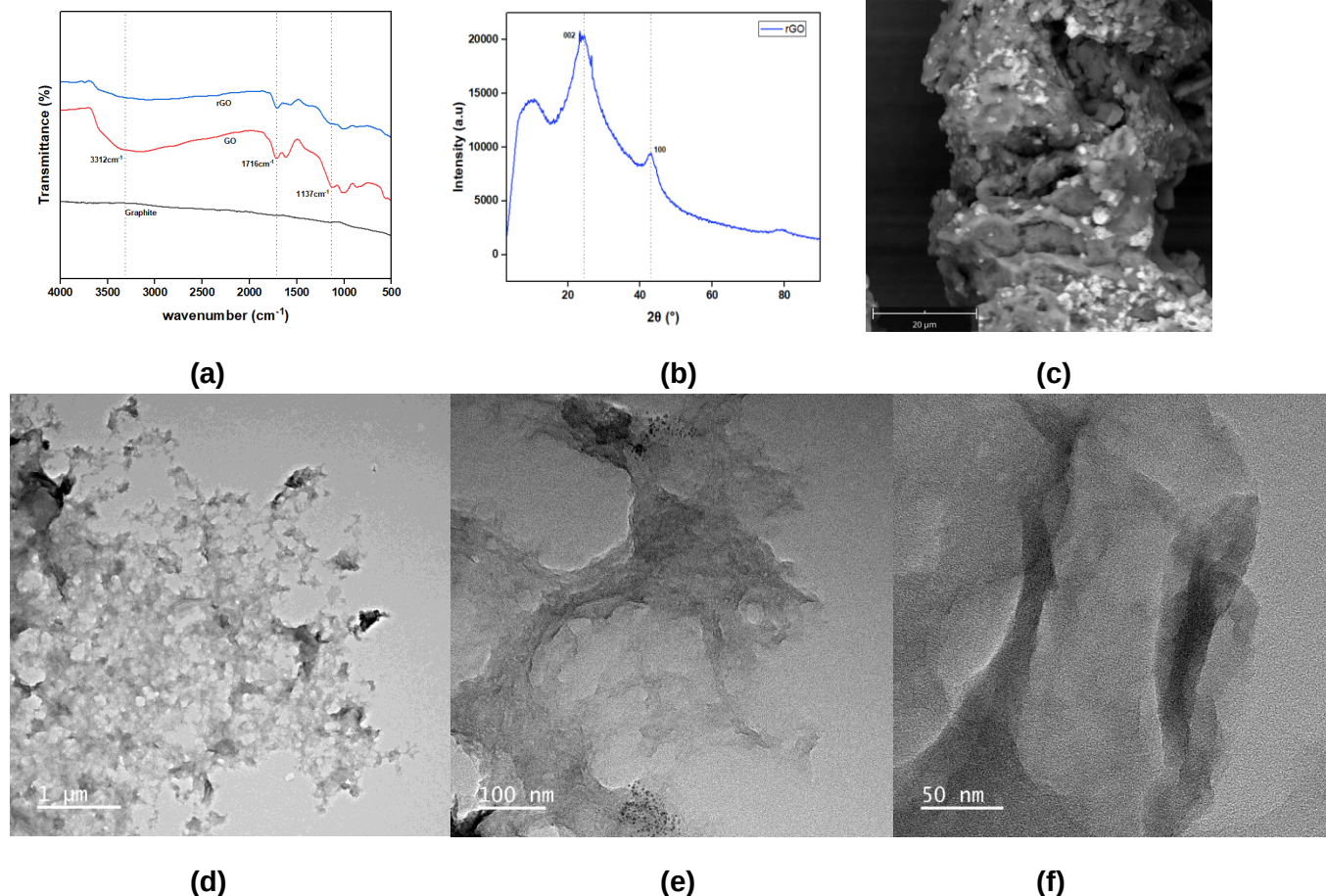


**Figure 48:** Reduced graphene oxide: (a) IR spectrum; (b) XRD spectrum; (c) SEM; (d,e,f) TEM at different magnifications.

### 3.5.3 Holey fumaryl pillared graphene oxide **hGOFC0.15** – $d_{(002)} = 0.352$ nm

The broad OH stretching vibration in the IR spectrum (Figure 43(a)) is absent in the spectrum of the holey fumaryl pillared graphene oxide (**hGOFC0.15**), which means that the OH has been reduced. A band occurring at  $2348\text{ cm}^{-1}$  corresponds to the C-H stretch; a second band appears at  $1716\text{ cm}^{-1}$  corresponding to a C=O stretching vibration. The sharp (002) XRD peak (Figure 43(b)) is at  $2\theta = 25.25^\circ$  with  $d_{(002)} = 0.352$  nm. The interlayer spacing  $d_{(002)}$  increased from 0.337 nm in graphite to 0.352 nm in GO and **hGOFC0.15**.

The SEM image (Figure 43(c)) shows the stacked thin films with holes. The presence of pores is not clearly seen at the magnification of 4000X, but TEM (Figure 43(d,e,f)) exhibits large darker aggregated areas and a transparent sheet-like structure. Several pores can be seen in the higher-resolution TEM image; therefore, **hGOFC0.15** has been successfully synthesized.

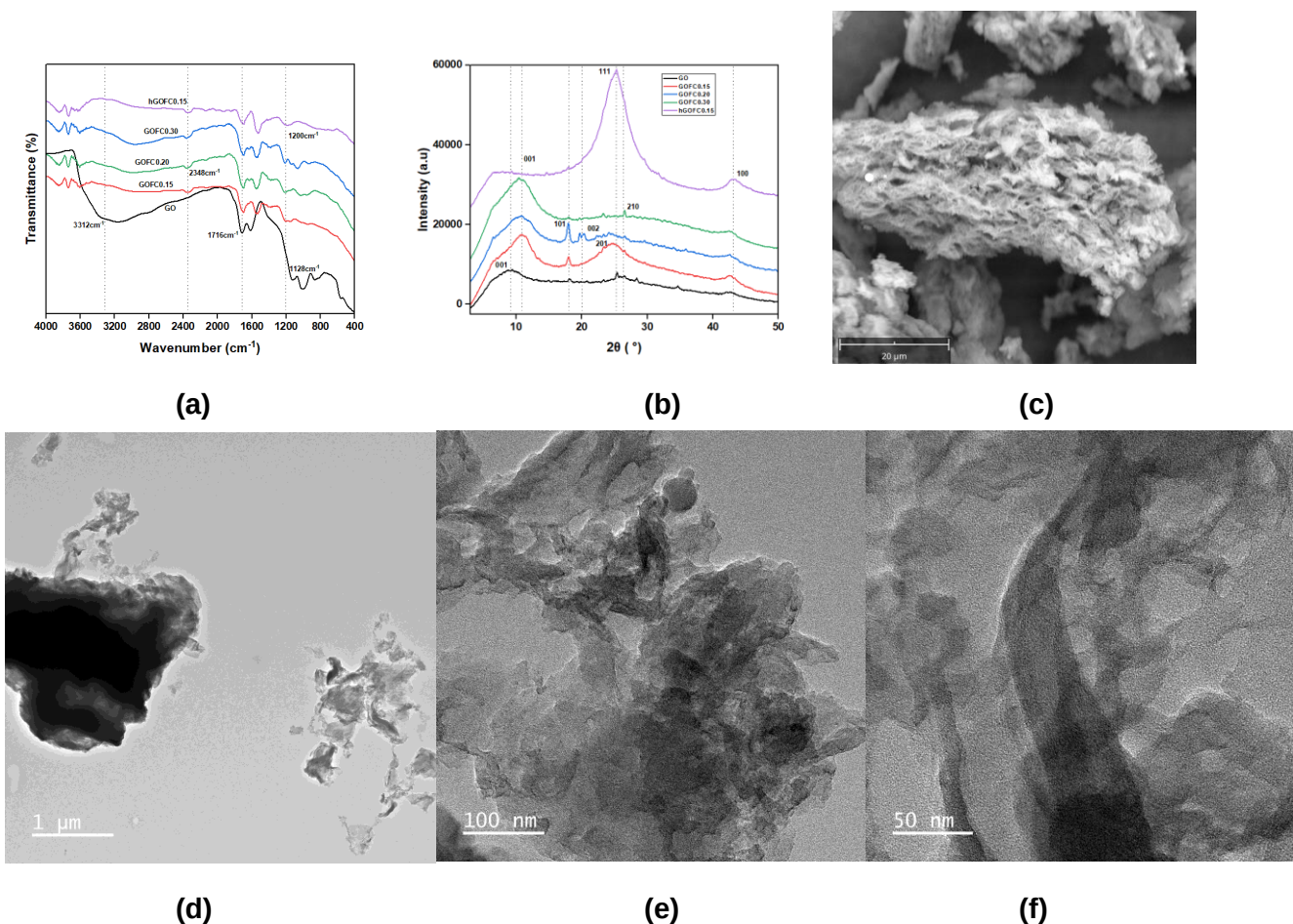


**Figure 49:** Holey fumaryl pillared graphene oxide **hGOFC0.15**: (a) IR spectrum; (b) XRD spectrum; (c) SEM; (d,e,f) TEM at different magnifications.

### 3.5.4 Holey fumaryl pillared reduced graphene oxide **hrGOFC0.15** – $d_{(002)} = 0.378$ nm

Infrared spectroscopy of **hrGOFC0.15** (Figure 44(a)) revealed a C-H stretching band at 2403 cm<sup>-1</sup> and the usual bands at 1777 cm<sup>-1</sup> (C=O), 1605 cm<sup>-1</sup> (C=C), and 1268 cm<sup>-1</sup> (C-O). The XRD (Figure 49(b)) shows a low-intensity sharp diffraction peak (110) at  $2\theta = 16.7^\circ$  with an interlayer spacing of 0.530 nm. The (002) interlayer spacing  $d_{(002)} = 0.378$  nm), greater than that of graphite and GO. The material is fairly crystalline.

The SEM image (Figure 44(c)) shows thick, rough grains with small scattered agglomerated flakes. The presence of pores is not clearly visible on this micrograph, but the TEM (Figure 44(d,e,f)) reveals an aggregated transparent sheet-like structure with several pores in the **hrGOFC0.15** sheets, showing that the pillared and holey graphene was successfully synthesized.

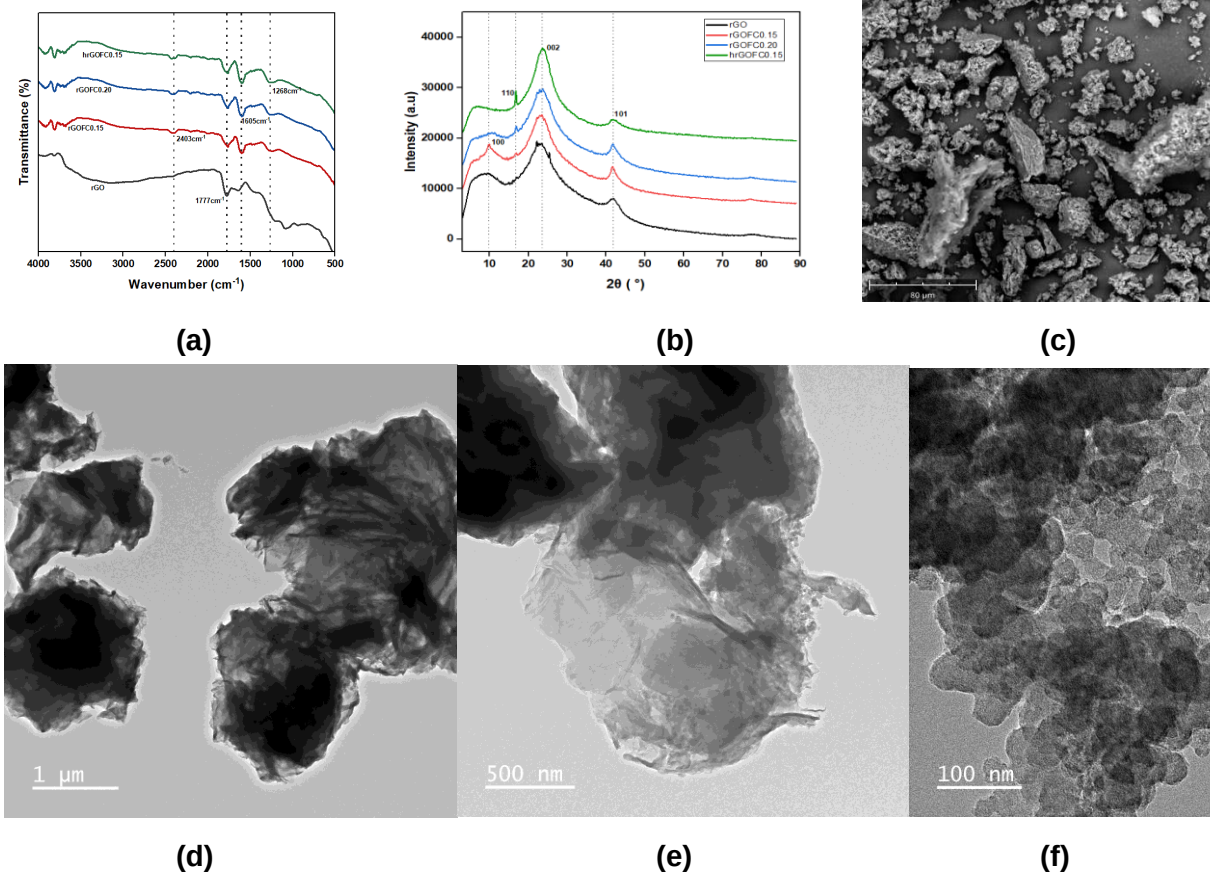


**Figure 50:** Holey fumaryl pillared reduced graphene oxide **hrGOFC0.15**: (a) IR spectrum; (b) XRD spectrum; (c) SEM; (d,e,f) TEM at different magnifications.

### 3.5.5 Holey maleoyl pillared graphene oxide **hGOMC0.15** – $d_{(002)} = 0.355$ nm

IR spectroscopy (Figure 45(a)) shows the absence of the broad OH band and the C-O vibration at  $1127\text{ cm}^{-1}$ , while the usual bands still appear at  $2342\text{ cm}^{-1}$  (C-H) and  $1700\text{ cm}^{-1}$  (C=O). These results show that GO, pillared graphene, and holey graphene were successfully synthesized. In the XRD (Figure 45(b)), the interlayer spacing remained virtually the same. The maleoyl pillars did not significantly alter the GO interlayer spacing and **hGOMC0.15** has small size effects and contains defects.

The SEM image (Figure 45(c)) shows aggregated grains of **hGOMC0.15** with pores; the TEM images (Figure 45(d,e,f)) show dark and transparent sheet-like structures. The transparent areas indicate thin films of a few layers of pillared graphene oxide clearly showing pores. Therefore, **hGOMC0.15** was successfully synthesized.

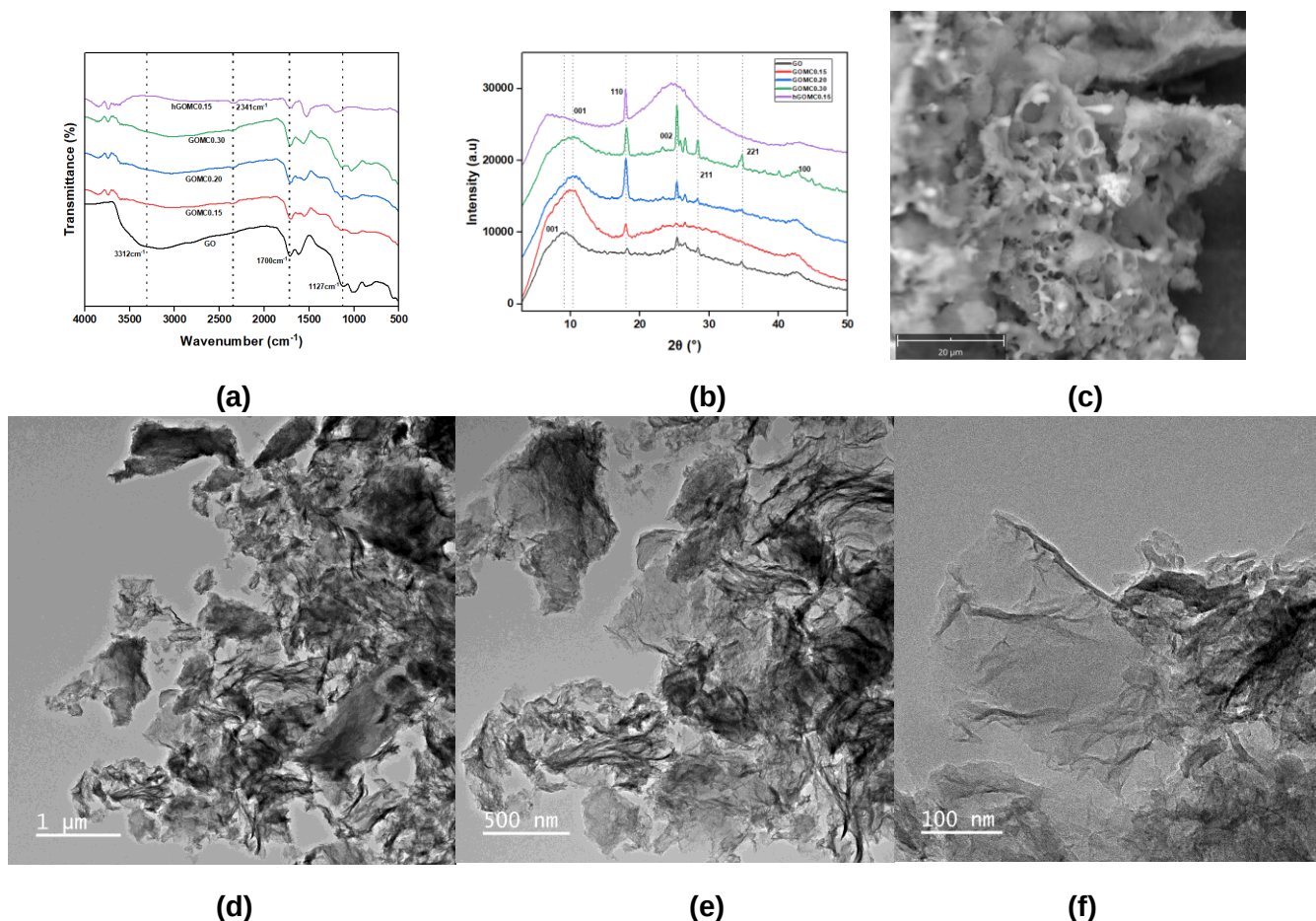


**Figure 51:** Holey maleoyl pillared graphene oxide **hGOMC0.15**: (a) IR spectrum; (b) XRD spectrum; (c) SEM; (d,e,f) TEM at different magnifications.

### 3.5.6 Holey maleoyl pillared reduced graphene oxide **hrGOMC0.20** – $d_{(002)} = 0.355$ nm

IR spectroscopy (Figure 46(a)) revealed a band at  $1815\text{ cm}^{-1}$  corresponding to a C=O stretching vibration. The XRD (Figure 46(b)) has a sharp (002) diffraction peak at  $2\theta = 25.00^\circ$  with  $d_{(002)} = 0.355$  nm.

The SEM (Figure 46(c)) shows thick worm-like films that are randomly aggregated. The presence of pores is not clear on this micrograph, but TEM images (Figure 46(d,e,f)) exhibit crumpled transparent sheet-like structures with several pores and crystalline areas.

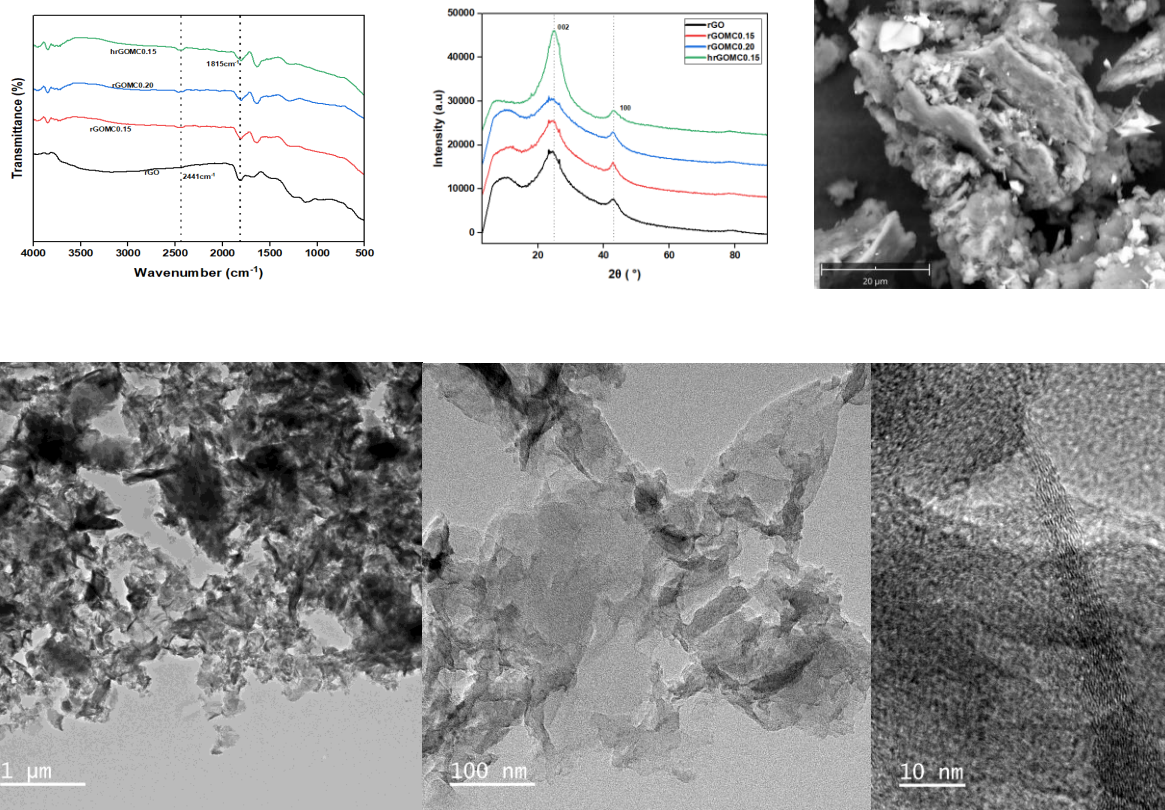


**Figure 52:** Holey maleoyl pillared reduced graphene oxide hrGOMC0.20: (a) IR spectrum; (b) XRD spectrum; (c) SEM; (d,e,f) TEM at different magnifications.

### 3.5.7 Holey oxalyl pillared graphene oxide hGOOC0.20 – $d_{(002)} = 0.355$ nm

IR spectroscopy (Figure 47(a)) shows the absence of the broad O-H stretching vibration, and a C=O band at  $1740\text{ cm}^{-1}$ . The XRD spectrum of **hGOOC0.15** (Figure 47(b)) exhibited a broad diffraction peak at  $2\theta = 25.09^\circ$  with  $d_{(002)} = 0.355$  nm, indicating a small particle size, that it is not highly crystalline, contains more structural disorder and has more defects.

The SEM image (Figure 47(c)) shows the scattered rough grains of **hGOOC0.15**. The presence of pores on the grains is evident. The TEM images (Figure 47(d,e,f)) show darker stacked and transparent sheet-like structures with wrinkles and scrolls on the surface.

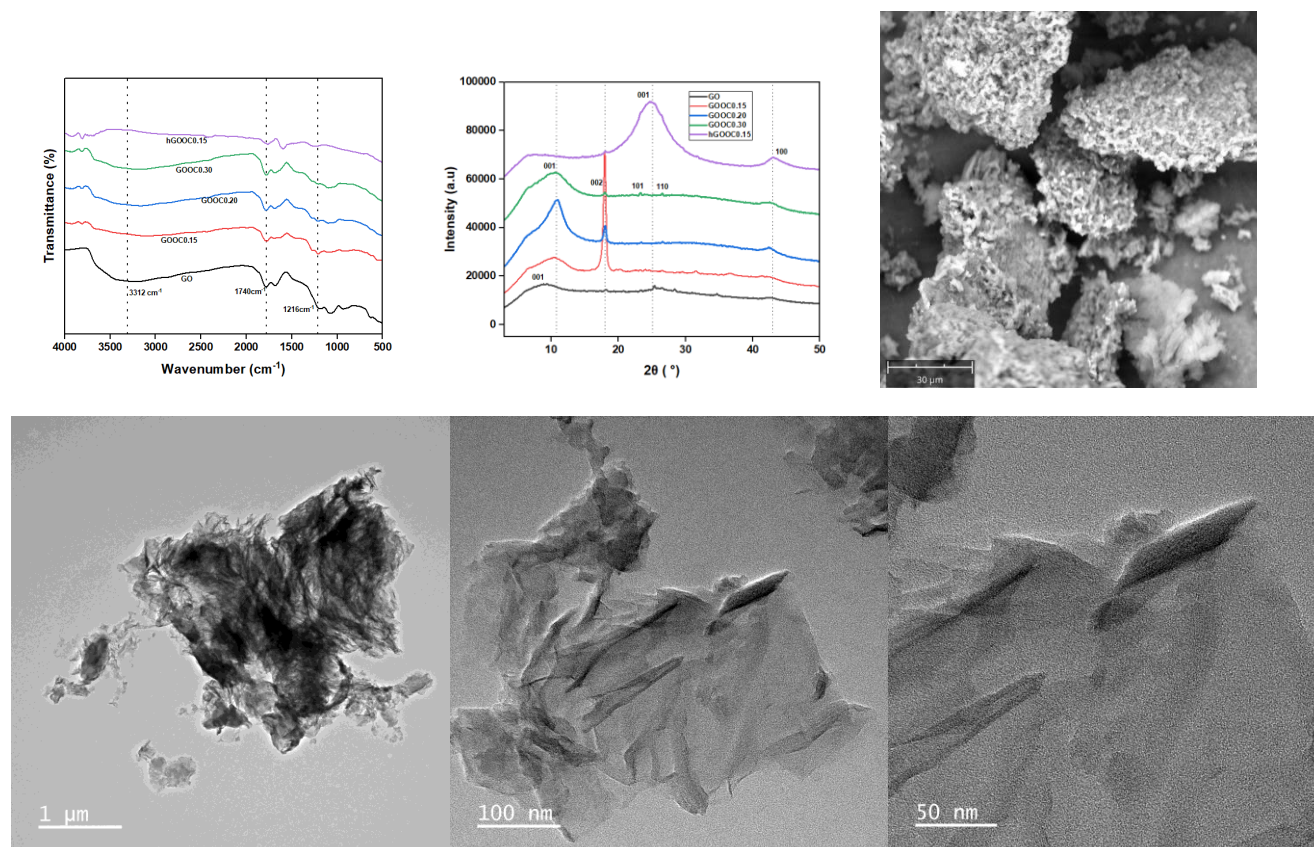


**Figure 53:** Holey oxalyl pillared graphene oxide **hGOOC0.20**: (a) IR spectrum; (b) XRD spectrum; (c) SEM; (d,e,f) TEM at different magnifications.

### 3.5.8 Holey oxalyl pillared reduced graphene oxide hrGOOC0.30 – $d_{(002)} = 0.378$ nm

The IR spectrum (Figure 48(a)) revealed the presence of a C-H stretching band at  $2341\text{ cm}^{-1}$  and the C=O band at  $1706\text{ cm}^{-1}$ . The XRD spectrum (Figure 48(b)) had a relatively sharp (002) diffraction peak at  $2\theta = 23.51^\circ$ , corresponding to  $d_{(002)} = 0.378$  nm and a low intensity reflective (100) peak at  $2\theta = 42.10^\circ$  with an interlayer spacing of 0.214 nm. The material is fairly crystalline and contains relatively few defects.

The SEM micrograph (Figure 48(c)) shows a wrinkled-like structure consisting of randomly aggregated thin films. The presence of pores is not clear in this micrograph, but TEM (Figure 48(d,e,f)) shows transparent sheet-like structures with randomly distributed holes, meaning that **hrGOOC0.15** was successfully synthesized.

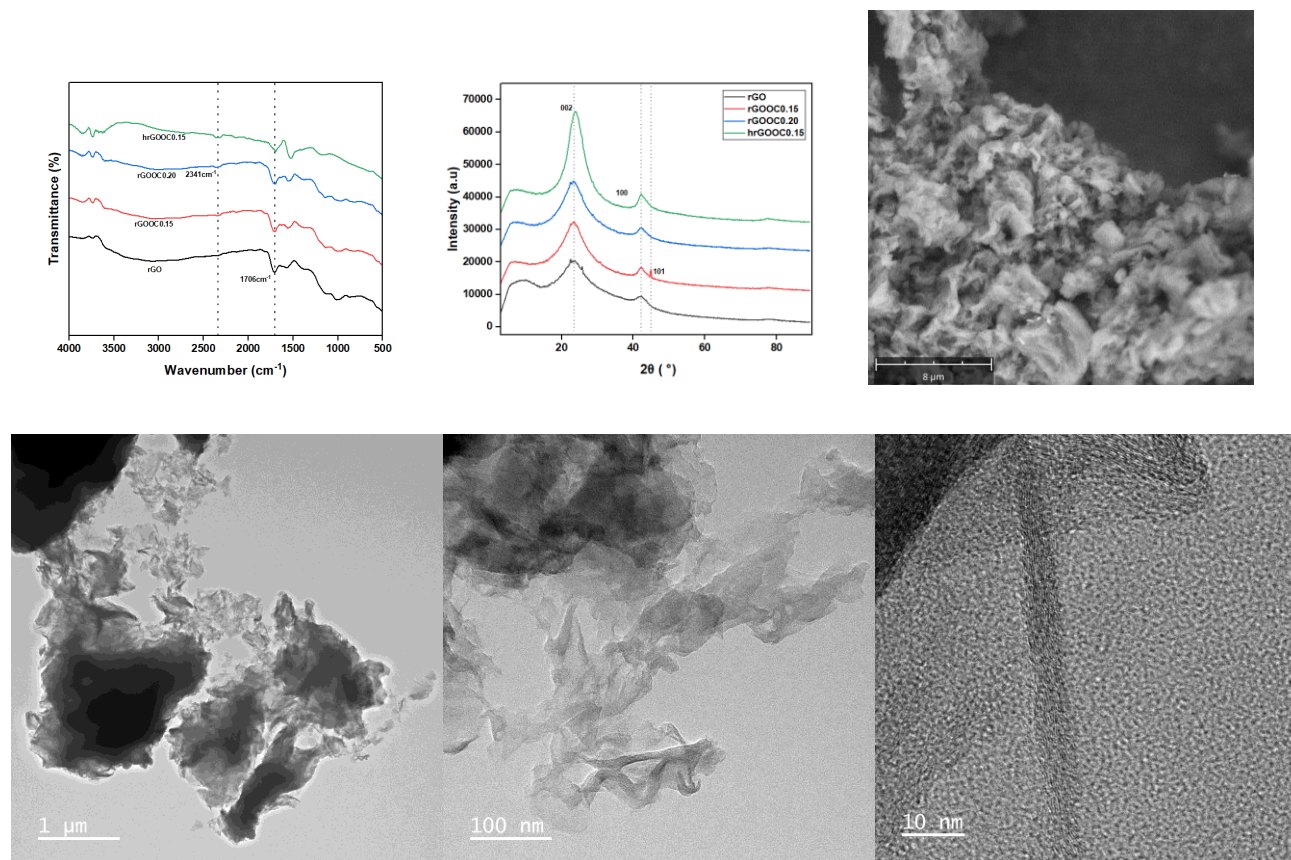


**Figure 54:** Holey oxalyl pillared reduced graphene oxide **hrGOOC0.30**: (a) IR spectrum; (b) XRD spectrum; (c) SEM; (d,e,f) TEM at different magnifications.

## CHAPTER 4: EXPERIMENTAL

### 4.1 GENERAL INSTRUMENTATION AND ANALYSIS TECHNIQUES

All reagents and solvents were Reagent Grade, purchased from Sigma-Aldrich. A Büchi rotatory evaporator was used to evaporate the solutions, and FTIR spectra were recorded using a Bruker Alpha Fourier Transform infrared spectrometer, with absorption maxima reported in terms of wavenumbers ( $\text{cm}^{-1}$ ). The structure and morphology of materials were characterized by X-Ray diffraction (XRD), Rigaku Smart lab X-ray diffractometer with  $\text{Cu } K_{\alpha}$  radiation,  $\lambda = 1.5406 \text{ \AA}$ , field-emission scanning electron microscope (FESEM, JEOL JEM-6701F), and transmission electron microscope (TEM, JEOL JEM-2100F), respectively. The interlayer spacing of GO and rGO and their derivatives were calculated by the formula:

$$d = \lambda / (2 \sin \theta_{(002)})$$

The morphology was determined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The specific surface area and pore size distribution was to be measured by a nitrogen adsorption/desorption analyzer (BET, JW-BK200C). Electrochemical characterization will be by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and galvanostatic charge-discharge cycling (GCD).

### 4.2 BET ANALYSIS CHARACTERISTICS

Due to time constraints, no BET results could be recorded. However, the expected results are briefly discussed. The adsorption-desorption analysis technique will be used to investigate the effect of pillars (fumaryl chloride, oxalyl chloride, and maleoyl chloride) between the GO/rGO sheets and calculate the pore size, and surface area. The theoretical value of the surface area of GO is  $2600 \text{ m}^2 \text{ g}^{-1}$ , so the expected results will be greater or less than the theoretical value of GO. The surface area of holey graphene and pore size distribution should be higher than that of GO and rGO because of the presence of spacers between the GO/rGO sheets. Xing *et al.* (2014) synthesized holey graphene with a specific surface area of  $1053.3 \text{ m}^2 \text{ g}^{-1}$  with a pore size distribution of 1.4-16.3 nm.

### 4.3 SYNTHESIS METHODS USED

### 4.3.1 Synthesis of Graphene Oxide

#### ***Synthesis of GO from commercial graphite flakes***

In Tour's method (Marcano *et al.*, 2010), concentrated sulphuric acid (90 ml, 98%) is mixed with concentrated ortho-phosphoric acid (10 ml) and the mixture is then added to graphite flakes (0.50 g). The mixture is stirred in an ice bath. Potassium permanganate (4.5 g) is added slowly to the mixture while stirring in the ice bath. Then the mixture is heated in a water bath at a controlled temperature of 50°C. The suspension is stirred continuously for 12 h at 50°C and is then cooled to room temperature followed by dilution with deionized water (250 ml) to interrupt the reaction. A 30% hydrogen peroxide solution (10 ml) is added as a reducing agent. The resulting mixture is filtered using filter paper and the precipitate is washed with aqueous HCl (16 ml of 5 % HCl and 84 ml H<sub>2</sub>O). After repeatedly rinsing with water, a black solid product is produced by centrifugation at 4000 rpm for 4 h, followed by decantation of the supernatant.

The black precipitate is then stirred in deionized water (100 ml) while heating for 12 h at 60 °C in a water bath. Thereafter the mixture is filtered collecting the black precipitate, which is dried in an oven at 60 °C for 24 h to obtain graphene oxide.

### 4.3.2 Synthesis of Reduced Graphene Oxide Using Ascorbic Acid

The graphene oxide (400 mg) is measured into a beaker and L-ascorbic acid (4 g) is dissolved in 400 ml of deionized water which is then added to the GO while stirring. The mixture is heated at 60°C for 30 minutes and the reduced product is then obtained by centrifugation at 4000 r/min for 40 minutes. The supernatant is discarded to obtain a black precipitate. Excess hydrogen peroxide (250 ml, 30% solution) is added for oxidation of the remaining LAA while stirring, and the mixture is heated 30 minutes at 60°C. After centrifuging 20 minutes at 4000 r/min, the liquid is decanted. The resultant black precipitate is then washed with ethanol (250 ml) followed by deionized water (250 ml): thereafter the precipitate is dried for 24 h at 120°C to obtain rGO.

### 4.3.3 Synthesis of Holey Graphene from Graphene Oxide

The gradual thermal annealing method (Walsh *et al.*, 2016; Han *et al.*, 2014; Lin *et al.*, 2015) was used to synthesize holey GO and rGO from GO and rGO powders, respectively. Holey graphenes have been made by direct heating of graphene in air at heating rates of ~10 °C min<sup>-1</sup> and holding isothermally at <500 °C for a specified time. The defects in the non-crystalline areas of the basal plane react with oxygen to produce holes in the graphene sheets.

#### 4.3.4 Synthesis of Pillared Reduced Graphene Oxide from rGO using Friedel-Crafts Acylation

Different pillar: rGO weight ratios were tested to determine the optimal composition. Three different pillars were used: fumaryl chloride, oxalyl chloride and maleoyl chloride; these chlorides were used at different concentrations 0.15 mmol, 0.20 mmol and 0.30 mmol to determine the optimal composition. Reduced graphene oxide reacts with a bifunctional acyl chloride in the presence of a Lewis acid catalyst ( $\text{AlCl}_3$ ) to form a graphene-based polymer. The reaction involves the acylation of the aromatic rings in rGO with the acyl chlorides, which results in a covalently functionalized graphene material. The graphene surface is functionally modified to increase its chemical reactivity and possible uses, enhanced mechanical, thermal, or electrical properties are shown in the resulting material. The bifunctional nature of these chlorides allows cross-linking, which results in a stronger and more stable material.

##### 4.3.4.1 *Friedel-Crafts acylation of rGO with fumaryl chloride*

Anhydrous  $\text{AlCl}_3$  (0.47g, 0.35 mmol) was stirred in 50 ml of 1,2-dichloroethane in a two-necked round-bottomed flask fitted with a drying tube, cooled in ice/water mixture, and fumaryl chloride (1.63 ml, 0.15 mmol) was added. Thereafter, 80 mg rGO was carefully added while stirring, and stirring continued overnight. The mixture was then poured onto ice to acidify the solution and to dissolve possible formed aluminium hydroxide. The product was collected by vacuum filtration, and the solid was washed three times with water, followed by acetone. The product was dried in the oven at 110 °C to obtain fumaryl functionalized rGO.

This method was repeated using 0.20 mmol fumaryl chloride (2.2 ml) 0.47 mmol anhydrous  $\text{AlCl}_3$  (0.63 g) and also 0.30 mmol fumaryl chloride (3.18 ml) and 0.70 mmol anhydrous  $\text{AlCl}_3$  (0.93 g)

##### 4.3.4.2 *Friedel-Crafts acylation of rGO with oxalyl chloride*

Anhydrous  $\text{AlCl}_3$  (0.47 g, 0.35 mmol) was stirred in 50 ml of 1,2-dichloroethane in a two-necked round bottom flask fitted with a drying tube which was cooled in ice/water mixture, then added oxalyl chloride (1.3 ml, 0.15 mmol). Thereafter, 80 mg rGO was carefully added while stirring, and stirring continued overnight. Then the mixture was poured onto ice to acidify the solution and to dissolve possible formed aluminium hydroxide. The product was collected by vacuum filtration and washed three times with water, followed by acetone. The product was dried in the oven at 110 °C to obtain oxalyl functionalized rGO.

This method was repeated using 0.20 mmol oxalyl chloride (1.7 ml), 0.47 mmol anhydrous  $\text{AlCl}_3$  (0.63 g), and also 0.30 mmol oxalyl chloride (2.6 ml) and 0.70 mmol anhydrous  $\text{AlCl}_3$  (0.93 g).

#### 4.3.4.3 *Friedel-Crafts acylation of rGO with maleoyl chloride*

Anhydrous  $\text{AlCl}_3$  (0.47 g, 0.35 mmol) was stirred in 50 ml 1,2-dichloroethane in a two-necked round bottom flask fitted with a drying tube, cooled in ice/water mixture, and then maleoyl chloride (1.6 ml, 0.15 mmol) was added. Thereafter, 80 mg rGO was added while stirring, and the mixture was stirred overnight. Then the mixture was poured onto ice to dissolve excess aluminium chloride and aluminium hydroxide. The product was collected by vacuum filtration and washed three times with water, followed by acetone. The product was dried in the oven at 110 °C to obtain maleoyl functionalized rGO.

This method was repeated using 0.20 mmol maleoyl chloride (2.2 ml), 0.47 mmol anhydrous  $\text{AlCl}_3$  (0.63 g), 0.30 mmol oxalyl chloride (3.2 ml), and 0.70 mmol anhydrous  $\text{AlCl}_3$  (0.93 g).

#### 4.3.5 Synthesis of hRGO from rGO

Han *et al.* (2014) and Walsh *et al.* (2016) used gradual thermal annealing to produce hG from graphene by removing non-crystalline areas from the graphene (Fig. 49). This method avoids the use of any specific chemicals or catalysts and was found to be relatively robust, easily scaled-up and environmentally friendly.

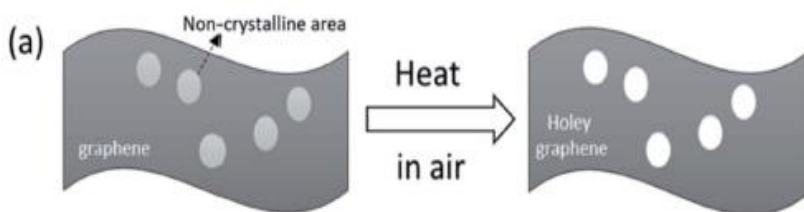


**Figure 55:** Schematic representation of holey graphene synthesis from graphene sheets (Han *et al.*, 2014).

Reduced graphene oxide (rGO) powder (1.0 g) was added to a crucible and the crucible was heated inside a muffle furnace at 350 °C for 30 minutes. The crucible was removed and allowed to cool down to room temperature to obtain **hrGO**; thereafter the crucible was placed in a desiccator. This method was repeated using the fumaryl functionalized rGO, oxalyl functionalized rGO and maleoyl functionalized rGO.

## CHAPTER 5: SUMMARY, CONCLUSIONS AND FUTURE WORK

### 5.1 SUMMARY

Graphene oxide (GO) was successfully synthesized by oxidizing graphite flakes using Tour's method. This method has been demonstrated to be efficient and less hazardous than legacy methods, but it yields a smaller amount of graphene oxide. Ascorbic acid has successfully reduced GO to rGO using ascorbic acid, which is the first and most efficient green reductant to date, it is a mildly reducing, inexpensive, and nontoxic reducing agent. This study revealed a cheaper and scalable method of producing high-quality graphene oxide from natural graphite, as well as a more environmentally friendly and controllable method of producing reduced graphene oxide from ascorbic. The Friedel–Crafts acylation was efficient in inserting the pillaring agents onto the sheets of rGO and GO using three different pillars (maleoyl chloride, fumaryl chloride, and oxalyl chloride). The gradual thermal annealing method was used to create holes in the functionalized graphene sheets. The literature review reveals that the pillared graphene and holey graphene were developed to minimize the restacking and agglomeration of the graphene sheets.

The study achieved the following objectives:

- Synthesis of pillared and holey graphene using low-cost efficient methods.
- Characterization of the prepared samples using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) spectroscopy.
- Synthesis and characterization of novel electrode materials.

FTIR spectroscopy was used to study and identify functional groups in GO, rGO, pillared graphene, and holey graphene. FTIR analysis revealed that during the oxidation, several oxygen-containing functional groups were introduced in the graphitic layers thus confirming the formation of graphene oxide, after chemical reduction, the GO was reduced to form reduced graphene oxide. IR analysis also showed the formation of pillared graphenes after the application of the Friedel-Crafts acylation method, and the formation of holey graphene after the gradual thermal heating method. XRD was used to examine the crystalline structure of GO, rGO, pillared graphene, and holey graphene. SEM and TEM were used to investigate the

surface morphology of GO, rGO, and the holey graphenes. BET will be used to measure the surface area and porosity of the synthesized materials and reported in a forthcoming article.

## 5.2 CONCLUSION

Friedel-Crafts acylation efficiently synthesized pillared graphenes using three pillars (fumaryl, oxalyl, and maleoyl chloride) with three different concentrations per 80 mg of GO and rGO. Gradual thermal annealing also efficiently synthesized holey graphene. FTIR analysis revealed several oxygen-containing functional groups in graphene oxide, reduced graphene oxide, pillared graphene, and holey graphene sheets. The pillared and holey graphene materials are fairly crystalline as evidenced by the XRD spectra; the SEM micrographs confirmed that the pillared and holey graphene materials are amorphous, while TEM further provided the information that pillared and holey graphenes were synthesized successfully, as shown by the presence of pores on the images. Using a low-energy ball mill may be necessary to eliminate large agglomerates. Overall, this research has explored an inexpensive and scalable way to produce high-quality graphene oxide from natural graphite. It also offers a more environmentally friendly and controlled method to produce reduced graphene oxide using ascorbic acid. Both GO and rGO give good results when used as a precursor to synthesize pillared graphene and holey graphene. Overall, the synthesis of pillared graphene and holey graphene was successful, and the aim and major objectives of this study have been met.

## 5.3 FUTURE WORK

For future work, the synthesized materials will be applied in a lithium-ion battery (CR2032 coin-type) cell where electrochemical studies of the three selected samples with high interlayer spacing and high surface area will be used to study:

- Cyclic voltammetry (CV), to investigate the reduction and oxidation processes.
- Electrochemical impedance spectroscopy (EIS), to investigate the ion transport dynamics of the synthesized materials.
- Galvanic charge and discharge cycling, to investigate the materials' charge storage capacity and performance in a Li-ion battery.

The three selected samples are:

- **GOFC0.20**, which has an interlayer spacing of 0.439 nm.
- **hrGOOC0.15**, which has an interlayer spacing of 0.378 nm.
- **GOOC0.20**, which has an interlayer spacing of 0.493 nm.

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